

Supporting information:

**Room Temperature Gibbs Energies of Hydrogen
Bonded Alcohol Dimethylselenide Complexes**

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S1 Computational Details

Optimized geometries at the ω B97X-D/aug-cc-pVTZ level of theory are shown in Figures S1 to S6. The structures are arranged from the lowest energy conformer to the highest. An asterisk is used to indicate if the structure was optimized using *opt=tight* convergence criteria instead of *opt=verytight* in Gaussian09, Revision D.01. The conformers of ethanol are written shorthand as EtOH(g) and EtOH(t) for the *gauche* and *trans* conformers, respectively. In Section S1.6, we give the zero point corrected relative energy, ΔE , in kJ/mol of different conformers, relative to the lowest energy conformer, of the various complexes. Also shown is the integrated kinetic energy density within the reduced gradient volume $s = 0.4$ a.u., $G(s_{0.4})$. In Table S2, we give the calculated wavenumber for the fundamental OH stretch of the complexes and in Table S3 the associated oscillator strength. In Table S4, the fundamental OH stretch and associated oscillator strength for each of the alcohols is shown.

S1.1 MeOH complexes

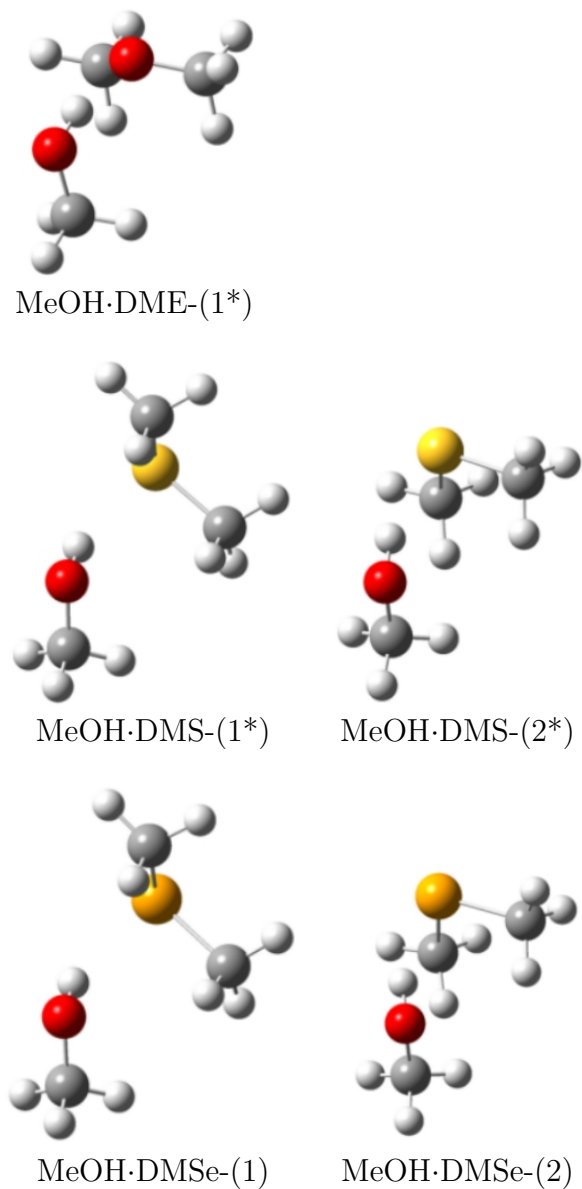


Figure S1: Optimized ω B97X-D/aug-cc-pVTZ geometries of MeOH·DME, MeOH·DMS and MeOH·DMSe.

S1.2 EtOH complexes

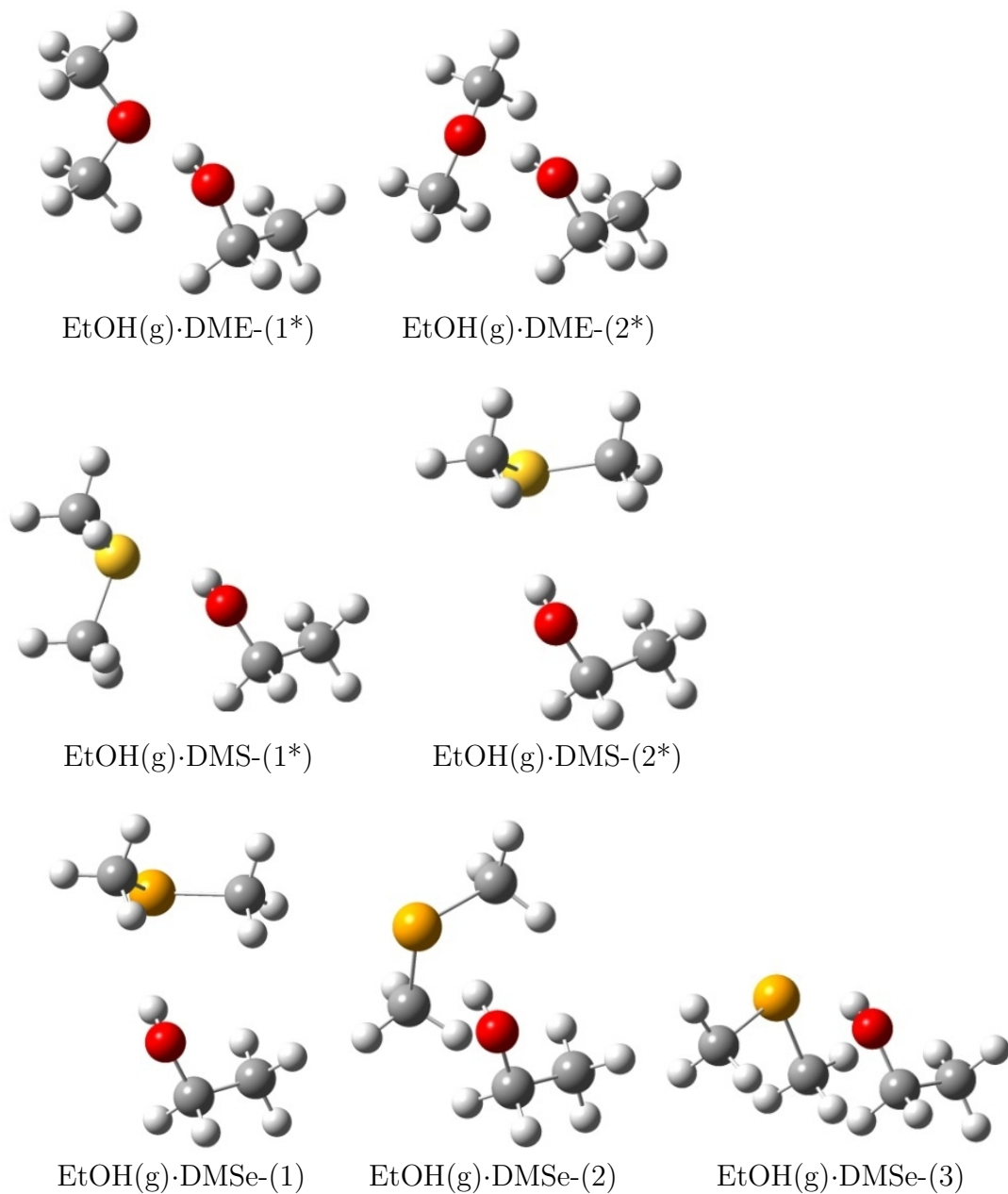
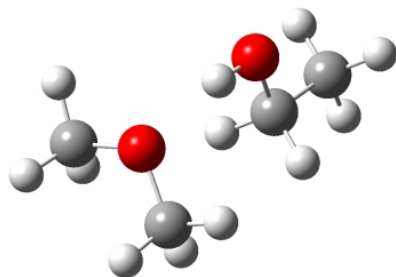
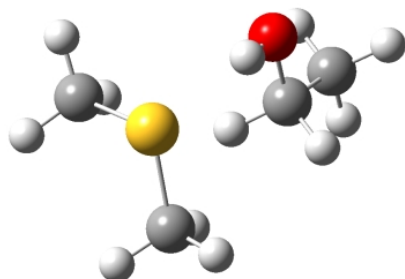


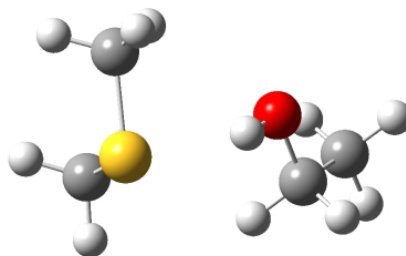
Figure S2: Optimized ω B97X-D/aug-cc-pVTZ geometries of EtOH(g)·DME, EtOH(g)·DMS and EtOH(g)·DMSe.



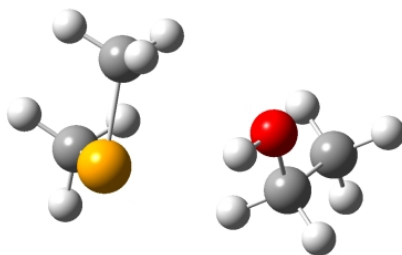
EtOH(t)·DME-(1*)



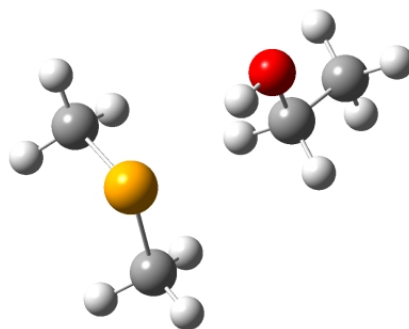
EtOH(t)·DMS-(1*)



EtOH(t)·DMS-(2*)



EtOH(t)·DMSe-(1)



EtOH(t)·DMSe-(2)

Figure S3: Optimized ω B97X-D/aug-cc-pVTZ geometries of EtOH(t)·DME, EtOH(t)·DMS and EtOH(t)·DMSe.

