Supporting Information:

Hybridization of Nitrogen Determines Hydrogen Bond Acceptor Strength: Gas Phase Comparison of Redshifts and Equilibrium Constants

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S1 Equilibrium Constant Determination

S1.1 Effect of Condensation of AN

Figure S1 shows the pressure measured using the Agilent Technologies capacitance diaphragm CDG-500 pressure gauge attached to a closed 10 cm cell filled with 59 Torr AN. The observed pressure decrease is ascribed condensation of AN.



Figure S1. Pressure of AN in the 10 cm cell as a function of time. The observed decrease in pressure is ascribed condensation.

S1.2 Spectral Subtraction of Water

Despite purging of the spectrometer with dry N_2 , absorbance from water in the ambient air surrounding the cell was still visible in the recorded alcohol-acetonitrile spectra. To reduce the effect of the water absorbance, a spectrum of ambient air was recorded and subtracted from the measured spectrum of the complex. During subtraction, the spectrum of the air was scaled to most fully remove the water absorption peaks. The resulting spectra show only little water absorbance. An illustration of the effect of the spectral water subtraction is given in Figure S2.



Figure S2. Fundamental OH-stretch of the TFE-AN complex before and after water subtraction and the subtracted water spectrum. The spectrum was recorded with 1.61 Torr TFE and 24.74 Torr AN at 295.1 K in the 2.4 m cell (corresponding to Expt. A in Table S17). The spectra are offset for clarity.

S1.3 Detailed Description

The equilibrium constant for the complex formation, K_P , is defined as:

$$K_P = \frac{P_{complex}}{P_{momo1} \times P_{mono2}} \times P^{\ominus} ,$$

where $P_{complex}$ is the pressure of the complex and P_{mono1} and P_{mono2} are the pressures of the two monomers. P^{\ominus} is the standard pressure of 750.06 Torr. The pressures of the monomers are determined from the monomer pressures measured when recording the monomer spectra. In the mixture used for recording the spectra of the complexes, it is difficult to obtain the exact same pressures of the two monomers as used for their individual measurements. The monomer pressures are therefore obtained by subtracting the reference monomer spectra from the spectrum of the complex by using scaling factors to obtain a flat baseline in regions where the complex does not absorb. The monomer pressures are then obtained by multiplying the measured pressures of the reference spectra by the scaling factor.

As reference spectra cannot be obtained for the complex, its pressure needs to be obtained indirectly. This is done using the experimentally observed integrated absorbance of the OH-stretching band in the complex, $\int A(\tilde{v})d\tilde{v}$ and a calculated oscillator strength, f_{calc} , using the following equation:

$$P_{complex} = 2.6935 \times 10^{-9} \left[\text{K}^{-1} \text{ Torr m cm} \right] \frac{T \int A(\tilde{v}) d\tilde{v}}{f_{calc} \times l},$$

where *T* is the absolute temperature in K and *l* is the optical path length in m. Upon formation of the expected 1:1 complex, a plot of $P_{complex}$ as a function of $P_{mono1} \times P_{mono2}$ should yield a straight line. The slope of this line multiplied by the standard pressure yields the equilibrium constant of complex formation. Slopes are obtained by linear least square fits forced through (0,0). For each complex, the equilibrium constant is determined using an average of the temperatures of the individual measurements, see Table S22.

S1.4 Pressure Correction Pyr Complexes

For the alcohol-Pyr experiments pressures were measured with a Varian Pirani capacitance diaphragm (PCG750) gas-type dependent (below 10 mbar) pressure gauge. The pressures were corrected by fitting the vacuum line with both the PCG750 and a gas-type independent (Agilent Technologies capacitance diaphragm CDG-500) pressure gauge and filling the vacuum line with sample pressure corresponding to values originally measured with the PCG750 gauge. The pressure measured with the CDG-500 gauge is the corrected pressure and is within 0.6 Torr of that measured with the PCG750 pressure gauge for all measurements.

S2 Vibrational Coupling in TFE-TMA

For the TFE-TMA complex, the 2D LM and LMPT models show a very large effective coupling between redshifted fundamental OH-stretching and the first overtone of the COH-bend. This induced by the known overestimation of the redshift in the 1D LM basis.¹⁻ The overestimated redshift of the OH-stretch caused the two calculated band positions to be nearly degenerate leading to two bands separated by 274 cm⁻¹ with nearly equal contribution from the two original bands and of comparable intensity, see Table S9 and Table S10. The oscillator strength of the OH-stretch calculated using the 1D LMPT model (3.06×10^{-4}) is very similar to the total oscillator strength of the two bands in the 2D LMPT model (2.97×10^{-4}) suggesting that the OH-stretch provides nearly all the intensity. For the other TMA complexes, the 1D LMPT model provides results comparable to the 2D LMPT model, but with slightly higher (~10%) oscillator strengths, see Section S12.

