

# Effect of Fluorine Insertion in Alcohol-Amine Complexes

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## FTIR of complexes

Complexes were formed by mixing two monomers in a vacuum line.



The amount of complex formed was determined using Fourier Transform Infrared (FTIR) spectroscopy and *ab initio* calculations.

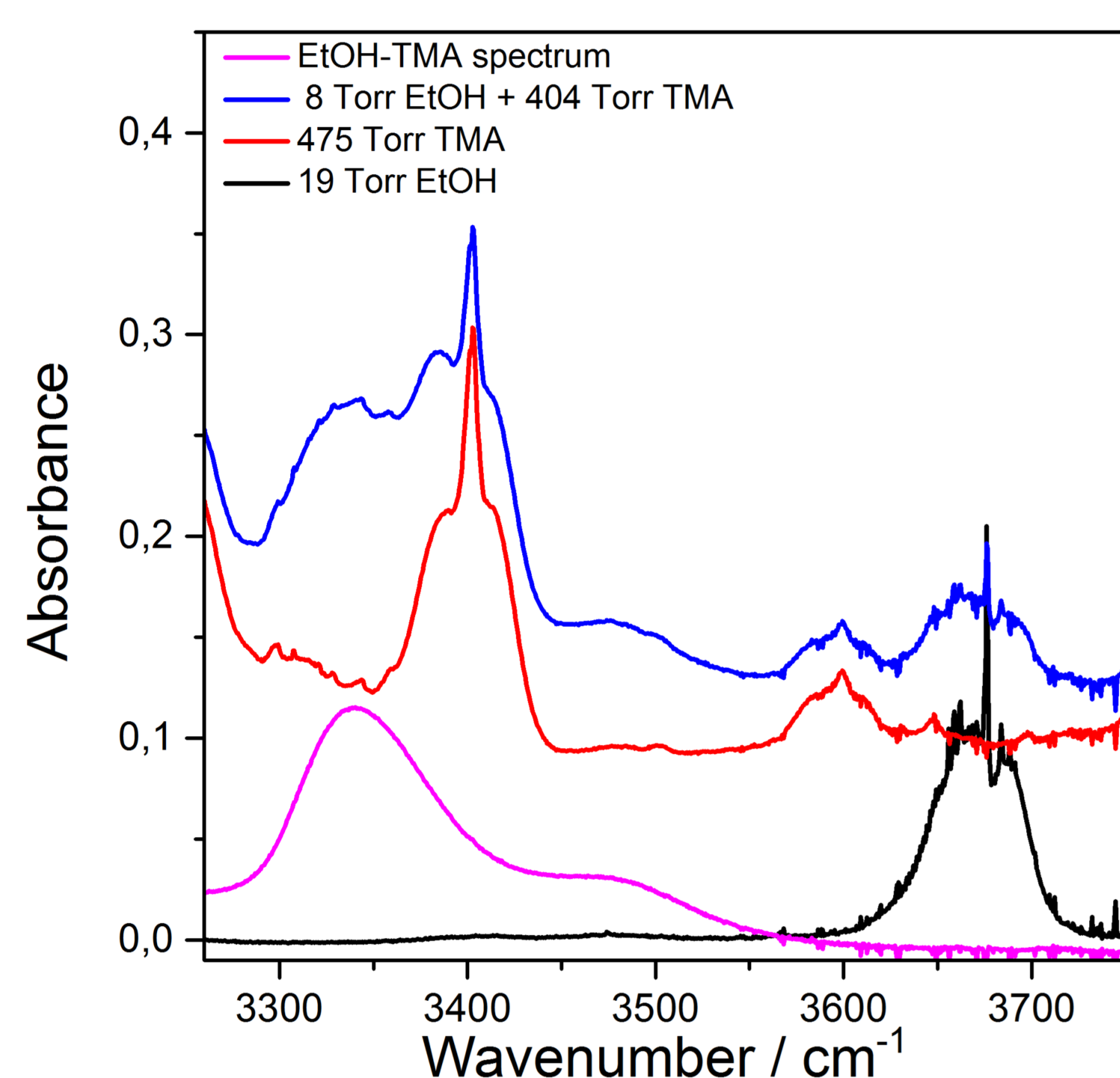


Figure 1: The spectrum of the complex has been made using spectral subtraction.

The pressure of the formed complex is very low and cannot be measured directly. The pressure of the complex can be determined by combining the calculated oscillator strength and the integrated absorbance of the complex:

$$P_C = 2.6935 \cdot 10^{-9} \text{ K}^{-1} \text{ Torr m cm} \frac{T \int A(\tilde{\nu}) d\tilde{\nu}}{f_{calc} \cdot l}$$

From this, the equilibrium constant upon complexation can be determined:

$$K_V = \frac{P_C}{P_{M1} \cdot P_{M2}} \cdot P^\ominus$$

## Complex formation

Some of the recognized characteristics of complex formation include OH-bond elongation, redshift of the fundamental OH-stretching transition and an intensity enhancement of this transition. All these characteristics were observed and confirms the formation of the complexes. The optimized structures of the complexes with dimethylamine (DMA) as acceptor are shown in Figure 2. The complexes with trimethylamine (TMA) as acceptor look similar.