S1.3 t-BuOH complexes

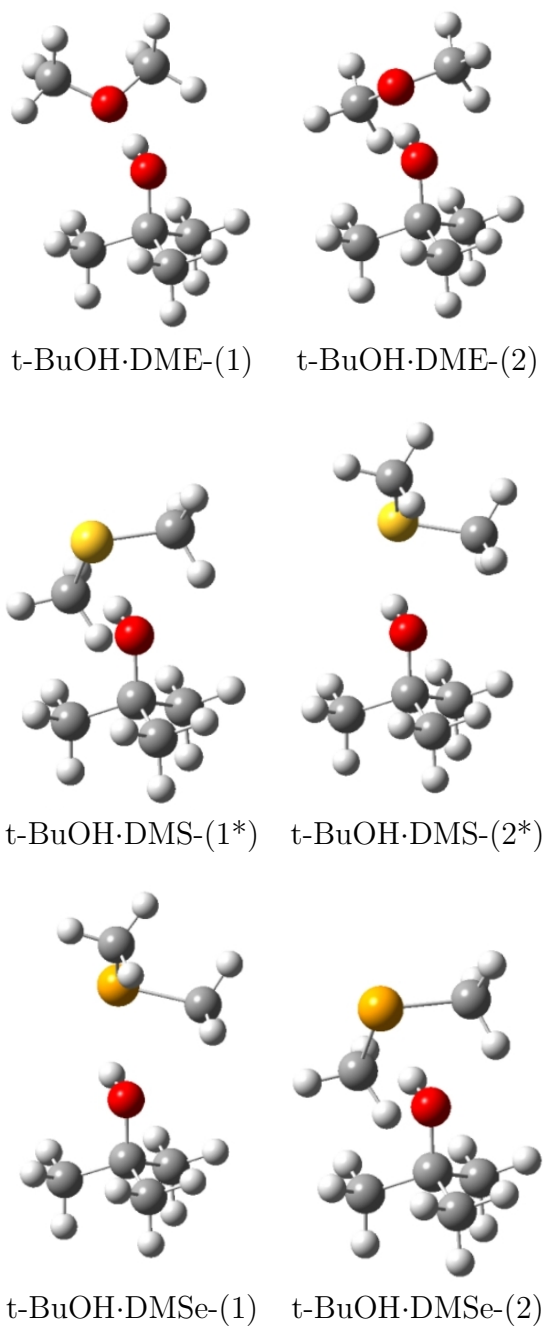


Figure S4: Optimized ω B97X-D/aug-cc-pVTZ geometries of t-BuOH·DME, t-BuOH·DMS and t-BuOH·DMSe.

S1.4 TFE complexes

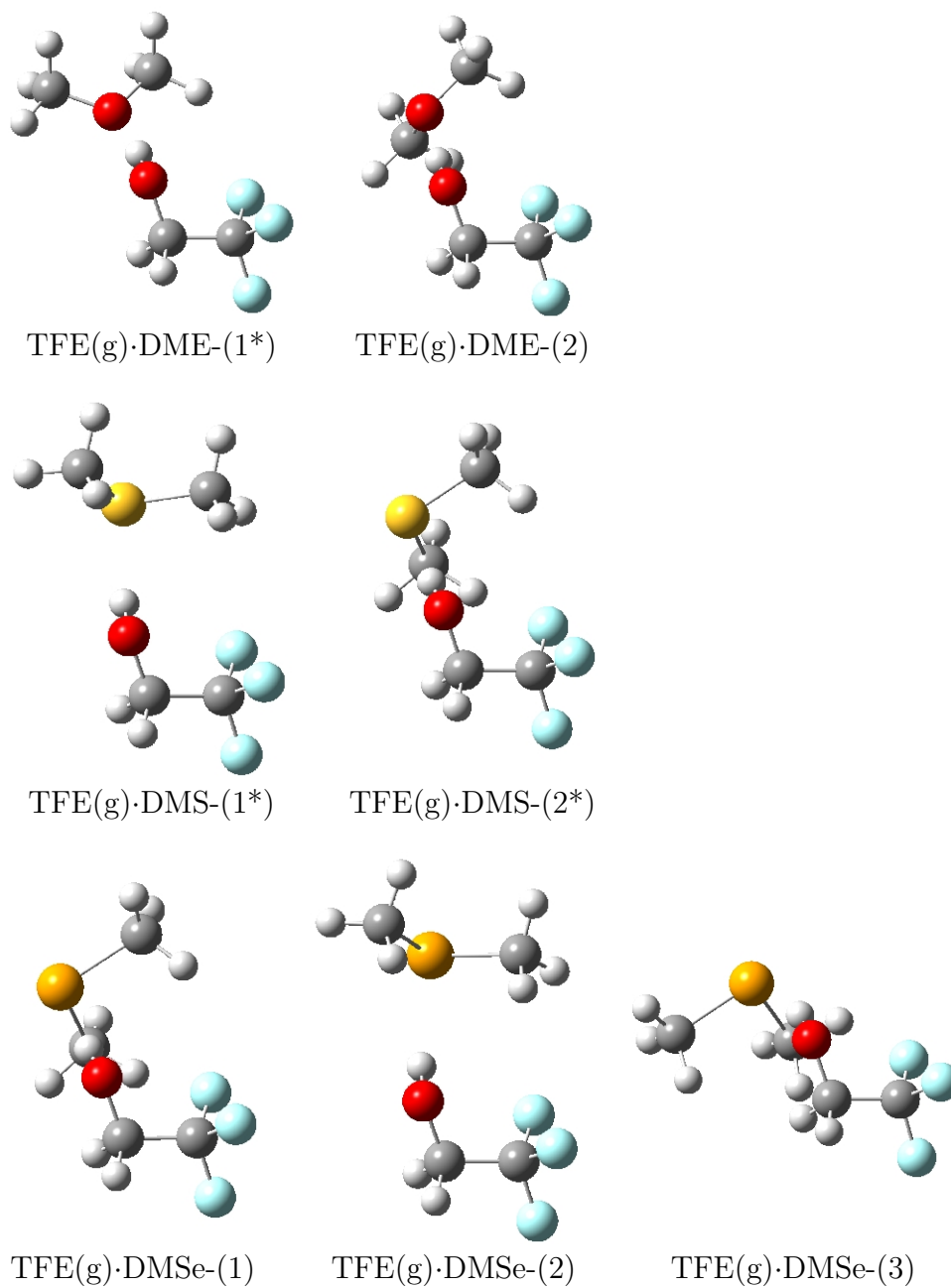


Figure S5: Optimized ω B97X-D/aug-cc-pVTZ geometries of TFE(g)·DME, TFE(g)·DMS and TFE(g)·DMSe.

S1.5 PhOH complexes

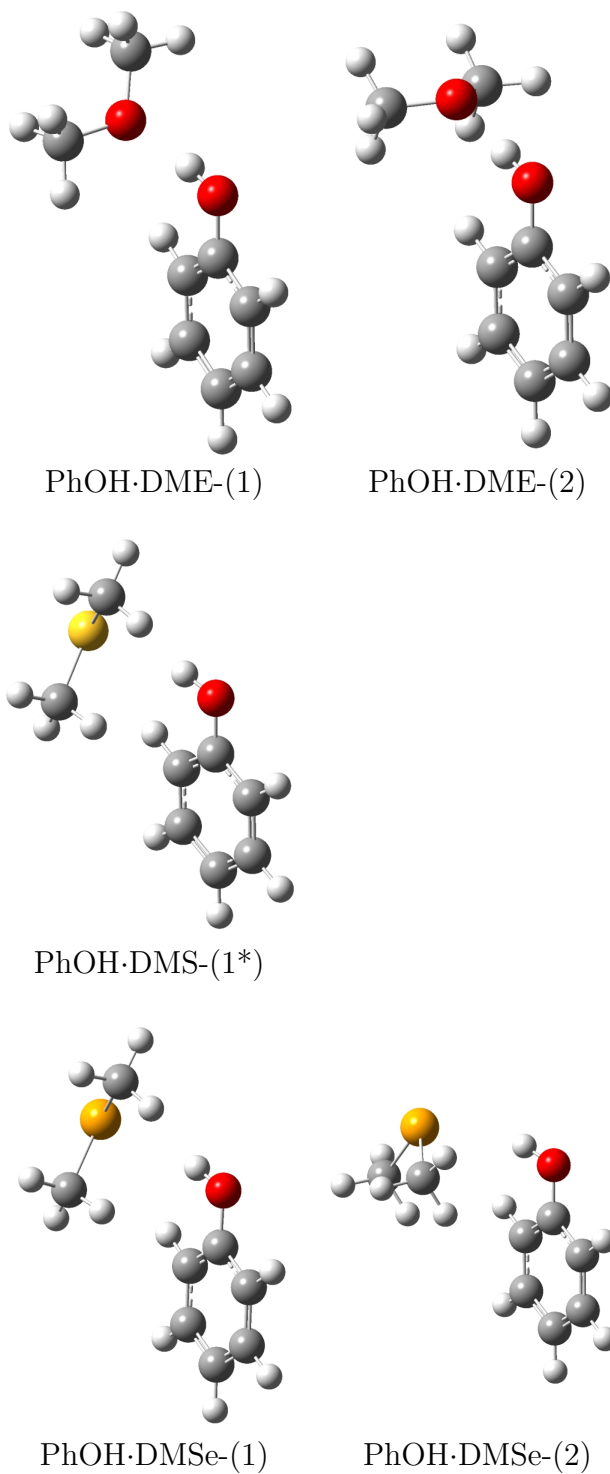


Figure S6: Optimized ω B97X-D/aug-cc-pVTZ geometries of PhOH·DME, PhOH·DMS and PhOH·DMSe.

S1.6 Calculated parameters

Table S1: The ω B97X-D/aug-cc-pVTZ relative electronic energy, ΔE , from the lowest energy conformer, given in kJ/mol, calculated Gibbs energies given in kJ/mol and the integrated kinetic energy density $G(s_{0.4})$ in a.u., for the hydrogen bonded interaction for each conformer of all complexes. The asterisk (*) indicate the structure were optimized using *opt=tight* critieria in Gaussian instead of *opt=verytight*.

