Electronic supplementary material

Hydrogen Bonding in the Alcohol−Ethylene Oxide and Alcohol−Ethylene Sulfide Complexes

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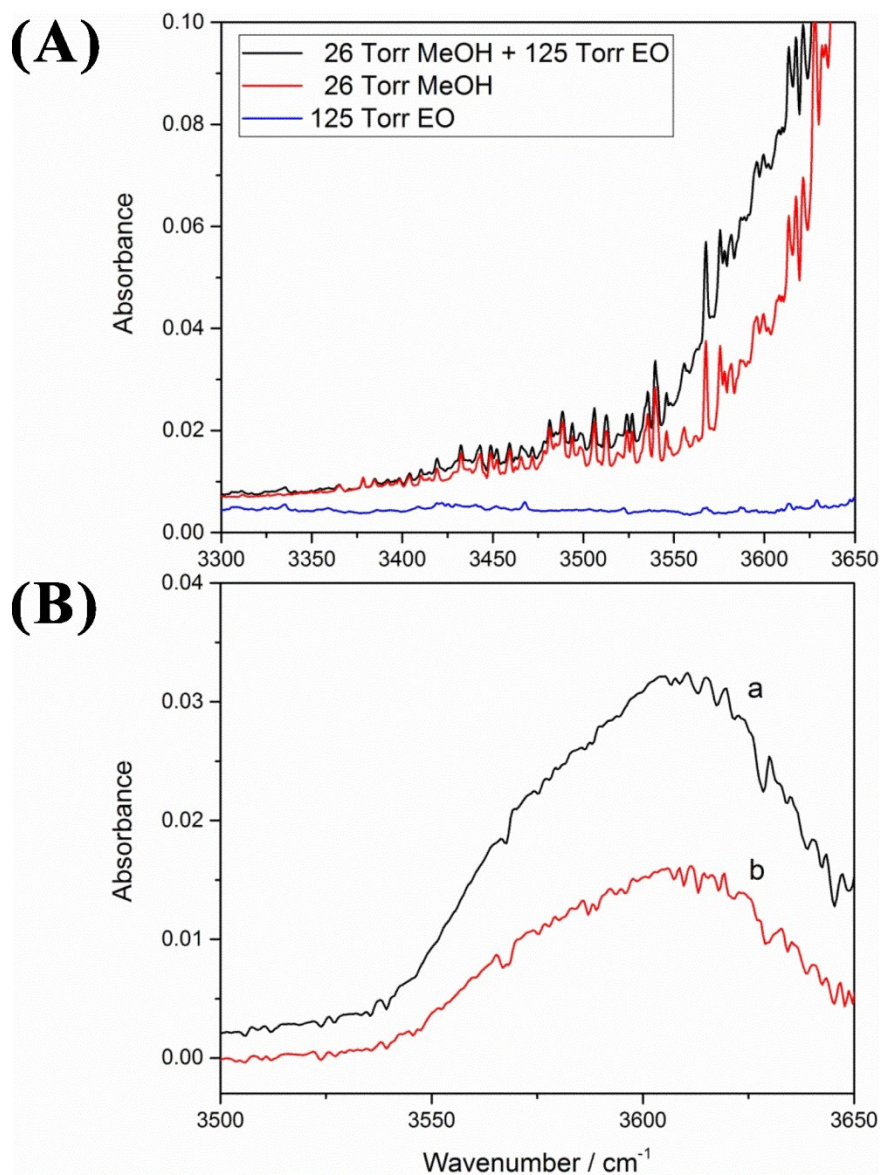
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Figure S1. (A) Spectra of MeOH, EO, and their mixture in the 3300-3650 cm^{-1} region. A 20 cm path length cell was used. (B) Spectra of the MeOH−EO complex in the ν_{OH} band region. (a) 26 Torr MeOH + 125 Torr EO; (b) 20 Torr MeOH + 90 Torr EO.
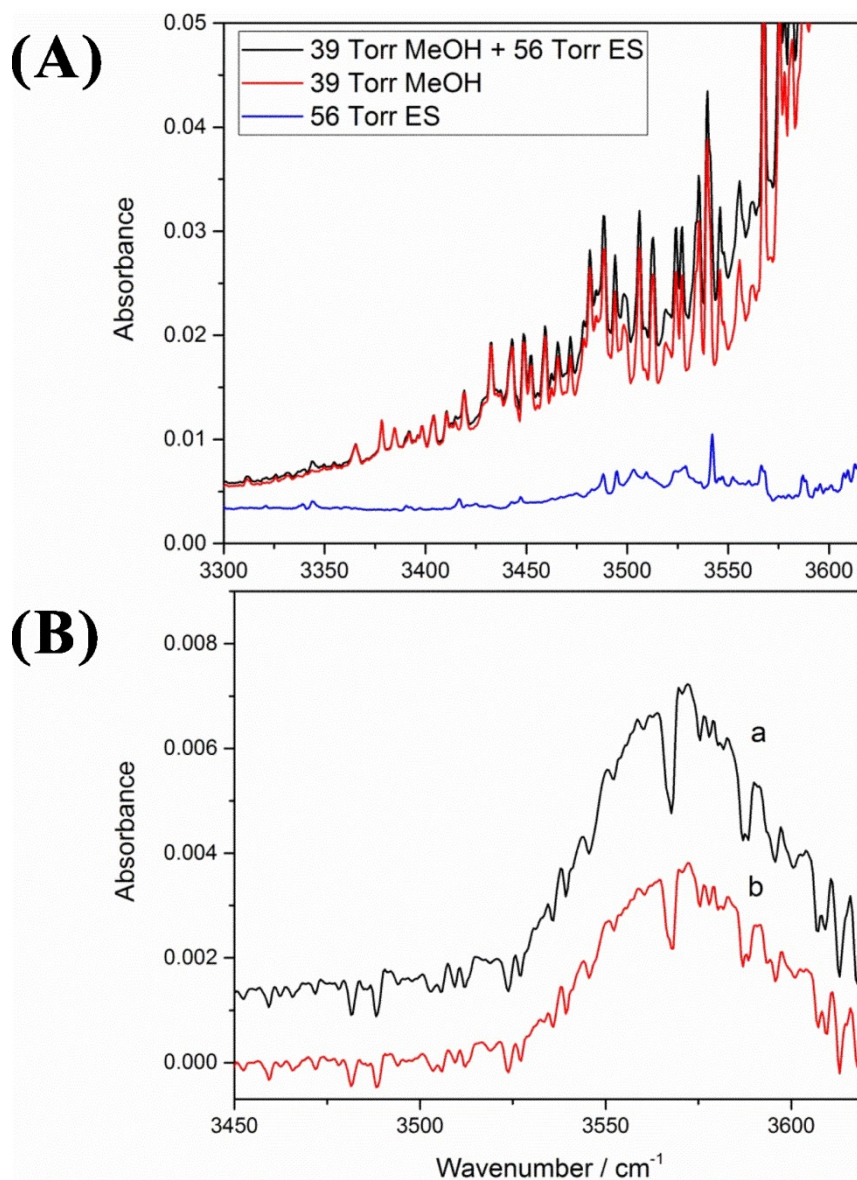
Figure S2. (A) Spectra of MeOH, ES, and their mixture in the 3300-3620 cm^{-1} region. A 20 cm path length cell was used. (B) Spectra of the MeOH−ES complex in the ν_{OH} band region. (a) 39 Torr MeOH + 56 Torr ES; (b) 30 Torr MeOH + 49 Torr ES.