S3 Non-Covalent Interactions (NCI)

The geometries of the conformers of the MeOH-AN and EtOH-AN complexes suggest that the linear (A) conformers are dominated by an OH-N H-bond, while the bent (B) conformers are dominated more by dispersion interactions and an OH- π H-bond. This assignment seems to be confirmed by non-covalent interactions, NCI, calculations. This is exemplified for the two conformers of MeOH-AN in Figure S3. MeOH-AN (A) assigned as dominated by an OH-N hydrogen bond shows only one NCI interaction between the two monomers, which is between the hydrogen and nitrogen atoms consistent with an OH-N H-bond. For MeOH-AN (B), the region of strong (blue) interaction between the hydrogen atom and the C=N bond suggests an OH- π hydrogen bond, while the region of weaker (green) interactions suggest dispersion interactions. For the EtOH-AN and TFE-AN complexes, the same trend is observed. For the gauche conformers of EtOH-AN and especially TFE-AN, other regions of dispersion interactions are also observed.



Figure S3. NCI isosurfaces for MeOH-AN at the ω B97X-D/aug-cc-pVTZ level of theory. The range of $\lambda_2 \times \rho(r)$ used for color-coding the NCI isosurfaces is -0.015 to 0.015 au at s = 0.5 au, where $s = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla \rho(r)|}{\rho(r)^{4/3}}$. The color-coding of the atoms is: white = H, gray = C, blue = N and red = O.



Figure S4. NCI isosurfaces for the EtOH-AN complexes at the ω B97X-D/aug-cc-pVTZ level of theory. The range of $\lambda_2 \times \rho(r)$ used for color-coding the NCI isosurfaces is -0.015 to 0.015 au at s = 0.5 au, where $s = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla \rho(r)|}{\rho(r)^{4/3}}$. The color-coding of the atoms is: white = H, gray = C, blue = N and red = O.



Figure S5. NCI isosurface for TFE-AN at the ω B97X-D/aug-cc-pVTZ level of theory. The range of $\lambda_2 \times \rho(r)$ used for color-coding the NCI isosurfaces is -0.015 to 0.015 au at s = 0.5 au, where $s = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla \rho(r)|}{\rho(r)^{4/3}}$. The color-coding of the atoms is: white = H, gray = C, blue = N, red = O and cyan = F.

S4 Relative Conformational Energies

S4.1 Monomers

Table S1. Relative conformational zero-point vibrational corrected electronic energy (Rel. E) calculated at the ω B97X-D/aug-cc-pVTZ level (ω B97X-D) or (where available) using the electronic energies of the CCSD-F12a/VDZ-F12 optimized structures combined with the ω B97X-D/aug-cc-pVTZ zero-point vibrational energy (F12) of the alcohol monomer conformers. Values are calculated relative to the most stable (lowest-energy) conformer.

Compound	Conformer	ωB97X-D Rel. E	F12 Rel. E
MeOH		_ ^a	_ ^a
EtOH	t-EtOH	0.0	0.0
	g-EtOH	0.047	0.49
TFE	t-TFE	7.0	_ ^b
	g-TFE	0.0	_ ^b
AN		- ^a	- ^a
Pyr		_ ^a	_ ^a
TMA		_ ^a	_ ^a

^a Only one conformer.

^bF12 calculation not conducted.

S4.2 Complexes

Table S2. Relative conformational zero-point vibrational corrected electronic energy (Rel. E) calculated at the ω B97X-D/aug-cc-pVTZ level (ω B97X-D) or (where available) using the electronic energies of the CCSD-F12a/VDZ-F12 optimized structures combined with the ω B97X-D/aug-cc-pVTZ zero-point vibrational energy (F12). Values are calculated relative to the most stable (lowest-energy) conformer. Structures are given in the main manuscript, Figure S6 and Figure S7.

Compound	Conformer	ωB97X-D Rel. E	F12 Rel. E
MeOH-AN	MeOH-AN (A)	0.0	0.21
	MeOH-AN (B)	1.1	0.0
EtOH-AN	t-EtOH-AN (A)	0.47	0.60
	g-EtOH-AN (A)	0.31	0.91
	t-EtOH-AN (B)	0.89	0.0
	g-EtOH-AN (B)	0.0	1.59
TFE-AN		_ ^a	_ ^a
MeOH-Pyr	MeOH-Pyr (N)	0.0	_ ^b
	MeOH-Pyr (π)	13	_ ^b
EtOH-Pyr	<i>t</i> -EtOH-Pyr	1.3	_ ^b
	g-EtOH-Pyr	0.0	_ ^b
TFE-Pyr		_ ^a	_ ^a
MeOH-TMA		_ ^a	_ ^a
EtOH-TMA	t-EtOH-TMA	1.0	_ ^b
	g-EtOH-TMA	0.0	_ ^b
TFE-TMA		_ ^a	_ ^a

^a Only one conformer.

^bF12 calculation not conducted.



Figure S6. Structures of the conformers of the alcohol-pyridine complexes optimized at the ω B97X-D/aug-cc-pVTZ level of theory. The dashed line represents the OH-N hydrogen bond. The color-coding of the atoms is: gray = C, red = O, white = H and blue = N.



Figure S7. Structures of the conformers of the alcohol-TMA complexes optimized at the ω B97X-D/aug-cc-pVTZ level of theory. The dashed line represents the OH-N hydrogen bond. The color-coding of the atoms is: gray = C, red = O, white = H and blue = N.