Complex	ΔE	ΔG_{calc}^a	Boltzmann weight ^b	$G(s_{0.4})^c$
MeOH·DME-(1*)	0.00	-	1.00	2.82
MeOH·DMS-(1*)	0.00	-	0.68	2.92 (2.96)
MeOH·DMS-(2*)	1.85	-	0.32	2.61 (2.55)
MeOH·DMSe-(1)	0.00	-	0.68	2.83
MeOH·DMSe-(2)	1.82	-	0.32	2.48
EtOH(g)·DME-(1*)	0.00	-	0.47	2.69
EtOH(g)·DME-(2*)	1.07	-	0.30	2.74
EtOH(g)·DMS-(1*)	0.00	-	0.40	2.85 (2.79)
EtOH(g)·DMS-(2*)	0.86	-	0.28	2.78 (2.81)
EtOH(g)·DMSe-(1)	0.00	-	0.36	2.68
EtOH(g)·DMSe-(2)	1.16	-	0.23	2.26
EtOH(g)·DMSe-(3)	2.61	-	0.13	2.19
EtOH(t)·DME-(1*)	1.76	-	0.21	2.80
EtOH(t)·DMS-(1*)	1.57	-	0.11	2.85 (2.55)
EtOH(t)·DMS-(2*)	3.20	-	0.21	2.57 (2.72)
EtOH(t)·DMSe-(1)	1.58	-	0.19	2.77
EtOH(t)·DMSe-(2)	3.31	-	0.10	2.46
t-BuOH-DME-(1)	0.00	4.3	0.55	2.86
t-BuOH-DME-(2)	0.47	8.1	0.45	2.69
t-BuOH-DMS-(1*)	0.00	21.5	0.74	2.84 (2.81)
t-BuOH-DMS-(2*)	2.62	7.8	0.26	2.39 (2.40)
t-BuOH-DMSe-(1)	0.00	12.0	0.72	2.70
t-BuOH-DMSe-(2)	1.64	5.1	0.28	2.22

Continued on next page.

TFE(g)·DME-(1*)	0.00	-1.0	0.53	3.76
TFE(g)·DME-(2)	0.25	2.4	0.47	3.74
TFE(g)·DMS-(1*)	0.00	6.9	0.58	3.86 (3.92)
TFE(g)·DMS-(2*)	0.78	5.4	0.42	3.51 (3.47)
TFE(g)·DMSe-(1)	0.00	2.7	0.46	3.17
TFE(g)·DMSe-(2)	0.23	3.6	0.39	3.68
TFE(g)·DMSe-(3)	2.64	1.3	0.14	3.34
PhOH·DME-(1)	0.00	-	0.54	3.57
PhOH·DME-(2)	0.36	-	0.46	3.60
PhOH·DMS-(1*)	0.00	-	1.00	3.33 (3.37)
PhOH·DMSe-(1)	0.00	-	0.57	3.15
PhOH·DMSe-(2)	0.80	-	0.43	2.56

a: Gibbs energies calculated using rigid rotor and harmonic oscillator approximations.

b: Boltzmann weights of EtOH complexes including both EtOH(t) and EtOH(g) complex conformers, for example Boltzmann weights for EtOH·DME, include EtOH(g)·DME-(1*), EtOH(g)·DME-(2*) and EtOH(t)·DME-(1*). Calculated at 296 K.

c: Values of $G(S_{0.4})$ should be multiplied by 10^{-3} . Example for MeOH·DME-(1*), $G(s_{0.4}) = 2.82 \times 10^{-3}$ a.u. Values in parenthesis calculated using ω B97X-D/aug-cc-pV(T+d)Z optimized geometries and densities.

Table S2: The ω B97X-D/aug-cc-pVTZ calculated wavenumbers in cm^{-1} for the fundamental OH stretching transition using different local mode models.

Complex	1D LM	2D LM	2D+2D LMPT
MeOH·DME-(1*)	3558	3535	3551
MeOH·DMS-(1)	3534	-	-
MeOH·DMS-(2)	3549	-	-
MeOH·DMSe-(1)	3552	-	-
MeOH·DMSe-(2)	3565	-	-
EtOH(g)·DME-(1*)	3548	3536	3572
EtOH(g)·DME-(2*)	3537	3556	3538
EtOH(g)·DMS-(1)	3524	-	-
EtOH(g)·DMS-(2)	3530	-	-
EtOH(g)·DMSe-(1)	3540	-	-
EtOH(g)·DMSe-(2)	3568	-	-
EtOH(g)·DMSe-(3)	3573	-	-
EtOH(t)·DME-(1*)	3557	3570	3541
EtOH(t)·DMS-(1)	3541	-	-
EtOH(t)·DMS-(2)	3551	-	-
EtOH(t)·DMSe-(1)	3560	-	-
EtOH(t)·DMSe-(2)	3566	-	-
t-BuOH·DME-(1)	3526	3530	3575
t-BuOH·DME-(2)	3534	3539	3575
t-BuOH·DMS-(1)	3517	3520	3553
t-BuOH·DMS-(2)	3529	3529	3555
t-BuOH·DMSe-(1)	3534	3533	3559
t-BuOH·DMSe-(2)	3543	3537	3553
TFE(g)·DME-(1*)	3404	3414	3473
TFE(g)·DME-(2)	3382	3400	3468
TFE(g)·DMS-(1*)	3400	3399	3420
TFE(g)·DMS-(2*)	3368	3361	3395
TFE(g)·DMSe-(1)	3427	3423	3442
TFE(g)·DMSe-(2)	3424	3433	3471
TFE(g)·DMSe-(3)	3455	3447	3458
PhOH·DME-(1)	3395	3409	3457
PhOH·DME-(2)	3381	3388	3442
PhOH·DMS-(1)	3428	-	-
PhOH·DMSe-(1)	3455	-	-
PhOH·DMSe-(2)	3514	-	-

Table S3: The ω B97X-D/aug-cc-pVTZ calculated oscillator strength of the fundamental OH stretching transition using different local mode models.

Complex	1D LM	2D LM	2D+2D LMPT
MeOH·DME-(1*)	8.81×10^{-5}	7.33×10^{-5}	5.88×10^{-5}
MeOH·DMS-(1)	7.89×10^{-5}	-	-
MeOH·DMS-(2)	7.56×10^{-5}	-	-
MeOH·DMSe-(1)	7.23×10^{-5}	-	-
MeOH·DMSe-(2)	6.94×10^{-5}	-	-
EtOH(g)·DME-(1*)	8.44×10^{-5}	7.92×10^{-5}	7.07×10^{-5}
EtOH(g)·DME-(2*)	9.22×10^{-5}	8.54×10^{-5}	8.07×10^{-5}
EtOH(g)·DMS-(1)	7.35×10^{-5}	-	-
EtOH(g)·DMS-(2)	7.07×10^{-5}	-	-
EtOH(g)·DMSe-(1)	6.88×10^{-5}	-	-
EtOH(g)·DMSe-(2)	6.91×10^{-5}	-	-
EtOH(g)·DMSe-(3)	5.20×10^{-5}	-	-
EtOH(t)·DME-(1*)	9.05×10^{-5}	8.44×10^{-5}	6.95×10^{-5}
EtOH(t)·DMS-(1)	7.78×10^{-5}	-	-
EtOH(t)·DMS-(2)	7.79×10^{-5}	-	-
EtOH(t)·DMSe-(1)	6.94×10^{-5}	-	-
EtOH(t)·DMSe-(2)	7.18×10^{-5}	-	-
t-BuOH·DME-(1)	1.03×10^{-4}	9.65×10^{-5}	7.81×10^{-5}
t-BuOH·DME-(2)	8.69×10^{-5}	7.98×10^{-5}	6.74×10^{-5}
t-BuOH·DMS-(1)	7.21×10^{-5}	6.77×10^{-5}	5.62×10^{-5}
t-BuOH·DMS-(2)	8.00×10^{-5}	7.53×10^{-5}	6.49×10^{-5}
t-BuOH·DMSe-(1)	6.66×10^{-5}	6.43×10^{-5}	5.39×10^{-5}
t-BuOH·DMSe-(2)	7.50×10^{-5}	7.13×10^{-5}	6.32×10^{-5}
TFE(g)·DME-(1*)	1.79×10^{-4}	1.66×10^{-4}	1.45×10^{-4}
TFE(g)·DME-(2)	1.70×10^{-4}	1.55×10^{-4}	1.38×10^{-4}
TFE(g)·DMS-(1*)	1.68×10^{-4}	1.58×10^{-4}	1.39×10^{-4}
TFE(g)·DMS-(2*)	1.63×10^{-4}	1.55×10^{-4}	1.31×10^{-4}
TFE(g)·DMSe-(1)	1.59×10^{-4}	1.54×10^{-4}	1.41×10^{-4}
TFE(g)·DMSe-(2)	1.51×10^{-4}	1.36×10^{-4}	1.15×10^{-4}
TFE(g)·DMSe-(3)	1.28×10^{-4}	1.20×10^{-4}	1.05×10^{-4}
PhOH·DME-(1)	1.97×10^{-4}	1.81×10^{-4}	1.54×10^{-4}
PhOH·DME-(2)	1.99×10^{-4}	1.83×10^{-4}	1.60×10^{-4}
PhOH·DMS-(1)	1.40×10^{-4}	-	-
PhOH·DMSe-(1)	1.29×10^{-4}	-	-
PhOH·DMSe-(2)	9.07×10^{-5}	-	-

Table S4: Calculated wavenumber, in cm^{-1} and oscillator strength for the fundamental OH stretching transition of the alcohol monomer using a 1D LM model.

Complex	f_{calc}	$\tilde{\nu}$
MeOH	4.25×10^{-6}	3756
EtOH(g)	3.59×10^{-6}	3736
EtOH(t)	2.89×10^{-6}	3755
t-BuOH	1.53×10^{-6}	3725
TFE(t)	8.23×10^{-6}	3756
TFE(g)	7.34×10^{-6}	3766
PhOH	8.40×10^{-6}	3749

S1.7 Basis set comparison

The effect of adding extra d functions to the aug-cc-pVTZ basis set [aug-cc-pV(T+d)Z] was tested for the t-BuOH·DMS-(2) conformer. In Table S5, we show the calculated OH stretching frequency and oscillator strength from the 2D+2D LMPT calculations, using either the aug-cc-pVTZ and aug-cc-pV(T+d)Z basis set. It can be seen that the effect of the different basis set is minimal.

Table S5: Effect of the aug-cc-pVTZ and aug-cc-pV(T+d)Z basis set on the 2D+2D LMPT oscillator strength, f_{calc} , and fundamental OH stretching frequency, $\tilde{\nu}_{OH}$ in cm^{-1} , for the t-BuOH·DMS-(2) conformer.