Figure S3. (A) Spectra of EtOH, EO, and their mixture in the 3300-3650 cm^{-1} region. A 20 cm path length cell was used. (B) Spectra of the EtOH−EO complex in the ν_{OH} band region. (a) 22 Torr EtOH + 127 Torr EO; (b) 18 Torr EtOH + 93 Torr EO.
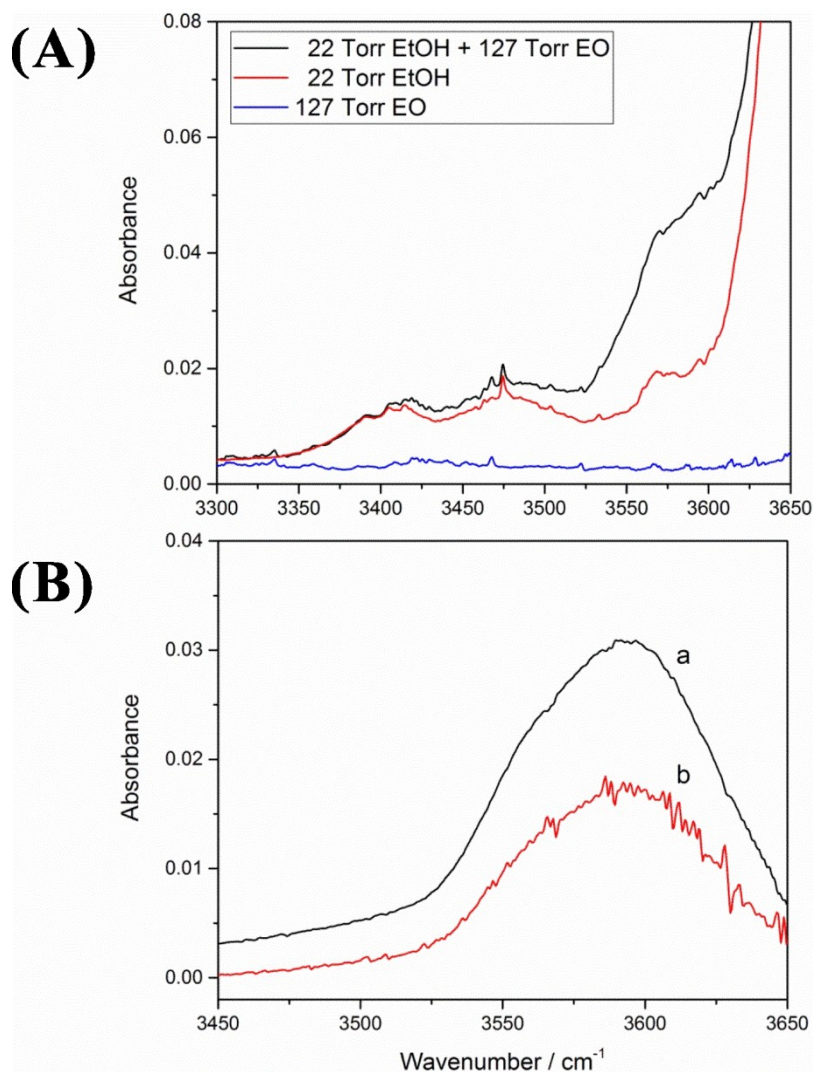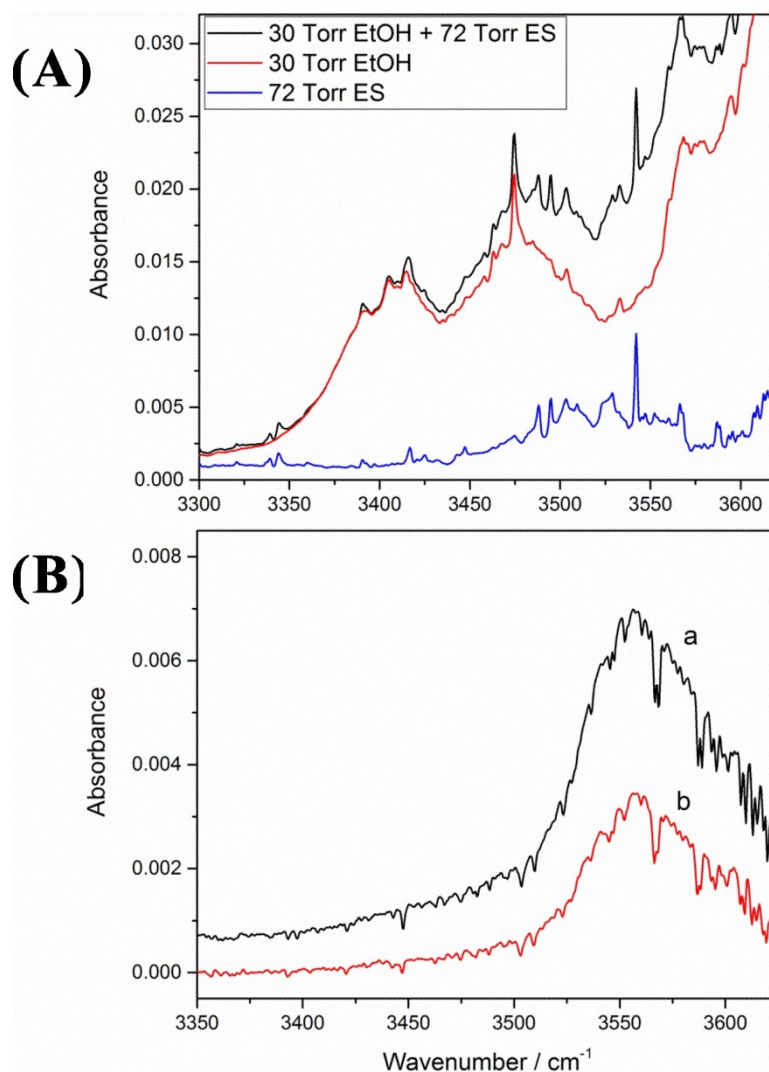
Figure S4. (A) Spectra of EtOH, ES, and their mixture in the 3300-3620 cm^{-1} region. A 20 cm path length cell was used. (B) Spectra of the EtOH−ES complex in the ν_{OH} band region. (a) 30 Torr EtOH + 72 Torr ES; (b) 21 Torr EtOH + 54 Torr ES.