S6 Calculated Gibbs Free Energies and Equilibrium Constants

Table S3. Calculated standard Gibbs free energies of complexation (kJ/mol) for the various complexes at 298.15 K. All values are calculated relative to the monomer conformer lowest in Gibbs free energy at the given level. All DFT values are calculated using the aug-cc-pVTZ basis set, while the F12 values use the cc-pVD-F12 basis set. The F12// ω B97X-D level employs F12 single-point calculations on the ω B97X-D geometry with thermal corrections at the ω B97X-D level. The F12 level is the same but using the F12 geometry. All calculations employ the rigid-rotor-harmonic-oscillator approximation.

Compound	Conformer	ωB97X-D	B3LYP	B3LYP-D3 ³	M06-2X ⁴	F12//ωB97X-D	F12
						(+ωB97X-D freq.)	(+ωB97X-D freq.)
MeOH-AN	MeOH-AN (A)	11.07	9.28	4.17	11.17	10.91	10.88
	MeOH-AN (B)	14.78	17.35	13.19	14.57	13.37	13.31
EtOH-AN	t-EtOH-AN (A)	9.91	9.90	21.18	10.60	9.52	9.49
	g-EtOH-AN (A)	11.07	11.91	22.94	11.03	11.11	11.08
	t-EtOH-AN (B)	14.13	18.31	13.35	13.90	12.71	12.65
	g-EtOH-AN (B)	17.65	19.12	15.38	18.33	18.97	18.65
TFE-AN		8.00	4.89	6.93	8.61	7.82	- ^a
MeOH-Pyr	MeOH-Pyr (N)	3.91	5.61	20.50	9.41	4.87	- ^a
	MeOH-Pyr (π)	19.55	17.22	16.94	20.87	20.71	- ^a
EtOH-Pyr	t-EtOH-Pyr	5.55	8.78	0.66	10.58	6.20	- ^a
	g-EtOH-Pyr	5.14	12.31	4.59	11.25	6.80	- ^a
TFE-Pyr		-4.88	5.32	-4.96	-1.17	-3.93	- ^a
MeOH-		0.63	11.35	-1.01	3.43	2.50	- ^a
TMA							
EtOH-TMA	t-EtOH-TMA	0.05	11.38	-1.22	5.98	1.80	_ ^a
	g-EtOH-TMA	5.73	14.78	3.88	9.03	8.85	- ^a
TFE-TMA		-3.30	8.31	-5.77	-5.82	-1.41	- ^a

^a Not optimized at the F12 level.

Table S4. Calculated equilibrium constants of complexation for the various complexes at 298.15 K. All values are calculated relative to the monomer conformer lowest in Gibbs free energy at the given level. All DFT values are calculated using the aug-cc-pVTZ basis set, while the F12 values use the cc-pVD-F12 basis set. The F12// ω B97X-D level employs F12 single-point calculations on the ω B97X-D geometry with thermal corrections at the ω B97X-D level. The F12 level is the same but using the F12 geometry. All calculations employ the rigid-rotor-harmonic-oscillator approximation.

Compound	Conformer	ωB97X-D	B3LYP	B3LYP-D3	M06-2X	F12//ωB97X-D	F12
						(+ωB97X-D freq.)	(+ωB97X-D freq.)
MeOH-AN	MeOH-AN (A)	1.15×10 ⁻²	2.37×10 ⁻²	1.86×10 ⁻¹	1.10×10 ⁻²	1.22×10 ⁻²	1.24×10 ⁻²
	MeOH-AN (B)	2.58×10-3	9.13×10 ⁻⁴	4.88×10 ⁻³	2.81×10-3	4.55×10 ⁻³	4.67×10 ⁻³
EtOH-AN	t-EtOH-AN (A)	1.84×10 ⁻²	1.84×10 ⁻²	1.95×10 ⁻⁴	1.39×10 ⁻²	2.15×10 ⁻²	2.17×10 ⁻²
	g-EtOH-AN (A)	1.15×10 ⁻²	8.19×10 ⁻³	9.59×10 ⁻⁵	1.17×10 ⁻²	1.13×10 ⁻²	1.14×10 ⁻²
	t-EtOH-AN (B)	3.35×10 ⁻³	6.20×10 ⁻⁴	4.58×10-3	3.67×10-3	5.93×10 ⁻³	6.08×10 ⁻³
	g-EtOH-AN (B)	8.08×10 ⁻⁴	4.47×10 ⁻⁴	2.02×10-3	6.15×10 ⁻⁴	4.75×10 ⁻⁴	5.40×10 ⁻⁴
TFE-AN		3.97×10 ⁻²	1.39×10 ⁻¹	6.10×10 ⁻²	3.10×10 ⁻²	4.27×10 ⁻²	- ^a
MeOH-Pyr	MeOH-Pyr (N)	2.06×10 ⁻¹	1.04×10 ⁻¹	2.56×10-4	2.24×10 ⁻²	1.40×10 ⁻¹	- ^a
	MeOH-Pyr (π)	3.76×10 ⁻⁴	9.62×10 ⁻⁴	1.07×10-3	2.21×10 ⁻⁴	2.36×10 ⁻⁴	- ^a
EtOH-Pyr	t-EtOH-Pyr	1.07×10 ⁻¹	2.90×10 ⁻²	6.56×10 ⁻¹	1.40×10 ⁻²	8.22×10 ⁻²	- ^a
	g-EtOH-Pyr	1.26×10 ⁻¹	6.96×10 ⁻³	1.57×10 ⁻¹	1.07×10 ⁻²	6.44×10 ⁻²	- ^a
TFE-Pyr		7.16×10^{0}	1.17×10 ⁻¹	7.41×10^{0}	1.60×10^{0}	4.89×10^{0}	- ^a
MeOH-		7.75×10 ⁻¹	1.03×10 ⁻²	1.51×10^{0}	2.51×10 ⁻¹	3.65×10 ⁻¹	- ^a
TMA							
EtOH-TMA	t-EtOH-TMA	9.80×10 ⁻¹	1.02×10 ⁻²	1.63×10^{0}	8.97×10 ⁻²	4.85×10 ⁻¹	_ ^a
	g-EtOH-TMA	9.90×10 ⁻²	2.57×10-3	2.09×10 ⁻¹	2.62×10 ⁻²	2.81×10 ⁻²	_ ^a
TFE-TMA		3.79×10^{0}	3.49×10 ⁻²	1.03×10^{1}	1.04×10^{1}	1.77×10^{0}	- ^a