Basis set	f_{calc}	$\tilde{\nu}_{OH}$
aug-cc-pVTZ	6.45×10^{-5}	3530
aug-cc-pV(T+d)Z	6.49×10^{-5}	3532

S2 Jet-cooled PhOH·DMS and PhOH·DMSe

Jet experiments by Biswal et al.¹ and Mishra et al.² observed the $\tilde{\nu}_{OH}$ band of the PhOH·DMS and PhOH·DMSe complexes and determined the associated redshift. Mishra et al. calculated the OH stretching frequencies of the PhOH·DMS complex. We have attempted to reproduce their calculations, using the same Gaussian09 revision D.01 software³, and were successful for their B97-D/aug-cc-pVTZ calculations. However, we are not able to reproduce their B97-D/6-311++G(d,p) calculated frequencies. In Table S6, we give the B97-D/6-311++G(d,p) frequencies of the fundamental OH stretching transition, for the PhOH·DMS and PhOH·DMSe complexes. We compare the values reported by Mishra et al.² with our B97-D/6-311++G(d,p) calculated $\tilde{\nu}_{OH}$ frequency, using geometries reported by Mishra et al.² (which has imaginary frequencies), and after a structure optimization, which removed the imaginary frequencies. The observed $\tilde{\nu}_{OH}$ band from jet-cooled experiments are included. From our optimized geometries of Mishra et al.’s reported geometries. The two conformers found of the PhOH·DMS and PhOH·DMSe complexes, show a difference in the OH stretching frequency of 73 and 74 cm^{-1} respectively. This difference should be enough to observe both conformers spectrally. Though for the two PhOH·DMSe complexes, the difference in zero point corrected electronic energy is 1.01 kJ/mol, between the two conformers. At a temperature of ~ 50 K in the jet, the relative population is 92% for the lower energy state. Similarly, for PhOH·DMS, with an energy difference of 1.5 kJ/mol, corresponding to 97% of the population as the lower energy conformer. This is in agreement with only one peak observed in the PhOH·DMS and PhOH·DMSe jet-cooled spectra.

Table S6: Calculated and experimental frequencies, in cm^{-1} , of the hydrogen bonded OH stretch of PhOH·DMS and PhOH·DMSe. Calculations performed at B97-D/6-311++G(d,p) level, with the OH stretching frequencies multiplied by 0.9609.

	PhOH·DMS-A	PhOH·DMS-B	PhOH·DMSe-A	PhOH·DMSe-B
Mishra et al. ^a	3538	3328	3418	3332
Calculated ^b	3498	3280	3366	3292
Calculated (Optimized) ^c	3353	3280	3365	3291
Observed	3527 ^d	-	3414 ^e	-

a: B97-D/6-311++G(d,p) calculated OH stretching frequencies, from Mishra et al.,² scaled by 0.9609.

b: B97-D/6-311++G(d,p) calculated OH stretching frequencies, scaled by 0.9609, using reported geometries by Mishra et al.² for which we observed imaginary frequencies in PhOH·DMS-A (-44 cm^{-1}), PhOH·DMS-B (-5 cm^{-1}) and PhOH·DMSe-B (-15 cm^{-1}).

c: Calculated OH stretching frequency after performing a geometry optimization, using the *opt=tight* and *int=ultrafine* keywords in gaussian.

d: Experimental value, Biswal et al.¹

e: Experimental value, Mishra et al.²

S3 Experimental Details

In total, three pressure gauges were used. Two were from the Agilent CDG-500 series, fullscale 10 and 1000 Torr, respectively, and one was an Agilent PCG-750 Pirani Capacitance Diaphragm Gauge. Pressures below 10 Torr were recorded using the Agilent CDG-500 fullscale 10 Torr gauge, and pressures above 10 Torr were recorded using the Agilent CDG-500 fullscale 1000 Torr, except for MeOH·DMSe where pressures above 10 Torr were measured with a Agilent PCG-750. Experiments from Du et al.⁴ used an Agilent PCG-750 Pirani gauge.

S3.1 Spectral subtraction

To obtain a spectrum of the hydrogen bonded complex, a total of three spectra are recorded. Reference spectra of the donor and acceptor units are recorded individually, as well as a spectrum of the mixture of the two. The spectrum of the complex is obtained by scaling and subtracting the reference spectra of the donor and acceptor from the spectrum of the mixture.

$$A_C(\tilde{\nu}) = A_{Mix}(\tilde{\nu}) - c_1 \times A_D(\tilde{\nu}) - c_2 \times A_A(\tilde{\nu}), \quad (1)$$

where $A_C(\tilde{\nu})$ is the absorbance of the hydrogen bonded complex at the wavenumber $\tilde{\nu}$, and where $A_D(\tilde{\nu})$, $A_A(\tilde{\nu})$ and $A_{Mix}(\tilde{\nu})$, likewise are the absorbances of the donor, acceptor and the mixture of the two, respectively, at the wavenumber $\tilde{\nu}$. The parameters c_1 and c_2 are scale factors that are introduced to account for small differences in the absorbance, which comes from the difference in pressure, between the spectrum of the references and that present in the spectrum of the mixture.

S3.2 Overview of complexes

A total of fifteen complexes are studied by considering all combinations of using one of five alcohol donors: MeOH, EtOH, t-BuOH, TFE and PhOH together with one of three

dimethylchalcogens acceptors DME, DMS and DMSe. The observed redshift of the $\tilde{\nu}_{OH}$ band upon complexization was determined for the t-BuOH·DME, PhOH·DME, t-BuOH·DMS, PhOH·DMS, MeOH·DMSe, EtOH·DMSe, t-BuOH·DMSe, PhOH·DMSe and TFE·DMSe complexes. These nine are complimented with spectra of the six complexes formed between MeOH, EtOH and TFE as donor molecules and DME and DMS as acceptors, which have been published previously.⁴ In this work, the equilibrium constant for the formation of the hydrogen bonded complex have been obtained for five of these complexes: t-BuOH·DME, PhOH·DME, t-BuOH·DMS, t-BuOH·DMSe and TFE·DMSe.

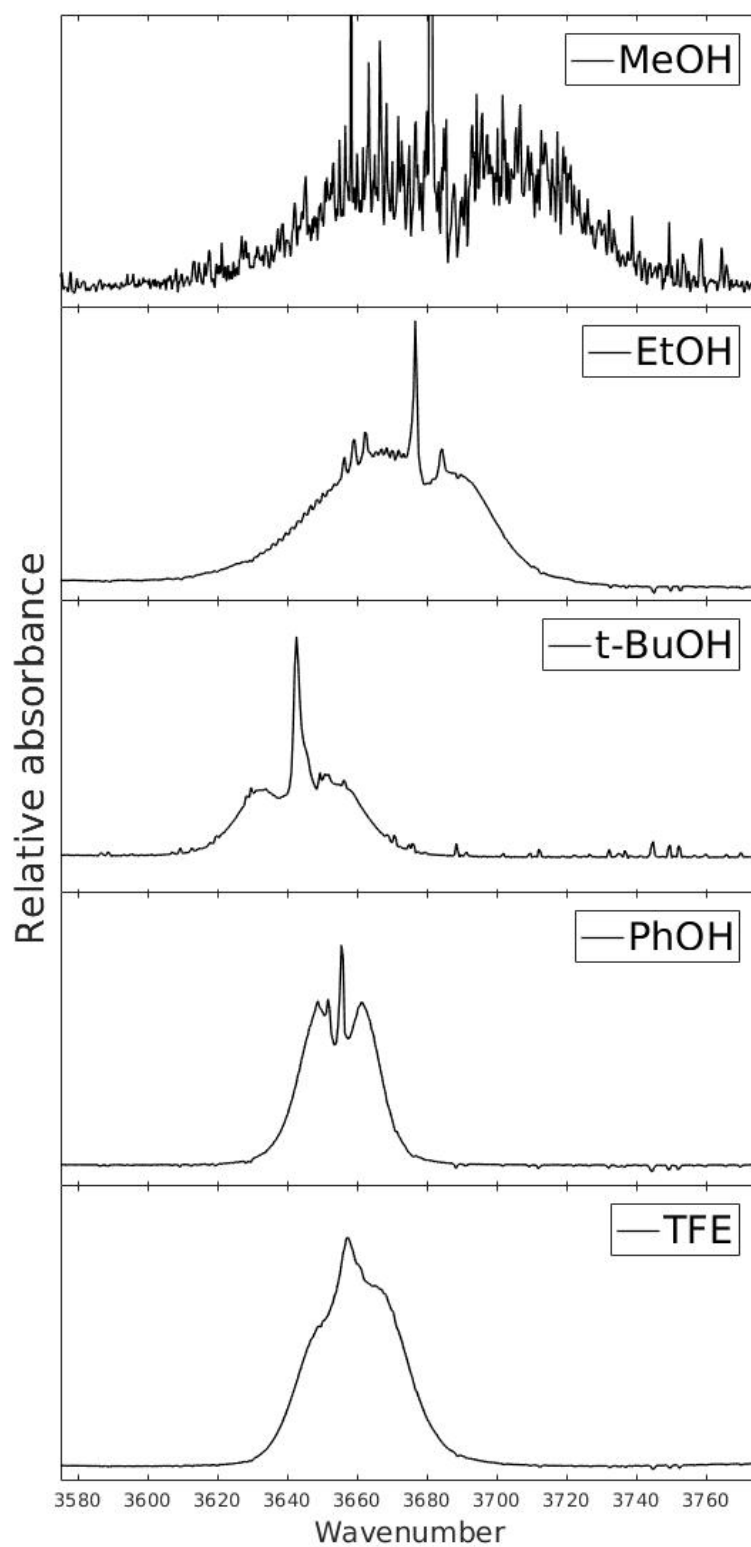


Figure S7: Spectra of the fundamental OH stretching band of each alcohol monomer, spectra of MeOH were recorded with 0.5 cm^{-1} resolution and for the other spectra, with a 1 cm^{-1} resolution.