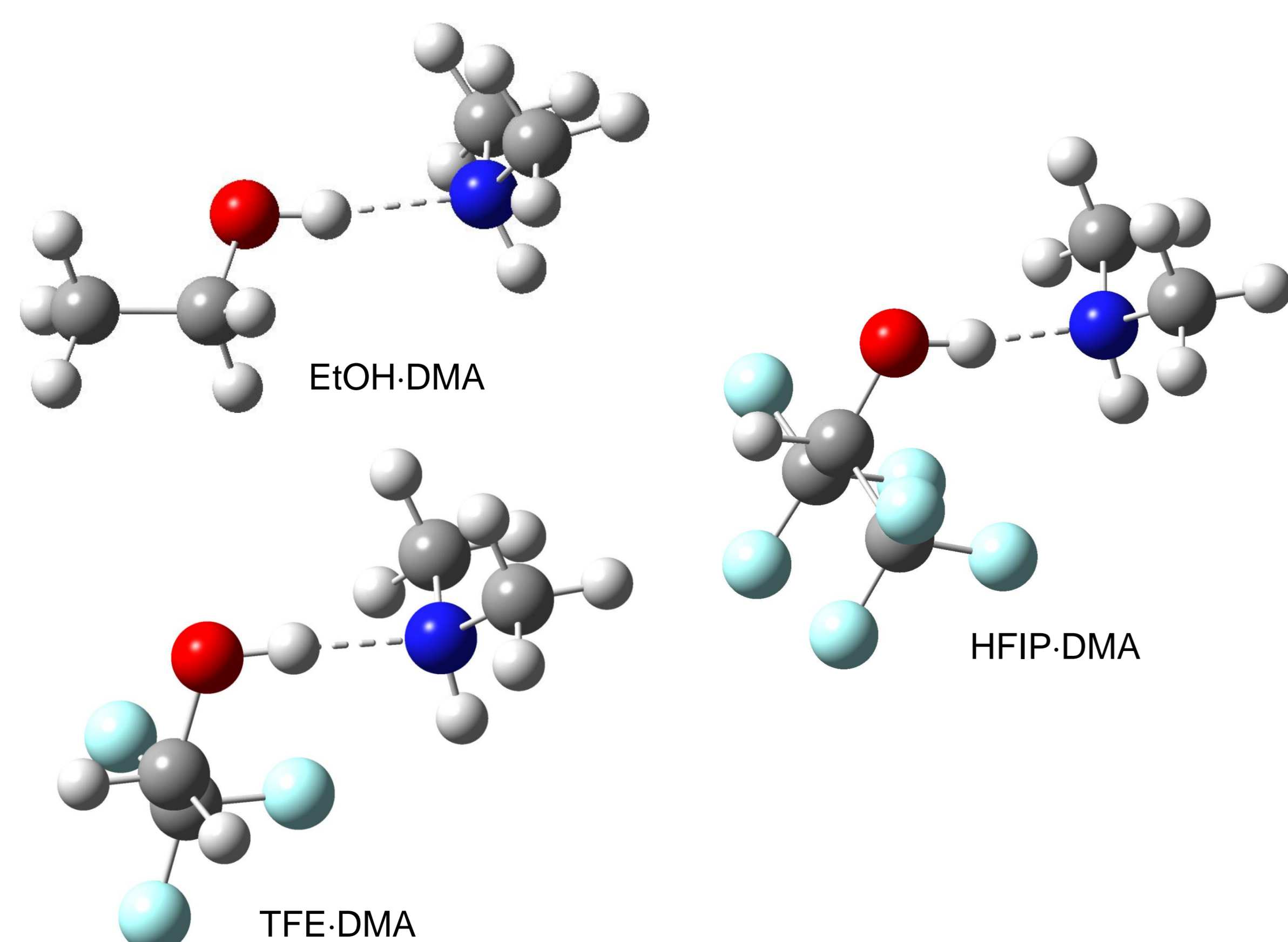


Figure 2: Optimized structures of EtOH-DMA, HFIP-DMA and TFE-DMA.

## Fluorine insertion

From the spectra in Figure 3, it is clear that the fundamental OH-stretching transition is redshifted upon complex formation. From the left panel, it is seen that the redshift increases as the number of fluorine atoms in the donor increases. The OH-stretching transition occurs at nearly the same frequency in the three monomers as shown in the right panel of Figure 3.