Figure S5. (A) The integrated absorbance of the OH-stretching band in the MeOH-EO, EtOH−EO and TFE−EO complexes as a function of the product of the MeOH/EtOH/TFE and EO pressures. A 20 cm path length cell was used. The integration regions for MeOH-EO, EtOH−EO and 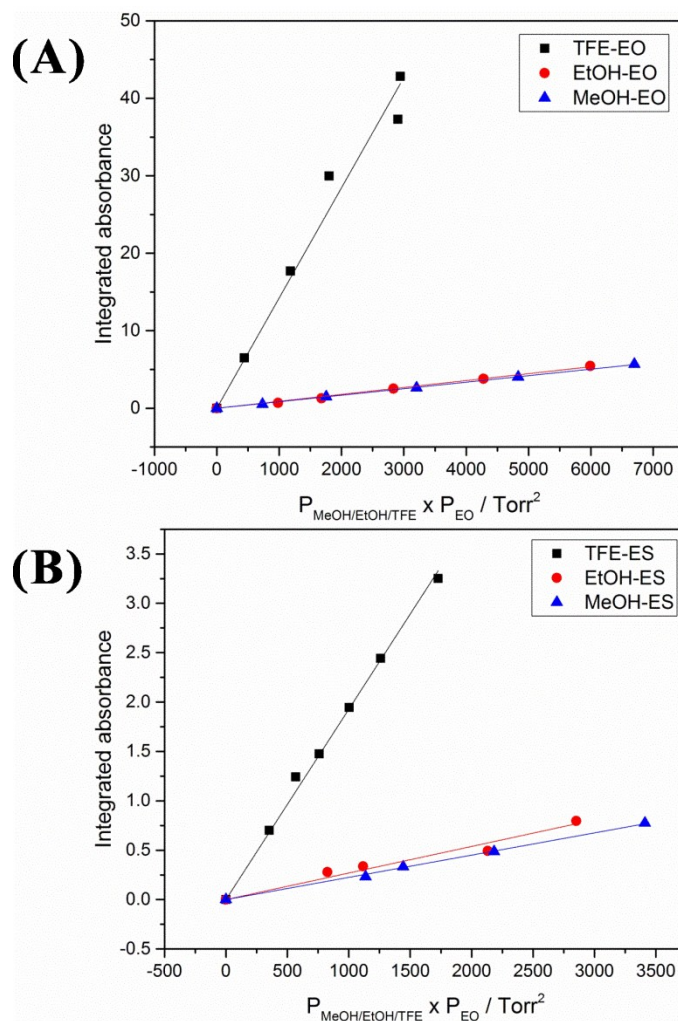TFE−EO are 3398-3674, 3397-3658 and 3219-3659 cm^{-1}, respectively; (B) The integrated absorbance of the OH-stretching band in the MeOH-ES, EtOH−ES and TFE−ES complexes as a function of the product of the MeOH/EtOH/TFE and ES pressures. A 20 cm path length