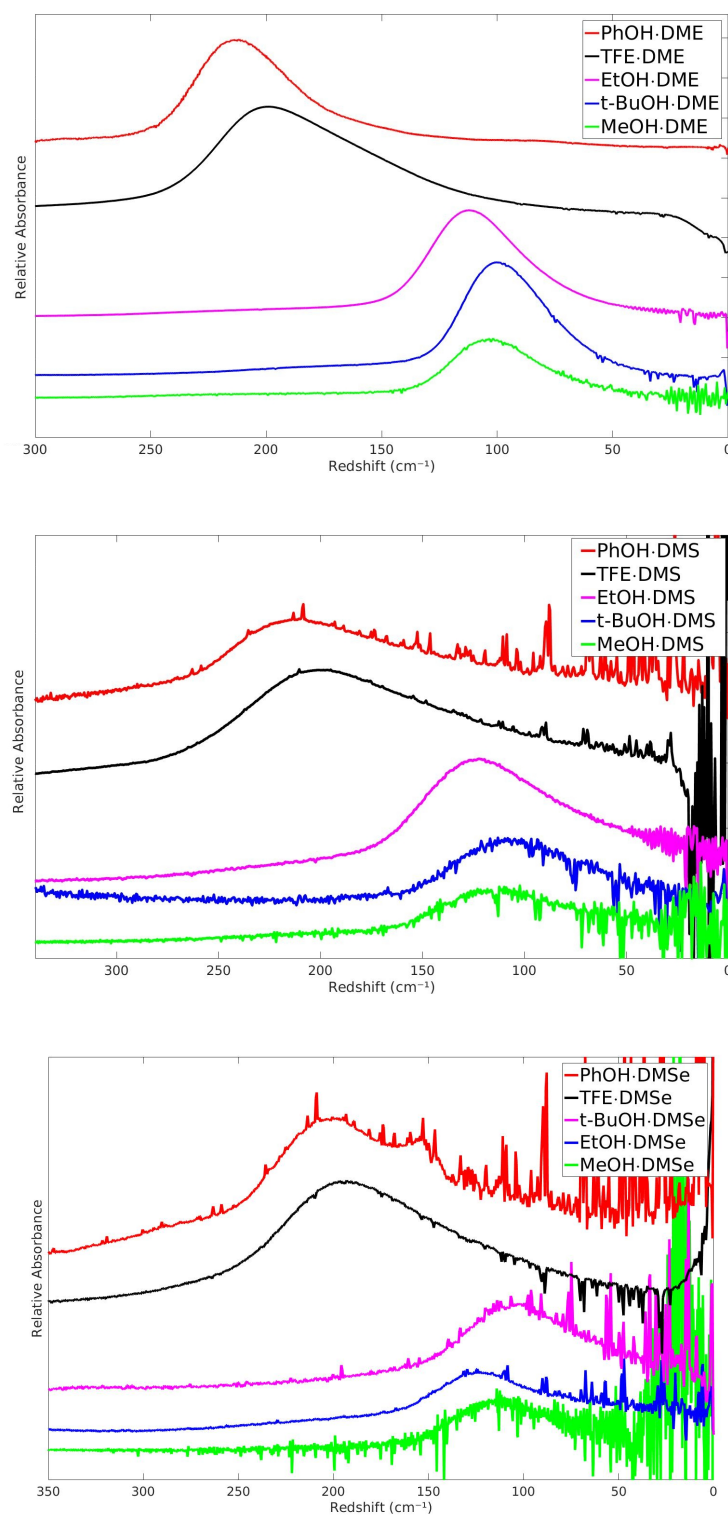


Figure S8: Spectra of the complexes, grouped by each acceptor unit, illustrating the redshift of the OH stretching band in the complexes.

Table S7: Experimental parameters for Figures 1 and 2 in manuscript. Pressures^a of the donor and acceptor is in Torr and optical pathlength in m.

Donor	Acceptor	Donor Pressure	Acceptor Pressure	Optical Pathlength
MeOH	DME	20	267	0.10
	DMS	14	95	0.20
	DMS _e	9.1	104.4	2.4
EtOH	DME	14	237	0.20
	DMS	11	90	0.20
	DMS _e	33.3	106.0	0.10
t-BuOH	DME	29.4	605.5	0.19
	DMS	1.8	191.5	2.4
	DMS _e	3.4	43.3	2.4
TFE	DME	18	102	0.20
	DMS	19	22	6
	DMS _e	3.1	81.7	2.4
PhOH	DME	0.14	132.4	16
	DMS	0.062	153.4	16
	DMS _e	0.061	100.0	16

a: The difference in significant digits between some of the experiments is because different pressure gauges were used between our experiments and those of Du et al.⁴

S3.3 Error propagation

Several sources of experimental and theoretical uncertainties are included in our experiments and the final uncertainty was calculated as the propagated error, calculated by:

$$Prop. Uncertainty\% = \sqrt{\sum_i x_i^2}, \quad (2)$$

Where *Prop. Uncertainty*% is the relative propagated uncertainty, and x_i is the relative uncertainty from each source of uncertainty. For MeOH·DME, the relative uncertainties are 35% from the oscillator strength, 10% from the integrated absorbance and 7% from the fitting. Here the propagated uncertainty becomes:

$$\sqrt{0.35^2 + 0.1^2 + 0.07^2} = 0.37 = 37\%. \quad (3)$$

S3.4 Alcohol DME complexes

Experimental details used for spectral subtraction and equilibrium constant determination are included for the various complexes. For all complexes were included a 35% uncertainty from the calculated oscillator strength.

S3.4.1 MeOH·DME

For experimental details see ref.⁴ Uncertainty for integrated absorbance is estimated to be 10% and two standard deviations on the linear fit is 7%. Propagated uncertainty of 37%

S3.4.2 EtOH·DME

For experimental details see ref.⁴ Uncertainty for integrated absorbance is estimated to be 10% and two standard deviations on the linear fit is 6%. Propagated uncertainty of 37%

S3.4.3 t-BuOH·DME

The cell path length for the experiment was 10 cm. The integrated absorbance was measured from 3267 to 3652 cm^{-1} and is estimated to have a 7% uncertainty and two standard deviations on the linear fit is 5%. Propagated uncertainty of 36%

Table S8: Experimental details for t-BuOH·DME.

Experiment	A	B	C	D	E
P(DME) ^a	61.7	165.3	231.9	354.0	606.4
P(t-BuOH) ^a	32.3	32.3	32.1	32.3	32.3
Scalefactor DME	1.159	0.972	1.01	1.001	0.998
Scalefactor t-BuOH	0.995	0.964	0.953	0.951	0.91
Temperature ^b	295	295	295	295	295
Int. Abs. ^c	1.354	2.575	3.588	5.399	9.194

a: Pressure before multiplication with corresponding scalefactor, given in Torr.

b: Temperature given in K.

c: Given in cm^{-1} .

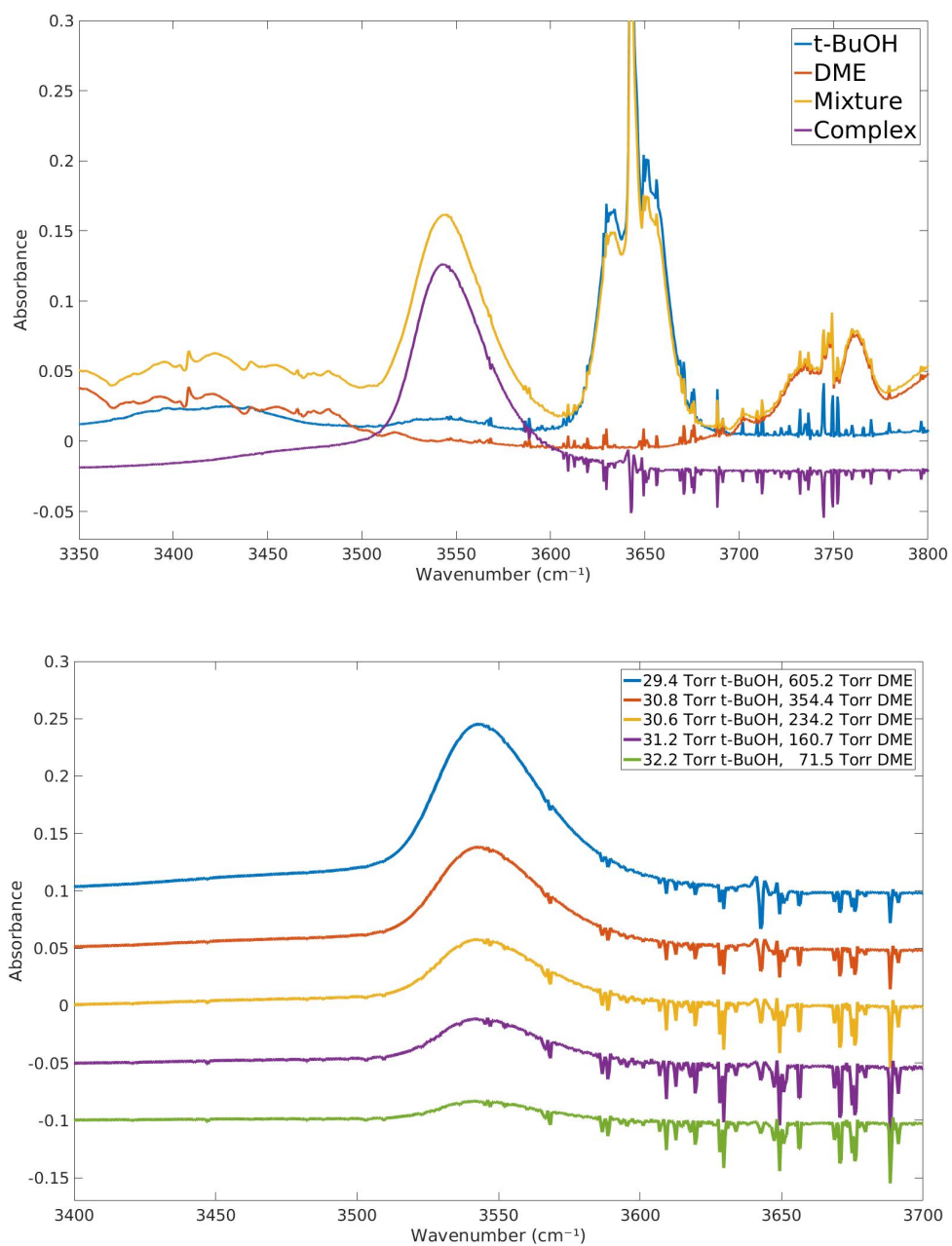


Figure S9: **Top:** Spectra of t-BuOH, DME, the mixture of the two and the complex spectrum (shown for experiment E, Table S8). **Bottom:** Spectra of t-BuOH·DME using various pressure combination of t-BuOH and DME. The spectra are off-set vertically for clarity.