^a Not optimized at the F12 level.

S7 Pressures and Temperatures for Spectra Shown in Figure 3 of the Main Manuscript

Table S5. Temperature (K) and scaled monomer pressures (Torr) for the spectra shown in Figure 3 of the main manuscript.

Complex	Temperature	Pressure alcohol	Pressure acetonitrile
MeOH-AN	296.3	1.90	40.78
EtOH-AN	296.5	1.49	54.47
TFE-AN	295.6	1.32	32.66



S8 MeOH-AN Spectrum in Larger Spectral Range

Figure S8. Spectrum of the MeOH-AN complex from experiment C, Table S14, showing larger spectral range than the corresponding spectrum in Figure 3 of the main manuscript.



S9 Lorentzian Fit of MeOH-AN

Figure S9. Fundamental OH-stretching transition in the MeOH-AN complex (black) and Lorentzian function (red) fitted to obtain the wavenumber. Temperature and pressures are given in Table S5.

S10 Calculated Wavenumbers and Oscillator Strengths

S10.1 Monomers

Table S6. ω B97X-D/aug-cc-pVTZ and CCSD(T)-F12a/VDZ-F12 2D local mode wavenumbers ($\tilde{\nu}$, cm⁻¹) and oscillator strengths (f) of the alcohol monomers.

		ĩ	f	
MeOH	ωB97X-D	3748	4.35×10 ⁻⁶	
	F12	3691	2.90×10 ⁻⁶	
g-EtOH	ωB97X-D	3728	3.02×10 ⁻⁶	
	F12	3661	2.60×10 ⁻⁶	
t-EtOH	ωB97X-D	3746	3.66×10 ⁻⁶	
	F12	3677	2.93×10 ⁻⁶	
g-TFE	ωB97X-D	3725	7.52×10 ⁻⁶	
	F12	-	-	
t-TFE	ωB97X-D	3757	8.27×10 ⁻⁶	
	F12	-	-	

S10.2 Complexes

S10.2.1 2D LMPT Results AN Complexes

Table S7. ω B97X-D/aug-cc-pVTZ and CCSD(T)-F12a/VDZ-F12 2D LMPT wavenumbers ($\tilde{\nu}$, cm⁻¹) and oscillator strengths (*f*) of the alcohol-AN complexes. No values are given for the (B) conformers, as the LMPT model has not been validated for this kind of complexes. No F12 values have been calculated for the TFE complex due to computational limitations.

		ν	f
MeOH-AN (A)	ωB97X-D	3651	7.48×10 ⁻⁵
	F12	3626	5.97×10 ⁻⁵
MeOH-AN (B)	ωB97X-D	-	-
	F12	-	-
t-EtOH-AN (A)	ωB97X-D	3650	8.09×10 ⁻⁵
	F12	3617	6.42×10 ⁻⁵
g-EtOH-AN (A)	ωB97X-D	3641	6.24×10 ⁻⁵
	F12	3610	5.36×10 ⁻⁵
t-EtOH-AN (B)	ωB97X-D	-	-
	F12	-	-
g-EtOH-AN (B)	ωB97X-D	-	-
	F12	-	-
TFE-AN (A)	ωB97X-D	3579	7.82×10 ⁻⁵
	F12	-	-

S10.2.2 2D LM Results AN Complexes

Table S8. ω B97X-D/aug-cc-pVTZ and CCSD(T)-F12a/VDZ-F12 2D LM wavenumbers ($\tilde{\nu}$, cm⁻¹) and oscillator strengths (f) of the alcohol-AN complexes.

		ĩ	f
		V	J
MeOH-AN (A)	ωB97X-D	3621	9.62×10 ⁻⁵
	F12	3603	7.97×10 ⁻⁵
MeOH-AN (B)	ωB97X-D	3688	2.03×10 ⁻⁵
	F12	3641	1.67×10 ⁻⁵
t-EtOH-AN (A)	ωB97X-D	3620	1.01×10 ⁻⁴
	F12	3595	8.46×10 ⁻⁵
g-EtOH-AN (A)	ωB97X-D	3618	8.18×10 ⁻⁵
	F12	3593	6.81×10 ⁻⁵
t-EtOH-AN (B)	ωB97X-D	3695	1.80×10 ⁻⁵
	F12	3635	1.52×10 ⁻⁵
g-EtOH-AN (B)	ωB97X-D	3680	1.09×10 ⁻⁵
	F12	3624	1.22×10 ⁻⁵
TFE-AN (A)	ωB97X-D	3553	8.91×10 ⁻⁵
	F12	-	-

S10.2.3 ωB97X-D/aug-cc-pVTZ 2D LM and LMPT Wavenumbers Pyr and TMA Complexes Table S9. ωB97X-D/aug-cc-pVTZ calculated 2D LM and LMPT and experimentally determined wavenumbers (cm⁻¹) of the fundamental OH-stretching band of the alcohol-Pyr and alcohol-TMA complexes.