cell was used. The integration regions for MeOH-ES, EtOH−ES and TFE−ES are 3420-3628, 3371-3629 and 3259-3626 cm^{-1}, respectively.
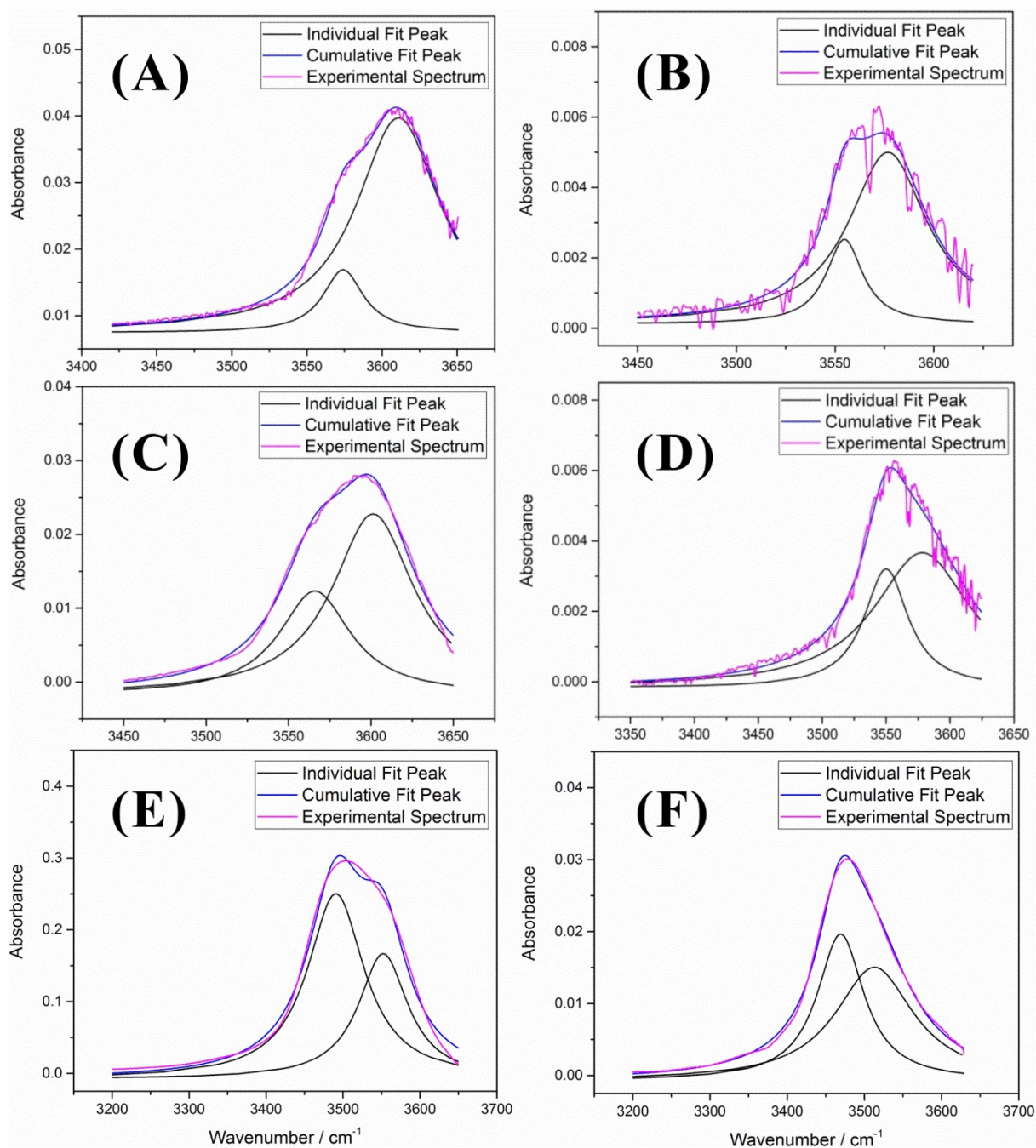
Figure S6. The deconvolution fittings of the OH-stretching fundamental transition bands of MeOH−EO (a), MeOH−ES (b), EtOH−EO (c), EtOH−ES (d). TFE−EO (e) and TFE−ES (f)
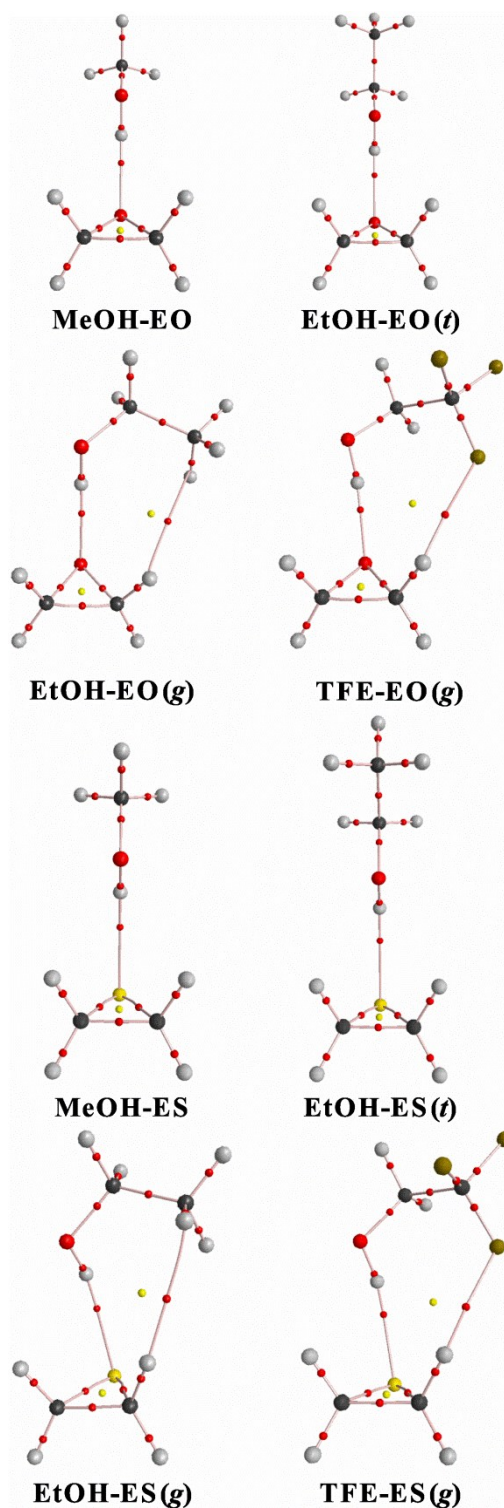
Figure S7. AIM plots of the complexes obtained with the B3LYP-D3 method. The bond critical points and ring critical points are presented by the red and yellow balls, respectively.