S3.4.4 TFE·DME

For experimental details see ref.⁴ Uncertainty for integrated absorbance is estimated at 10% and two standard deviations on the linear fit is 10%. Propagated uncertainty of 38%.

S3.4.5 PhOH·DME

The optical pathlength for the experiment was 16 m. The integrated absorbance was measured from 3282 to 3632 cm^{-1} and is estimated to have a 3% uncertainty and two standard deviations on the linear fit is 12%. Propagated uncertainty of 36%. Observed equilibrium constant $K = 0.26 \pm 0.09$ ($\Delta G = 3.3 \pm 1.0$ kJ/mol).

Table S9: Experimental details for PhOH·DME.

Experiment	A	B	C	D	E
P(DME) ^a	10.9	24.7	51.7	75.4	135.0
P(PhOH) ^a	0.233	0.240	0.239	0.247	0.226
Scalefactor DME	0.970	1.03	0.99	0.981	0.981
Scalefactor PhOH	0.614	0.681	0.705	0.700	0.651
Temperature ^b	296	296	295	296	295
Int. Abs. ^c	3.04	6.64	12.68	19.60	29.78

a: Pressure before multiplication with corresponding scalefactor, given in Torr.

b: Temperature given in K.

c: Given in cm^{-1} .

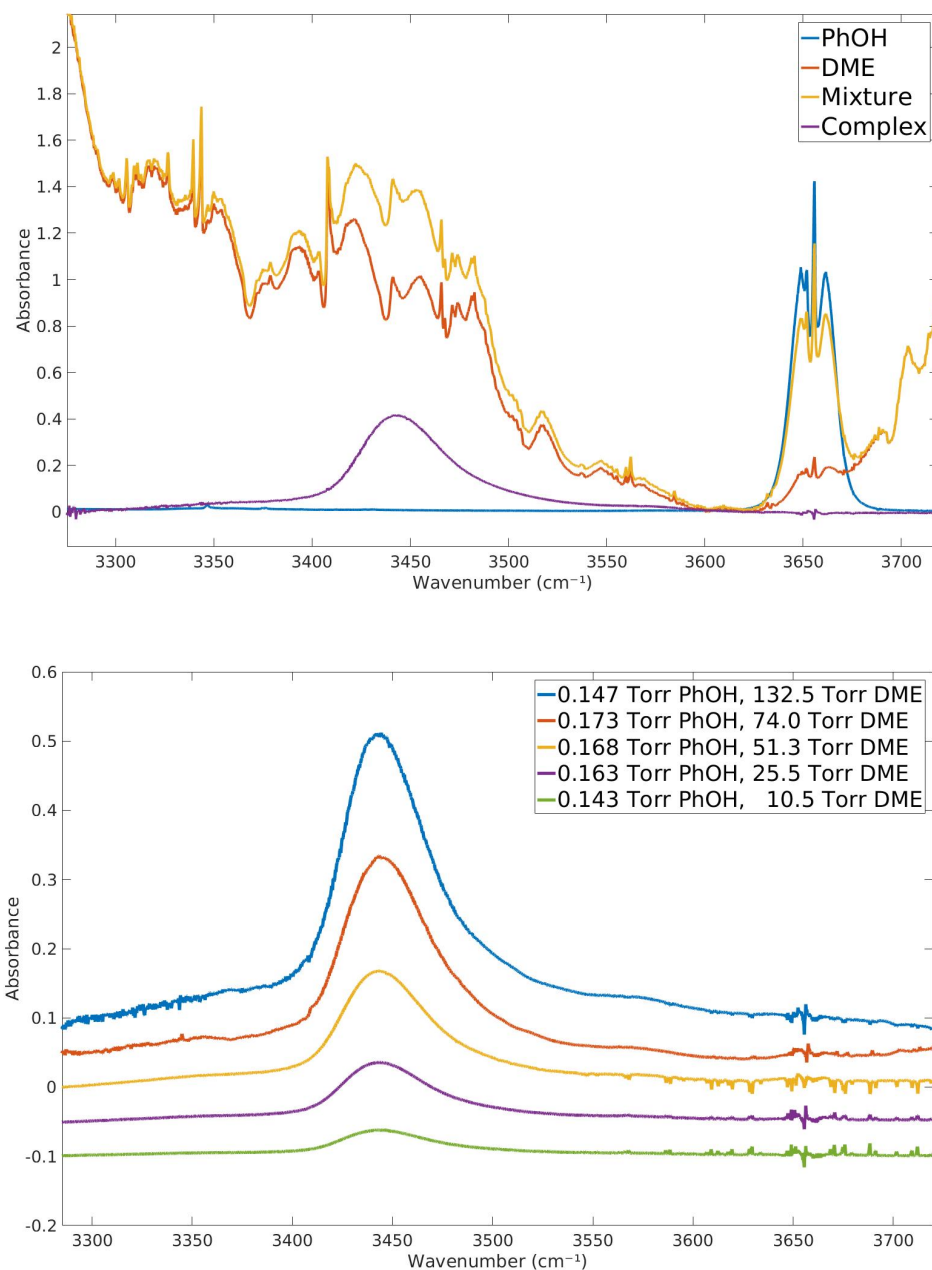


Figure S10: **Top:** Spectra of PhOH monomer, DME monomer, the mixture and the complex spectrum (shown for experiment E, Table S9). **Bottom:** Spectra of PhOH·DME using various pressure combination of PhOH and DME. The spectra are off-set vertically for clarity.

S3.5 Alcohol DMS complexes

S3.5.1 t-BuOH·DMS

The optical pathlength for the experiment was 2.4 m. The integrated absorbance was measured from 3340 to 3689 cm^{-1} and is estimated to have a 16% uncertainty and two standard deviations on the linear fit is 22%. Propagated uncertainty 44%.

Table S10: Experimental details for t-BuOH·DMS.

Experiment	A	B	C	D	E
P(DMS) ^a	24.2	50.5	105.5	152.5	181.9
P(t-BuOH) ^a	2.055	2.266	2.431	2.676	2.266
Scalefactor DMS	0.9325	1.277	0.93	0.99	1.053
Scalefactor t-BuOH	0.995	1.005	0.945	0.94	0.791
Temperature ^b	296	295	295	294	295
Int. Abs. ^c	0.166	0.656	1.044	1.383	1.405

a: Pressure before multiplication with corresponding scalefactor, given in Torr.

b: Given in Kelvin.

c: Given in cm^{-1} .

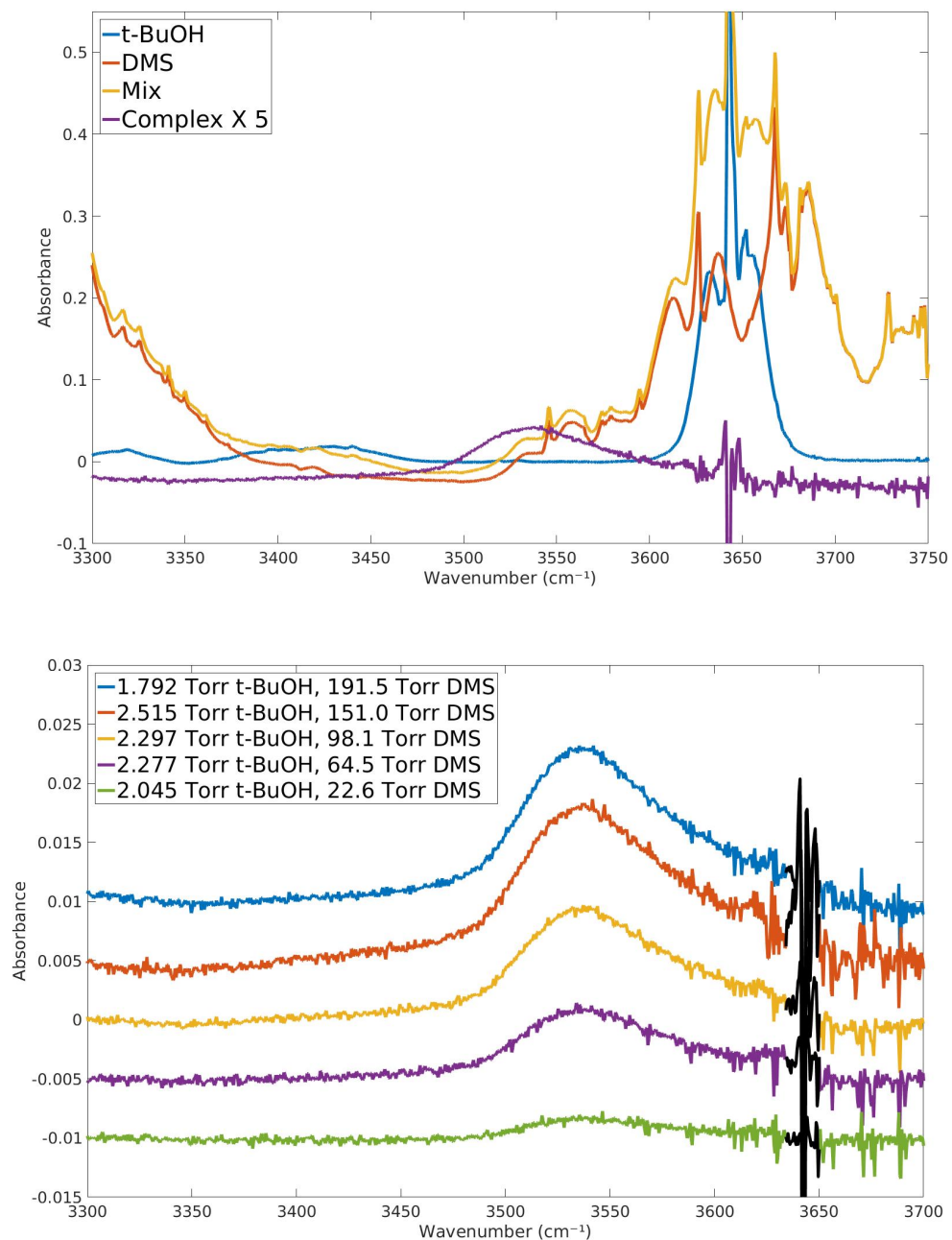


Figure S11: **Top:** Spectra of t-BuOH, DMS, the mixture of the two and the complex spectrum (experiment E, Table S10). **Bottom:** Spectra of t-BuOH·DMS using various pressure combination of t-BuOH and DMS. The spectra are off-set vertically for clarity. The black region comes from slight saturation of the alcohol OH stretch. The integrated absorbance is obtained by replacing the black region with a straight line.