	2D LM	2D LMPT	Expt.
MeOH-Pyr	3398	3465	3472
g-EtOH-Pyr	3390	3447	
t-EtOH-Pyr	3401	3465	3462
TFE-Pyr	3189	3255	3289
MeOH-TMA	3272	3350	
MeOH-TMA ^a	3260	3337	3355
g-EtOH-TMA	3271	3333	
t-EtOH-TMA	3270	3340	3345
TFE-TMA	2803/3074 ^b	2819/3093 ^b	3174

^a From reference ² at the CCSD(T)-F12a/VDZ-F12 level of theory.

^b Two values given due to resonance, see Section 2.

of the complexes.

S10.2.4 ωB97X-D/aug-cc-pVTZ 2D LM and LMPT Oscillator Strengths Pyr and TMA Complexes Table S10. ωB97X-D/aug-cc-pVTZ calculated 2D LM and LMPT oscillator strengths of the fundamental OH-stretching band

2D LM 2D LMPT MeOH-Pyr 1.93×10-4 1.70×10-4 g-EtOH-Pyr 1.84×10-4 1.66×10-4 t-EtOH-Pyr 2.02×10-4 1.78×10-4 TFE-Pyr 2.78×10⁻⁴ 2.54×10-4 MeOH-TMA 1.95×10-4 1.67×10-4 MeOH-TMA^a 1.86×10-4 1.58×10-4 g-EtOH-TMA 1.79×10-4 1.55×10-4 2.10×10-4 1.80×10-4 t-EtOH-TMA TFE-TMA 1.95×10⁻⁴/1.40×10^{-4, b} 1.72×10-4/1.25×10-4, b

^a From reference ² at the CCSD(T)-F12a/VDZ-F12 level of theory.

^b Two values given due to resonance, see Section 2.

S10.2.5 1D LM and LMPT Wavenumbers All Complexes

Table S11. ω B97X-D/aug-cc-pVTZ calculated 1D LM and LMPT wavenumbers (cm⁻¹) of the fundamental OH-stretching band of the complexes.

	1D LM	1D LMPT
MeOH-AN(A)	3622	3660
MeOH-AN(B)	3698	-
t-EtOH-AN(A)	3621	3664
g-EtOH-AN(A)	3620	3652
t-EtOH-AN(B)	3700	-
g-EtOH-AN(B)	3693	-
TFE-AN	3549	3585
MeOH-Pyr	3388	3469
g-EtOH-Pyr	3378	3451
t-EtOH-Pyr	3391	3476
TFE-Pyr	3153	3253
MeOH-TMA	3241	3346
g-EtOH-TMA	3240	3329
t-EtOH-TMA	3243	3343
TFE-TMA	2931	3066

S10.2.6 1D LM and LMPT Oscillator Strengths All Complexes

Table S12. ω B97X-D/aug-cc-pVTZ calculated 1D LM and LMPT oscillator strengths of the fundamental OH-stretching band of the complexes.

	1D LM	1D LMPT
MeOH-AN(A)	1.04×10 ⁻⁴	7.53×10 ⁻⁵
MeOH-AN(B)	1.95×10 ⁻⁵	-
t-EtOH-AN(A)	1.08×10 ⁻⁴	8.01×10 ⁻⁵
g-EtOH-AN(A)	8.80×10 ⁻⁵	6.11×10 ⁻⁵
t-EtOH-AN(B)	1.74×10 ⁻⁵	-
g-EtOH-AN(B)	1.14×10 ⁻⁵	-
TFE-AN	9.60×10 ⁻⁵	8.25×10 ⁻⁵
MeOH-Pyr	2.09×10 ⁻⁴	1.77×10 ⁻⁴
g-EtOH-Pyr	1.99×10 ⁻⁴	1.74×10 ⁻⁴
t-EtOH-Pyr	2.17×10 ⁻⁴	1.84×10 ⁻⁴
TFE-Pyr	3.32×10 ⁻⁴	2.95×10 ⁻⁴
MeOH-TMA	2.27×10 ⁻⁴	1.90×10 ⁻⁴
g-EtOH-TMA	2.07×10 ⁻⁴	1.73×10 ⁻⁴
t-EtOH-TMA	2.42×10 ⁻⁴	2.00×10 ⁻⁴
TFE-TMA	3.43×10 ⁻⁴	3.06×10 ⁻⁴

S11 Fundamental OH-stretching in EtOH-AN

Figure S10 shows the fundamental OH-stretching region of the EtOH-AN complex. The spectrum shows a single band, suggesting the presence of only one conformer.