Table S1. Selected optimized geometric parameters in the complexes (angles in degrees and bond lengths in Å)

Conformer	Method [a]	$r_{(OH)}$ [b]	$\Delta r_{(OH)}$ [c]	$r_{(HB)}$ [d]	$\theta_{(HB)}$ [e]
MeOH−EO	B3LYP	0.9693	0.0086	1.9205	161.6
	ωB97X-D	0.9654	0.0092	1.9069	156.9
EtOH−EO (*t*)	B3LYP	0.9695	0.0084	1.9278	161.3
	ωB97X-D	0.9655	0.0090	1.9119	156.3
EtOH−EO (*g*)	B3LYP	0.9699	0.0080	1.9357	160.3
	ωB97X-D	0.9660	0.0085	1.9211	158.3
TFE−EO (*g*)	B3LYP	0.9750	0.0121	1.8294	172.9
	ωB97X-D	0.9716	0.0132	1.8093	164.8
MeOH−ES	B3LYP	0.9692	0.0085	2.4401	151.5
	ωB97X-D	0.9647	0.0085	2.4172	149.8
EtOH−ES (*t*)	B3LYP	0.9693	0.0082	2.4515	151.1
	ωB97X-D	0.9646	0.0081	2.4326	147.7
EtOH−ES (*g*)	B3LYP	0.9696	0.0077	2.4676	149.5
	ωB97X-D	0.9655	0.0080	2.4261	152.2
TFE−ES (*g*)	B3LYP	0.9747	0.0118	2.3456	168.0
	ωB97X-D	0.9707	0.0123	2.3128	156.3

[a] aug-cc-pV(T+d)Z basis set for S and aug-cc-pVTZ basis set for the remaining atoms. [b] OH bond length. [c] $\Delta r_{(OH)} = r_{complex} - r_{alcohol}$, is the change in the OH bond length upon complexation. [d] Intermolecular hydrogen bond distance. [e] Intermolecular hydrogen bond angle, i.e., $\theta_{(O-H\cdots O)}$ and $\theta_{(O-H\cdots S)}$.