S3.5.2 TFE·DMS

For experimental details see reference.⁴ Uncertainty for integrated absorbance is estimated to be 10% and two standard deviations on the linear fit is 4%. Propagated uncertainty of 37%.

S3.5.3 PhOH·DMS

The cell path length for the experiment was 16 m.

Table S11: Experimental details for PhOH·DMS.

Experiment	A
P(DMS) ^a	153.4
P(PhOH) ^a	0.225
Scalefactor DMS	0.916
Scalefactor PhOH	0.275
Temperature ^b	296

a: Pressure before multiplication with corresponding scalefactor, given in Torr.

b: Temperature given in K.

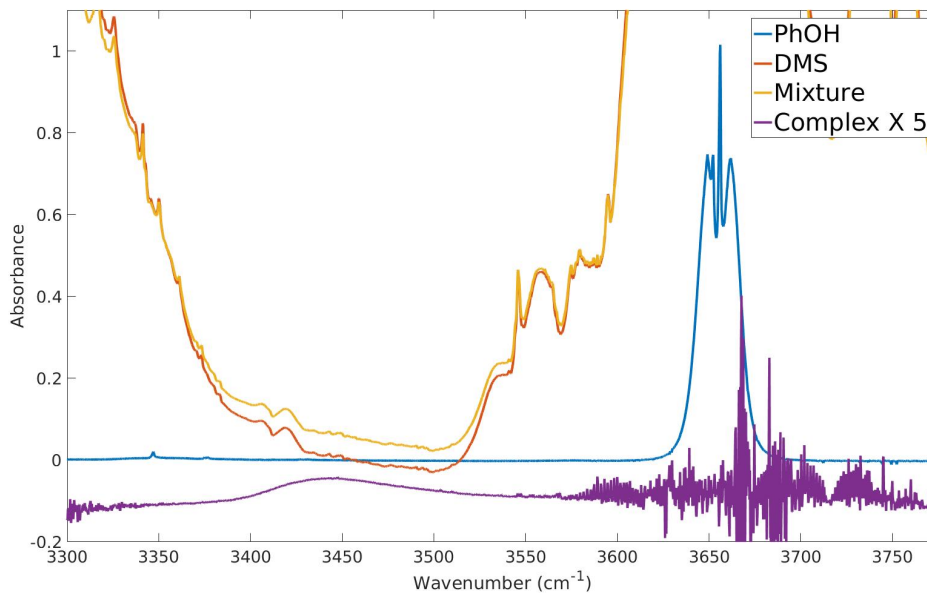


Figure S12: Spectra of PhOH, DMS, mixture and complex, the complex is upscaled by a factor of 5.

S3.6 Alcohol DMSe complexes

S3.6.1 MeOH·DMSe

The optical pathlength for the experiment was 2.4 m.

Table S12: Experimental details for MeOH·DMSe.

Experiment	A
P(DMSe) ^a	108
P(MeOH) ^a	8.70
Scalefactor DMSe	0.967
Scalefactor MeOH	1.05
Temperature ^b	291

a: Pressure before multiplication with corresponding scalefactor, given in Torr.

b: Temperature given in K.

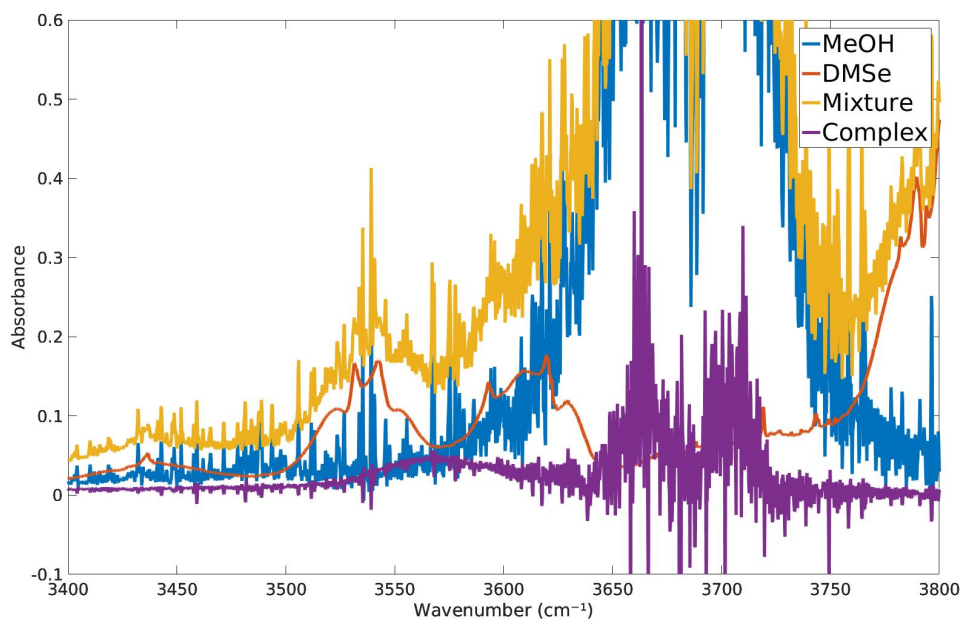


Figure S13: Spectra of MeOH, DMSe, mixture and complex.

S3.6.2 EtOH·DMSe

The optical pathlength for the experiment was 19 cm.

Table S13: Experimental details for EtOH·DMSe.

Experiment	A
P(DMSe) ^a	106.0
P(EtOH) ^a	40.8
Scalefactor DMSe	0.732
Scalefactor EtOH	0.817
Temperature ^b	296

a: Pressure before multiplication with corresponding scalefactor, given in Torr.

b: Temperature given in K.

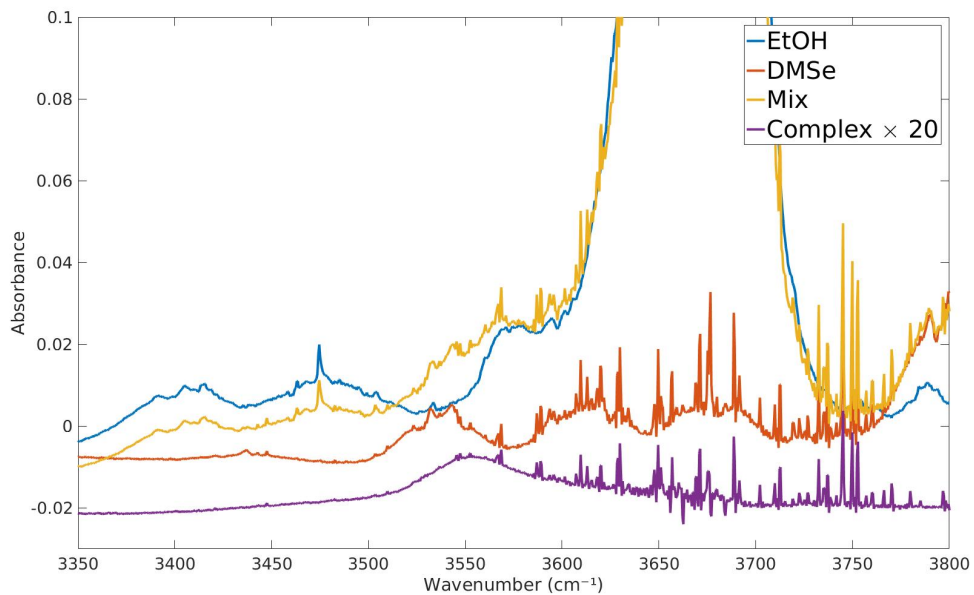


Figure S14: Spectra of EtOH, DMSe, mixture and complex. The Spectrum of the complex has been upscaled by a factor of 20.

S3.6.3 t-BuOH·DMSe

The optical pathlength for the experiment was 2.4 m. The integrated absorbance was measured from 3312 to 3695 cm^{-1} (3312 to 3623 cm^{-1} for experiment D due to negative absorbance from the water lines), and was estimated to have a 20% uncertainty from the integrated absorbance and two standard deviations on the linear fit is 55%. Propagated uncertainty of 68%.

Table S14: Experimental details for t-BuOH·DMSe.

Experiment	A	B	C	D	E
P(DMSe) ^a	40.2	44.3	71.9	108.2	149.0
P(t-BuOH) ^a	4.064	3.762	3.978	3.978	3.978
Scalefactor DMSe	0.978	0.979	1.005	0.99	0.976
Scalefactor t-BuOH	0.945	0.915	0.95	0.95	0.87
Temperature ^b	296	296	295	295	295
Int. Abs. ^c	0.76	0.45	1.18	1.18	2.49

a: Pressure before multiplication with corresponding scalefactor, given in Torr.

b: Temperature given in K.

c: Given in cm^{-1} .