Figure S10. Fundamental OH-stretching band of the EtOH-AN complex. The spectrum is recorded using 2.6 Torr EtOH, 42.5 Torr AN at 296.5 K corresponding to experiment B in Table S16. The optical path length is 0.1 m.

S12 Spectrum of TFE-Pyr

Figure S11 shows the spectrum of TFE-Pyr in the full range of Figure 4 in the main manuscript. The feature observed just below 3100 cm⁻¹ is caused by the aromatic CH-stretching of the pyridine monomer and cannot be subtracted due to signal saturation. The remaining regions of only monomer absorbance are fully subtracted.



Figure S11. Spectrum of TFE-Pyr in the full range of Figure 4 in the main manuscript. Experimental conditions are given in Table S13.

Table S13. Temperature (K) and scaled monomer pressures (Torr) for the spectra shown in Figure 4 of the main manuscript.

Complex	Temperature	Pressure alcohol	Pressure acetonitrile
TFE-AN	295.6	1.3	32.7
TFE-Pyr	299.5	5.7	0.64
TFE-TMA	297	1.2	183

S14 Experimental Details

S14.1 MeOH-AN

Recording the spectrum of this complex has proven difficult. The reason is the small redshift (52 cm^{-1}) combined with the weakness of the complex (max. absorbance 0.002) and the resolved strong rotational lines of the MeOH monomer. The small redshift and sharp rotational lines means that if we cannot get a good subtraction of the fundamental OH-stretching transition in the monomer, this will overlap with the fundamental OH-stretching transition in the complex. This greatly limits the maximum MeOH pressure possible and the weakness of the complex thus results in very little absorbance. Each integrated absorbance therefore has a large relative uncertainty.

Table S14. Temperature (T, K), optical path length (l, m), measured pressure ($P_{measured}$, Torr), scaling factor (s.f.), actual pressure (P_{actual} , Torr, product of $P_{measured}$ and s.f.) and integrated absorbance of the OH-stretching band of the complex (Int. Abs., cm⁻¹) for each of the experimental measurement of the MeOH-Pyr complex.

			Methanol			Acetonitrile			
Expt.	Т	1	Pmeasured	s.f.	Pactual	Pmeasured	s.f.	Pactual	Int. Abs. ^a
А	294.9	0.10	8.00	1.10	8.80	35.8	0.98	35.1	0.064
В	294.9	0.10	8.00	0.98	7.84	30.6	1.00	30.6	0.040
C ^b	296.3	2.4	2.72	0.70	1.90	42.5	0.96	40.8	0.492 ^c

^aIntegration range: 3578-3668 cm⁻¹

^bResolution of 0.2 cm⁻¹. The remaining spectra are recorded with a resolution of 1 cm⁻¹.

^cDetermined from a Lorentzian fit to the band due to noise.

Table S15. Product of monomer pressures ($P_{MeOH} \times P_{AN}$, Torr²), determined complex pressure ($P_{MeOH-AN}$, Torr) and equilibrium constant determined from both of the experiments of MeOH-AN. The pressure of the complex (and thus the equilibrium constant) is determined based on an average experimental temperature of 295.3 K and a 2D LMPT ω B97X-D/aug-cc-pVTZ oscillator strength of 7.50×10⁻⁵. The last row provides an average equilibrium constant. Note that this is only an approximate value due to the limited number of points and the experimental challenges in obtaining these.

Expt.	$P_{MeOH} \times P_{AN}$	P _{MeOH-AN}	K
Α	308.7	0.0069	0.017
В	239.9	0.0041	0.013
С	77.61	0.0022	0.021
Average			0.017



Figure S12. Pressure of the MeOH-AN complex plotted as a function of the product of monomer pressures. The pressure of the complex is determined based on an average experimental temperature of 295.3 K and a 2D LMPT ω B97X-D/aug-cc-pVTZ oscillator strength of 7.50×10⁻⁵.

S14.2 EtOH-AN

Similar to MeOH-AN, the spectra of EtOH-AN were difficult to record. Again, the small redshift and weakness of the complex greatly limits the maximum integrated absorbance. For this complex, two gas cells with different optical path lengths have been used to obtain data points in different regions and thus a better determination of the equilibrium constant. The shorter 0.1 m cell further reduced the issues of detector saturation. However, each integrated absorbance still has a reasonably large uncertainty and the linear fit is not perfect leading to a relatively large total uncertainty for the determined equilibrium constant. The seemingly non-linearity observed for the data in Figure S13 likely stems from this uncertainty, as the linear fit is within the error bars.

Table S16. Temperature (T, K), optical path length (l, m), measured pressure ($P_{measured}$, Torr), scaling factor (s.f.), actual pressure (P_{actual} , Torr, product of $P_{measured}$ and s.f.) and integrated absorbance of the OH-stretching band of the complex (Int. Abs., cm⁻¹) for each of the experimental measurements of the EtOH-AN complex.