Table S2. Calculated binding energy (*BE*), enthalpy of formation (ΔH^{θ}_{298K}), Gibbs free energy of formation (ΔG^{θ}_{calc}) and equilibrium constant (K^{calc}_{eq}) at 298 K for the complexes

Conformer	Method [a]	*BE* [b]	ZPVE	BSSE	ΔH^{θ}_{calc}	ΔG^{θ}_{calc}	K^{calc}_{eq}
MeOH−EO	B3LYP	-14.5	5.1	0.4	-13.6	16.8	1.2×10^{-3}
	ωB97X-D	-19.3	5.5	0.6	-18.8	13.0	5.2×10^{-3}
EtOH−EO (*t*)	B3LYP	-14.4	4.6	0.4	-13.1	17.4	9.0×10^{-4}
	ωB97X-D	-19.3	5.2	0.6	-18.6	14.9	2.4×10^{-3}
EtOH−EO (*g*)	B3LYP	-14.1	4.8	0.4	-12.8	17.9	7.3×10^{-4}
	ωB97X-D	-19.9	6.3	0.7	-19.9	18.6	5.4×10^{-4}
TFE−EO (*g*)	B3LYP	-21.1	4.7	0.7	-20.2	14.7	2.7×10^{-3}
	ωB97X-D	-27.3	5.3	1.2	-27.2	10.2	1.6×10^{-2}
MeOH−ES	B3LYP	-12.3	3.9	0.4	-10.9	18.8	5.1×10^{-4}
	ωB97X-D	-18.5	4.7	0.5	-17.8	16.8	1.1×10^{-3}
EtOH−ES (*t*)	B3LYP	-12.1	3.5	0.5	-10.4	19.4	4.0×10^{-4}
	ωB97X-D	-18.9	4.5	0.5	-18.0	18.1	6.6×10^{-4}
EtOH−ES (*g*)	B3LYP	-11.8	3.6	0.4	-10.1	20.5	2.6×10^{-4}
	ωB97X-D	-19.8	5.1	0.6	-19.3	19.4	4.1×10^{-4}
TFE−ES (*g*)	B3LYP	-16.8	3.2	0.7	-15.4	18.5	5.7×10^{-4}
	ωB97X-D	-25.0	3.9	1.1	-24.4	13.6	4.1×10^{-3}

[a] aug-cc-pV(T+d)Z basis set for S and aug-cc-pVTZ basis set for the remaining atoms. Energies are in kJ mol^{-1}. [b] *BE* corrected with ZPVE and BSSE.

Table S3. Calculated harmonic OH-stretching wavenumbers and oscillator strengths [a]

Conformer		B3LYP	ωB97X-D
MeOH	$\tilde{\nu}$ / cm^{-1}	3829	3918
	f_{MeOH}	5.8×10^{-6}	6.4×10^{-6}
EtOH (t)	$\tilde{\nu}$ / cm^{-1}	3825	3914
	$f_{EtOH\,(t)}$	5.4×10^{-6}	6.0×10^{-6}
EtOH (g)	$\tilde{\nu}$ / cm^{-1}	3810	3896
	$f_{EtOH\,(g)}$	4.2×10^{-6}	4.6×10^{-6}
TFE (g)	$\tilde{\nu}$ / cm^{-1}	3806	3892
	$f_{TFE\,(g)}$	9.2×10^{-6}	9.5×10^{-6}
MeOH−EO	$\tilde{\nu}$ / cm^{-1}	3656	3737
	$\Delta\tilde{\nu}$ / cm^{-1} [b]	173	181
	f	9.5×10^{-5}	8.7×10^{-5}
	f/f_{MeOH}	16.4	13.6
EtOH−EO (t)	$\tilde{\nu}$ / cm^{-1}	3655	3736
	$\Delta\tilde{\nu}$ / cm^{-1} [b]	170	178
	f	1.0×10^{-4}	9.1×10^{-5}
	$f/f_{EtOH\,(t)}$	18.6	15.1
EtOH−EO (g)	$\tilde{\nu}$ / cm^{-1}	3649	3733
	$\Delta\tilde{\nu}$ / cm^{-1} [b]	161	163
	f	8.6×10^{-5}	6.9×10^{-5}
	$f/f_{EtOH\,(g)}$	20.2	15.0
TFE−EO (g)	$\tilde{\nu}$ / cm^{-1}	3553	3621
	$\Delta\tilde{\nu}$ / cm^{-1} [b]	253	271
	f	1.5×10^{-4}	1.4×10^{-4}
	$f/f_{TFE\,(g)}$	16.5	14.3
MeOH−ES	$\tilde{\nu}$ / cm^{-1}	3651	3749
	$\Delta\tilde{\nu}$ / cm^{-1} [b]	177	169
	f	8.0×10^{-5}	6.1×10^{-5}
	f/f_{MeOH}	13.7	9.5
EtOH−ES (t)	$\tilde{\nu}$ / cm^{-1}	3654	3752
	$\Delta\tilde{\nu}$ / cm^{-1} [b]	171	162
	f	8.2×10^{-5}	5.9×10^{-5}
	$f/f_{EtOH\,(t)}$	15.2	9.8
EtOH−ES (g)	$\tilde{\nu}$ / cm^{-1}	3650	3736
	$\Delta\tilde{\nu}$ / cm^{-1} [b]	160	161
	f	7.0×10^{-5}	5.9×10^{-5}
	$f/f_{TFE\,(g)}$	16.5	12.7
TFE−ES (g)	$\tilde{\nu}$ / cm^{-1}	3547	3632
	$\Delta\tilde{\nu}$ / cm^{-1} [b]	259	259
	f	1.5×10^{-4}	1.2×10^{-4}
	$f/f_{TFE\,(g)}$	16.1	12.6