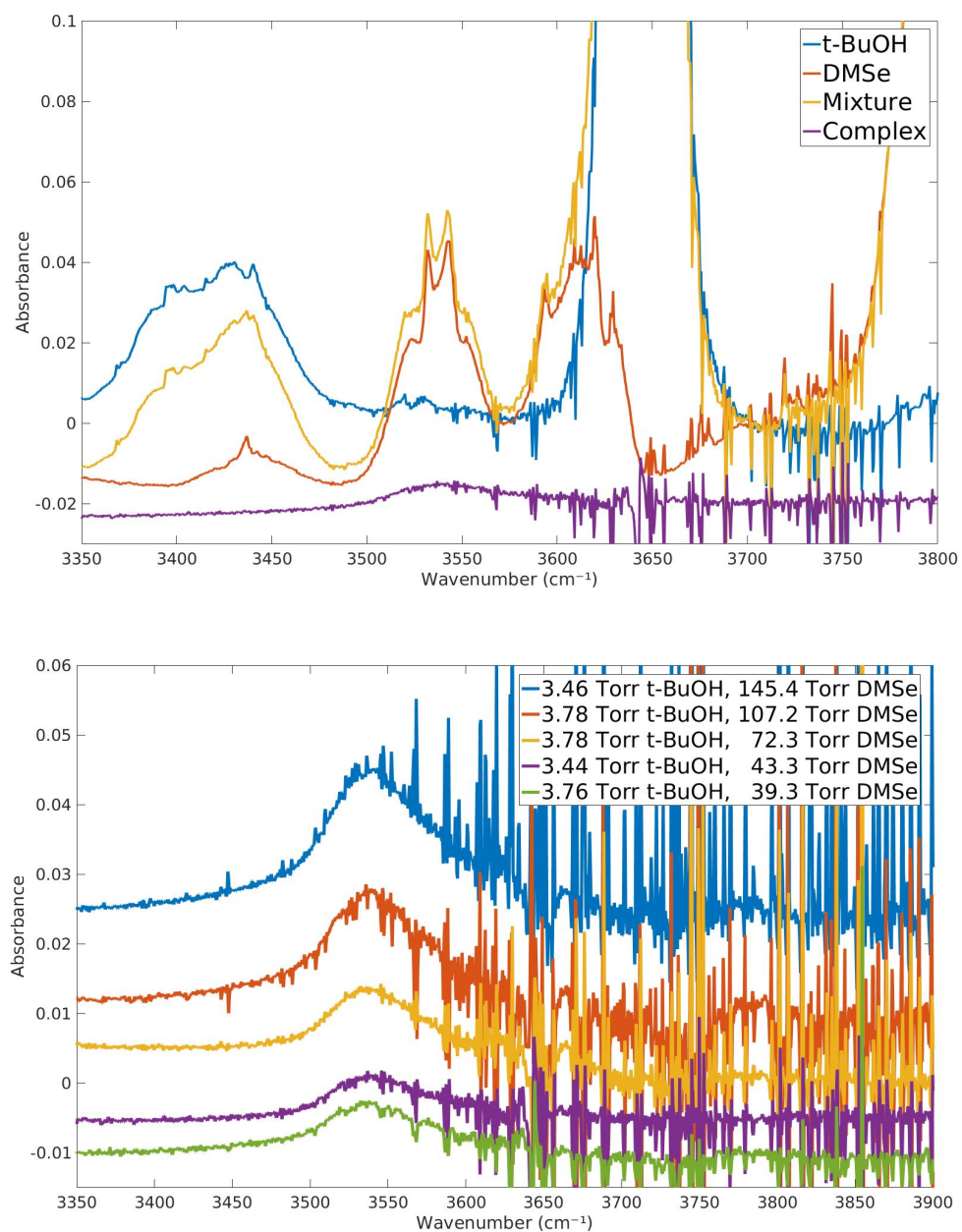


Figure S15: **Top:** spectra of t-BuOH monomer, DMSe monomer, the mixture and the complex spectrum (shown for experiment B, Table S14). **Bottom:** Spectra of t-BuOH·DMSe using various pressure combination of t-BuOH and DMSe. The spectra are off-set vertically for clarity.

S3.6.4 TFE·DMSe

The optical pathlength for the experiment was 2.4 m. The integrated absorbance was measured from 3196 to 3697 cm^{-1} and is estimated to have a 9% uncertainty and two standard deviations on the linear fit is 23%. Propagated uncertainty of 43%.

Table S15: Experimental details for TFE·DMSe.

Experiment	A	B	C	D	E
P(DMSe) ^a	36.2	96.3	47.0	57.3	115.1
P(TFE) ^a	1.03	2.28	2.41	2.41	3.16
Scalefactor DMSe	0.93	0.418	0.88	0.89	0.71
Scalefactor TFE	1	1.009	0.97	0.975	0.97
Temperature ^b	295	295	296	296	296
Int. Abs ^c	2.87	3.37	4.12	5.07	9.98

a: Pressure before multiplication with corresponding scalefactor, given in Torr.

b: Temperature given in K.

c: Given in cm^{-1} .

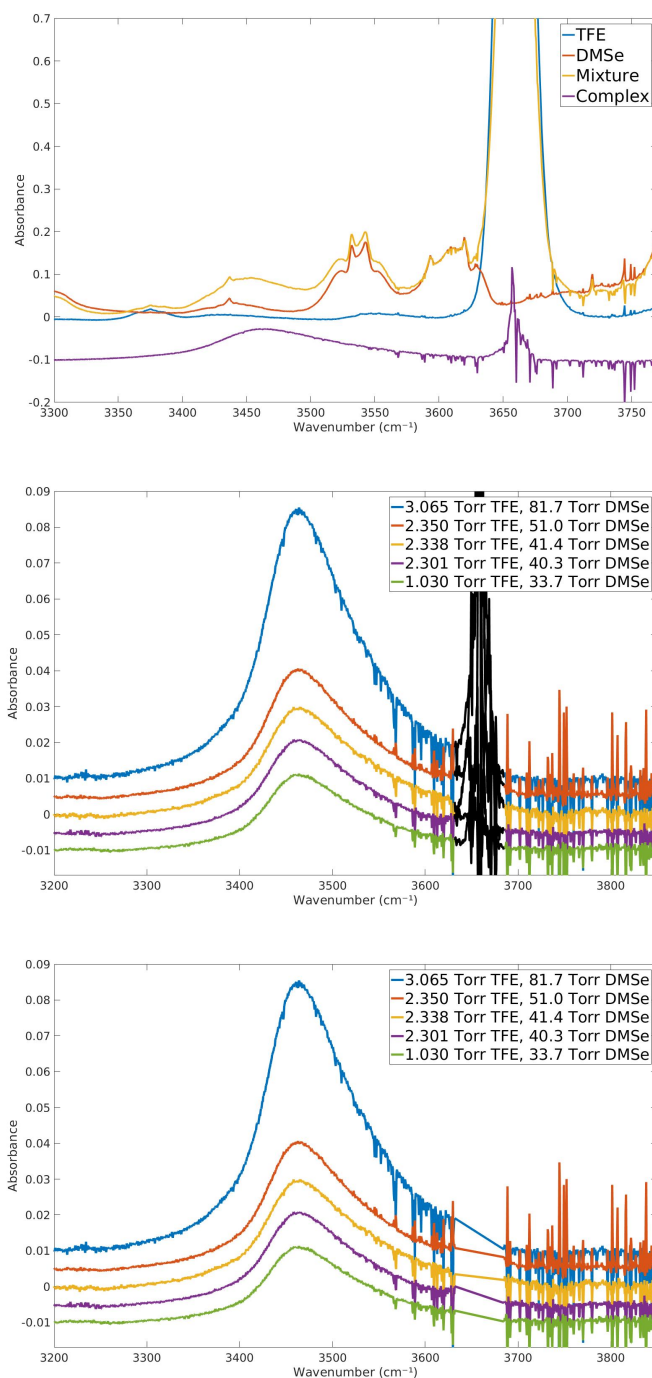


Figure S16: **Top:** Spectra of TFE, DMSe, the mixture of the two and the complex spectrum. **Middle:** Complex spectra of TFE·DMSe using various pressure combinations of TFE and DMSe. The black region is from the OH stretch of TFE, which is present because of over-saturation. **Bottom:** Spectra of the complex, which have been corrected for TFE monomer saturation, which were used to obtain integrated absorbances.

S3.6.5 PhOH·DMSe

The optical pathlength for the experiment was 16 m.

Table S16: Experimental details for PhOH·DMSe.

Experiment	A
P(DMSe) ^a	101.6
P(PhOH) ^a	0.325
Scalefactor DMSe	0.984
Scalefactor PhOH	0.187
Temperature ^b	296

a: Pressure before multiplication with corresponding scalefactor, given in Torr.

b: Temperature given in K.

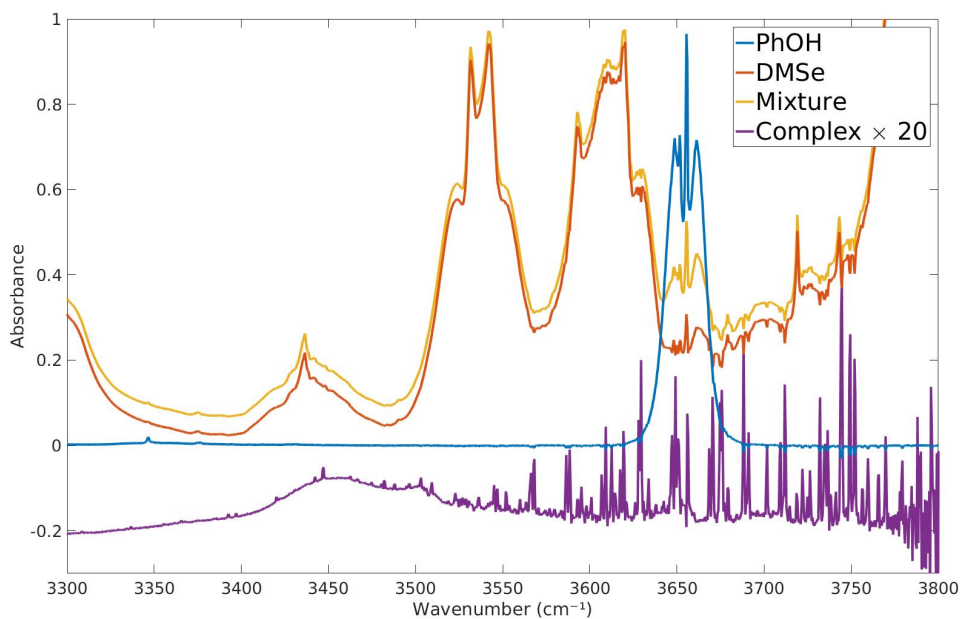


Figure S17: Spectra of PhOH, DMSe, the mixture of the two and the complex spectrum. The spectrum of the complex is upscaled by a factor of 20.

References

- (1) Biswal, H. S.; Chakraborty, S.; Wategaonkar, S. Experimental Evidence of O-H-S Hydrogen Bonding in Supersonic Jet. *J. Chem. Phys.* **2008**, *129*, 184311.
- (2) Mishra, K. K.; Singh, S. K.; Ghosh, P.; Ghosh, D.; Das, A. The Nature of Selenium Hydrogen Bonding: Gas Phase Spectroscopy and Quantum Chemistry Calculations. *Phys. Chem. Chem. Phys.* **2017**, *19*, 24179–24187.
- (3) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et. al, Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT. 2013.
- (4) Du, L.; Tang, S.; Hansen, A. S.; Frandsen, B. N.; Maroun, Z.; Kjaergaard, H. G. Subtle Differences in the Hydrogen Bonding of Alcohol to Divalent Oxygen and Sulfur. *Chem. Phys. Lett.* **2017**, *667*, 146–153.