			Ethanol			Acetonitr			
Expt.	Т	1	Pmeasured	s.f.	Pactual	Pmeasured	s.f.	Pactual	Int. Abs. ^a
А	297.2	2.4	3.46	0.850	2.94	35.58	1.150	40.92	1.16
В	296.5	2.4	3.46	0.750	2.60	43.81	0.970	42.50	0.90
С	296.5	2.4	3.46	0.870	3.01	29.00	1.065	30.89	0.68
D	296.5	2.4	3.46	0.430	1.49	57.04	0.955	54.47	0.39
Е	297.1	2.4	3.46	0.835	2.89	30.05	1.090	32.75	0.53
F	296.5	0.10	13.45	0.850	11.43	52.38	0.860	45.05	0.29
G	296.6	0.10	13.45	0.920	12.38	26.62	1.150	30.61	0.43
Н	296.7	0.10	32.23	1.085	34.97	26.62	0.720	19.17	0.40
Ι	296.1	0.10	13.45	0.870	11.70	13.50	1.000	13.50	0.06

^a Integration range: 3576-3742 cm⁻¹.



Figure S13. Pressure of the EtOH-AN complex plotted as a function of the product of monomer pressures. The pressure of the complex is determined based on an average experimental temperature of 296.6 K and a conformationally averaged 2D LMPT ω B97X-D/aug-cc-pVTZ oscillator strength of 7.17×10⁻⁵. The linear least square fit (red) is forced through (0,0). The two differently colored data sets represent two different gas cells used for the spectral recordings. The error bars represent a factor of 2.27 uncertainty estimated by summing the different factors providing uncertainty in the determined complex pressure, see text main manuscript.

S14.3 TFE-AN

Table S17. Temperature (T, K), optical path length (l, m), measured pressure ($P_{measured}$, Torr), scaling factor (s.f.), actual pressure (P_{actual} , Torr, product of $P_{measured}$ and s.f.) and integrated absorbance of the OH-stretching band of the complex (Int. Abs., cm⁻¹) for each of the experimental measurements of the TFE-AN complex.

			2,2,2-Triflouroethanol			Acetonitrile			
Expt.	Т	1	Pmeasured	s.f.	Pactual	Pmeasured	s.f.	Pactual	Int. Abs. ^a
А	295.1	2.4	1.73	0.935	1.61	29.10	0.850	24.74	3.20
В	295.8	2.4	1.73	1.005	1.74	11.05	0.975	10.77	1.52
С	295.3	2.4	1.73	0.918	1.59	20.03	1.083	21.69	2.86
D	297.3	2.4	1.73	0.390	0.67	44.49	0.950	42.27	2.81
Е	295.6	2.4	1.73	0.765	1.32	35.5	0.920	32.66	3.62



Figure S14. Pressure of the TFE-AN complex plotted as a function of the product of monomer pressures. The pressure of the complex is determined based on an average experimental temperature of 295.8 K and a 2D LMPT ω B97X-D/aug-cc-pVTZ oscillator strength of 7.82×10⁻⁵. The linear least square fit (red) is forced through (0,0).

S14.4 MeOH-Pyr

Table S18. Temperature (T, K), optical path length (l, m), measured pressure ($P_{measured}$, Torr), scaling factor (s.f.), actual pressure (P_{actual} , Torr, product of $P_{measured}$ and s.f.) and integrated absorbance of the OH-stretching band of the complex (Int. Abs., cm⁻¹) for each of the experimental measurements of the MeOH-Pyr complex.

			Methano	l		Pyridine			
Expt.	Т	1	Pmeasured	s.f.	Pactual	Pmeasured	s.f.	Pactual	Int. Abs. ^a
А	296.1	2.4	36.0	0.950	34.2	10.3	0.840	8.7	17.75
В	296.2	2.4	23.8	1.00	23.8	10.3	0.985	10.1	12.65
С	296.4	2.4	10.6	0.920	9.80	4.4	0.820	3.6	2.929
D	296.6	2.4	16.3	0.980	16.0	3.3	0.980	3.2	4.390
Е	295.3	2.4	18.3	1.01	18.5	6.2	0.890	5.5	6.390
F	295.5	2.4	24.3	1.01	24.5	6.2	0.910	5.6	8.634



Figure S15. Pressure of the MeOH-Pyr complex plotted as a function of the product of monomer pressures. The pressure of the complex is determined based on an average experimental temperature of 296.0 K and a 2D LMPT ω B97X-D/aug-cc-pVTZ oscillator strength of 1.70×10^{-4} . The linear least square fit (red) is forced through (0,0).

S14.5 EtOH-Pyr

Table S19. Temperature (T, K), optical path length (l, m), measured pressure ($P_{measured}$, Torr), scaling factor (s.f.), actual pressure (P_{actual} , Torr, product of $P_{measured}$ and s.f.) and integrated absorbance of the OH-stretching band of the complex (Int. Abs., cm⁻¹) for each of the experimental measurements of the EtOH-Pyr complex.

			Ethanol			Pyridine			
Expt.	Т	1	Pmeasured	s.f.	Pactual	Pmeasured	s.f.	Pactual	Int. Abs. ^a
А	298.6	16	4.06	0.99	4.02	4.11	0.965	3.97	7.457
В	298.0	16	9.54	1.01	9.64	3.36	1.035	3.48	13.68
С	298.4	16	11.4	0.97	11.1	4.11	0.918	3.77	18.68
D	298.7	16	13.5	1.045	14.1	4.11	1.040	4.27	26.60



Figure S16. Pressure of the EtOH-Pyr complex plotted as a function of the product of monomer pressures. The pressure of the complex is determined based on an average experimental temperature of 298.4 K and a conformationally averaged 2D LMPT ω B97X-D/aug-cc-pVTZ oscillator strength of 1.72×10^{-4} . The linear least square fit (red) is forced through (0,0).