[a] aug-cc-pV(T+d)Z basis set for S and aug-cc-pVTZ basis set for all the remaining atoms. [b] $\Delta\tilde{\nu}_{OH} = \tilde{\nu}_{alcohol} - \tilde{\nu}_{complex}$.

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Table S4. AIM parameters for the complexes (all values in a.u.) [a]

	Conformer		$\Delta q(H)$	$\Delta E(H)$	$\rho(BCP)$	$\nabla^2\rho(BCP)$
B3LYP	MeOH−EO	O−H···O	0.0365	0.0213	0.0278	0.0845
	EtOH−EO (*t*)	O−H···O	0.0363	0.0203	0.0273	0.0838
	EtOH−EO (*g*)	O−H···O	0.0398	0.0222	0.0268	0.0831
	TFE−EO (*g*)	O−H···O	0.0375	0.0240	0.0340	0.0908
	MeOH−ES	O−H···S	0.0043	0.0114	0.0186	0.0404
	EtOH−ES (*t*)	O−H···S	0.0095	0.0149	0.0182	0.0400
	EtOH−ES (*g*)	O−H···S	0.0119	0.0159	0.0176	0.0393
	TFE−ES (*g*)	O−H···S	-0.0035	0.0097	0.0231	0.0417
ωB97X-D	MeOH−EO	O−H···O	0.0399	0.0228	0.0288	0.0882
	EtOH−EO (*t*)	O−H···O	0.0328	0.0207	0.0285	0.0879
	EtOH−EO (*g*)	O−H···O	0.0416	0.0259	0.0281	0.0862
	TFE−EO (*g*)	O−H···O	0.0457	0.0326	0.0362	0.0954
	MeOH−ES	O−H···S	0.0136	0.0151	0.0195	0.0433
	EtOH−ES (*t*)	O−H···S	0.0065	0.0135	0.0189	0.0429
	EtOH−ES (*g*)	O−H···S	0.0120	0.0166	0.0190	0.0424
	TFE−ES (*g*)	O−H···S	0.0118	0.0224	0.0242	0.0459

[a] aug-cc-pV(T+d)Z basis set for S and aug-cc-pVTZ basis set for all the remaining atoms. All values are in a.u.

Table S5. NBO parameters for the alcohol−EO complexes at the B3LYP/aug-cc-pVTZ level [a]

NBO parameters	MeOH−EO	EtOH−EO (*t*)	EtOH−EO (*g*)	TFE−EO (*g*)
$\Delta q(H)$	0.02422	0.01856	0.01999	0.02087
$\Delta q(O)$	-0.02531	-0.02428	-0.02495	-0.03562
$\delta(n_O)$	1.986, 1.921	1.986, 1.921	1.986, 1.921	1.984, 1.919
$\delta(\sigma^*_{O-H})$	0.0233	0.0221	0.0239	0.0310
$E^{(2)}_{i \to j^*}$	31.76 (6.78+24.98)	31.00 (6.57+24.43)	30.34 (6.49+23.85)	48.87 (12.80+36.07)
$\varepsilon^{(0)}_{j^*} - \varepsilon^{(0)}_i$	2.01 (1.22+0.79)	2.02 (1.23+0.79)	2.01 (1.22+0.79)	1.98 (1.19+0.79)
$\langle \varphi^{(0)}_i \mid \hat{F}_{KS} \mid \varphi^{(0)}_{j^*} \rangle$	0.102 (0.04+0.062)	0.101 (0.039+0.062)	0.100 (0.039+0.061)	0.129 (0.054+0.075)

[a] The values in the parentheses give the individual contribution of the nonbonding orbitals of oxygen. The $\delta(n_{pO})$ values are for each of the two lone pairs. $E^{(2)}_{i \to j^*}$ is in kJ mol⁻¹, all other values are in a.u.