S14.6 TFE-Pyr

Table S20. Temperature (T, K), optical path length (l, m), measured pressure ($P_{measured}$, Torr), scaling factor (s.f.), actual pressure (P_{actual} , Torr, product of $P_{measured}$ and s.f.) and integrated absorbance of the OH-stretching band of the complex (Int. Abs., cm⁻¹) for each of the experimental measurements of the TFE-Pyr complex.

			2,2,2-Trifluoroethanol		Pyridine				
Expt.	Т	1	Pmeasured	s.f.	Pactual	Pmeasured	s.f.	Pactual	Int. Abs. ^a
А	299.2	16	2.06	1.100	2.27	0.715	0.990	0.708	28.79
В	299.5	16	6.00	0.945	5.67	0.715	0.900	0.644	64.15
С	299.3	16	4.80	0.940	4.51	1.60	0.850	1.36	100.2
D	299.1	16	3.67	1.005	3.69	0.715	0.980	0.701	48.41



Figure S17. Pressure of the TFE-Pyr complex plotted as a function of the product of monomer pressures. The pressure of the complex is determined based on an average experimental temperature of 299.3 K and a 2D LMPT ω B97X-D/aug-cc-pVTZ oscillator strength of 2.54×10⁻⁴. The linear least square fit (red) is forced through (0,0).

S14.7 Literature Data Alcohol-TMA Complexes

Table S21. Equilibrium constants (K_P) and calculated oscillator strengths (f_{calc}) extracted from reference ⁵ used to determine equilibrium constants with the oscillator strengths in this work. The oscillator strength for MeOH-TMA is calculated at the CCSD(T)-F21a/VDZ-F12 level of theory, while the other two oscillator strengths are calculated at the B3LYP/aug-cc-pVTZ level. The average oscillator strength for the two EtOH-TMA conformers was used. The equilibrium constants are re-determined here, by dividing the literature equilibrium constants by the literature oscillator strength and multiplying by the oscillator strength calculated here (Table S22).

Complex	K _P	fcalc
MeOH-TMA	0.12	2.2×10^{-4}
EtOH-TMA	0.14	2.3×10 ⁻⁴
TFE-TMA	3.5	3.4×10 ⁻⁴

S15 Oscillator Strengths and Temperatures for Determination of Equilibrium Constants

Table S22. Oscillator strengths (f) and temperatures (T, K) used to calculate equilibrium constants. The oscillator strengths are calculated at the 2D LMPT ω B97X-D/aug-cc-pVTZ level of theory. For cases with multiple conformers, an average of their two oscillator strengths is used. For the AN complexes, only the oscillator strengths of the N-bonded conformers are used.

	MeOH		EtOH		TFE	TFE	
	f	Т	f	Т	f	Т	
AN	7.50×10 ⁻⁵	295.3	7.17×10 ⁻⁵ (avg. of gauche: 8.09×10^{-5}) and trans: 6.24×10^{-5})	296.6	7.82×10 ⁻⁵	295.8	
Pyr	1.70×10 ⁻⁴	296.0	1.72×10 ⁻⁴ (avg. of gauche: 1.66×10^{-4} and trans: 1.78×10^{-4})	298.4	2.54×10 ⁻⁴	299.3	
TMA	1.67×10 ⁻⁴	297 ^b	1.68×10 ⁻⁴ (avg. of <i>gauche</i> : 1.55×10^{-4} and <i>trans</i> : 1.80×10^{-4})	296 ^b	3.06×10 ^{-4,a}	297 ^b	

^a At the 1D LMPT ωB97X-D/aug-cc-pVTZ level of theory due to coupling at the 2D LMPT level. ^b From reference ⁵.

S16 Uncertainties from Linear Fits

Table S23. Combined experimentally and theoretical equilibrium constants (K_P) for each of the five complexes along with the uncertainty from the linear least square fits. The uncertainty is calculated as a two-tailed 95% confidence interval assuming a t-distribution and calculated in percent of the equilibrium constant.

Complex	KP	Uncertainty (95% CI) in %
EtOH-AN	0.035	19.5
TFE-AN	0.26	6.63
MeOH-Pyr	0.086	10.8
EtOH-Pyr	0.096	6.09
TFE-Pyr	2.5	9.25

S17 Electron Density at Hydrogen Bond from Non Covalent Interactions (NCI)

Table S24 shows the electron density of the AIM bond critical point corresponding to the OH-N hydrogen bond. This is identified as located between the hydrogen and the nitrogen atom and connected to both of these by a bond path. For each donor, the charge density increases from AN to Pyr to TMA. Furthermore, for each acceptor, the density is greatest with TFE as a donor and comparable with MeOH and EtOH.

Table S24. Electron density (au) at the AIM bond critical	point (BCP) of the	OH-N hydrogen bond.
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	MeOH	EtOH	TFE
AN	0.0220	trans: 0.0218	0.0250
		gauche: 0.0210	
Pyr	0.0335	trans: 0.0331	0.0419
		gauche: 0.0330	
TMA	0.0388	trans: 0.0385	0.0479
		gauche: 0.0379	

S18 References

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