Table S6. NBO parameters for the alcohol−EO complexes at the ωB97X-D/aug-cc-pVTZ level [a]

NBO parameters	MeOH−EO	EtOH−EO (t)	EtOH−EO (g)	TFE−EO (g)
Δq(H)	0.02305	0.01775	0.01861	0.01803
Δq(O)	-0.02592	-0.02515	-0.02533	-0.02967
$\delta(n_O)$	1.987, 1.920	1.987, 1.920	1.987, 1.920	1.984, 1.916
$\delta(\sigma^*_{O\text{-}H})$	0.0232	0.0223	0.0240	0.0327
$E^{(2)}_{i\to j*}$	39.46 (7.49+31.97)	38.83 (7.32+31.51)	38.29 (7.45+30.84)	63.51 (13.01+50.50)
$\varepsilon^{(0)}_{j*} - \varepsilon^{(0)}_{i}$	2.35 (1.39+0.96)	2.36 (1.40+0.96)	2.35 (1.39+0.96)	2.31 (1.36+0.95)
$\langle \varphi^{(0)}_{i} \mid \hat{F}_{KS} \mid \varphi^{(0)}_{j*} \rangle$	0.123 (0.045+0.078)	0.121 (0.044+0.077)	0.121 (0.045+0.076)	0.155 (0.058+0.097)

[a] The values in the parentheses give the individual contribution of the nonbonding orbitals of oxygen. The $\delta(n_{pO})$ values are for each of the two lone pairs. $E^{(2)}_{i\to j*}$ is in kJ mol^{-1}, all other values are in a.u.

Table S7. NBO parameters for the alcohol−ES complexes at the B3LYP/aug-cc-pVTZ level [a] ($E^{(2)}_{i\to j*}$ is in kJ mol^{-1}, all other values are in a.u.)

NBO parameters	MeOH−ES	EtOH−ES (t)	EtOH−ES (g)	TFE−ES (g)
Δq(H)	0.00780	0.00669	0.00826	0.00371
Δq(S)	-0.02145	-0.02137	-0.02293	-0.01486
$\delta(n_S)$	1.996, 1.923	1.996, 1.924	1.996, 1.925	1.994, 1.911
$\delta(\sigma^*_{O\text{-}H})$	0.0286	0.0265	0.0280	0.0432
$E^{(2)}_{i\to j*}$	27.95 (1.63+26.32)	26.31 (1.42+24.89)	25.11 (1.51+23.60)	47.41 (3.31+44.10)
$\varepsilon^{(0)}_{j*} - \varepsilon^{(0)}_{i}$	1.83 (1.14+0.69)	1.84 (1.14+0.70)	1.83 (1.14+0.69)	1.80 (1.12+0.68)
$\langle \varphi^{(0)}_{i} \mid \hat{F}_{KS} \mid \varphi^{(0)}_{j*} \rangle$	0.037 (0.019+0.060)	0.076 (0.018+0.058)	0.074 (0.018+0.056)	0.104 (0.027+0.077)

[a] The values in the parentheses give the individual contribution of the nonbonding orbitals of oxygen. The $\delta(n_{pO})$ values are for each of the two lone pairs. $E^{(2)}_{i\to j*}$ is in kJ mol^{-1}, all other values are in a.u.

Table S8. NBO parameters for the alcohol−ES complexes at the ωB97X-D/aug-cc-pVTZ level ^{a} ($E_{i \to j*}^{(2)}$ is in kJ mol^{-1}, all other values are in a.u.)

NBO parameters	MeOH−ES	EtOH−ES (t)	EtOH−ES (g)	TFE−ES (g)
$\Delta q(H)$	0.00822	0.00777	0.00879	0.00453
$\Delta q(S)$	-0.02106	-0.02133	-0.02229	-0.01645
$\delta(n_S)$	1.996, 1.926	1.996, 1.927	1.995, 1.926	1.995, 1.913
$\delta(\sigma^*_{O-H})$	0.0270	0.0246	0.0280	0.0414
$E_{i \to j*}^{(2)}$	35.61 (2.22+33.39)	32.71 (1.92+30.79)	35.02 (2.26+32.76)	60.42 (3.81+56.61)
$\varepsilon_{j*}^{(0)} - \varepsilon_i^{(0)}$	2.17 (1.31+0.86)	2.18 (1.32+0.86)	2.17 (1.31+0.86)	2.12 (1.28+0.84)
$\langle \varphi_i^{(0)} | \hat{F}_{KS} | \varphi_{j*}^{(0)} \rangle$	0.099 (0.024+0.075)	0.094 (0.022+0.072)	0.098 (0.024+0.074)	0.127 (0.031+0.096)

^{a} The values in the parentheses give the individual contribution of the nonbonding orbitals of oxygen. The $\delta(n_{pO})$ values are for each of the two lone pairs. $E_{i \to j*}^{(2)}$ is in kJ mol^{-1}, all other values are in a.u.