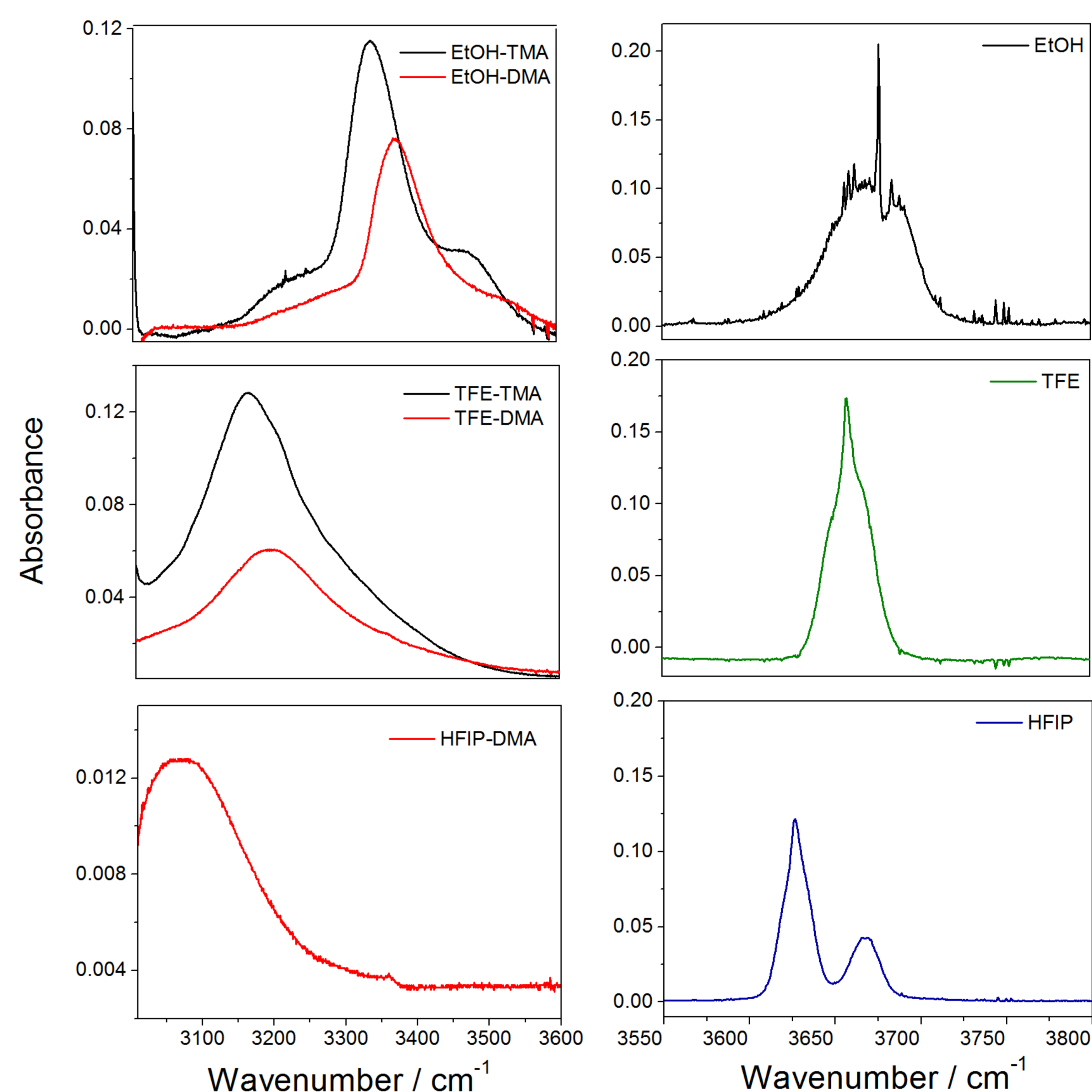


Figure 3: A series of recorded spectra. Different pressures have been used.

From Table 1, it is clearly seen that insertion of fluorine has an enhancing effect on the hydrogen bond strength. This is most likely due to the high electronegativity of the fluorine atoms, which draws electron density out of the OH-bond and hence weakens it.

	$\Delta R_{OH}$	$\Delta \nu_{OH} (obs)$	$K_V$
EtOH-DMA	0.015	296	0.11
TFE-DMA	0.030	460	3.6
HFIP-DMA	0.016	555	110
EtOH-TMA	0.016	331	0.14
TFE-TMA	0.031	485	3.5
HFIP-TMA	0.047	562	13.8

Table 1: The characteristics of hydrogen bond formation: The M06-2X/aug-cc-pVTZ calculated OH-bond elongation,  $\Delta R_{OH}$  (Å), the observed redshift,  $\Delta \nu_{OH}$  (cm<sup>-1</sup>), and the unitless equilibrium constant,  $K_V$ .

## Conclusion

The addition of a methyl group to the hydrogen bond acceptor has a limited effect on the hydrogen bond strength. However, substituting CH<sub>3</sub> with CF<sub>3</sub> in the donor has a large effect. Adding a second CF<sub>3</sub> group to the donor enhances the hydrogen bond strength even further.

## References

A. S. Hansen, L. Du, H. G. Kjaergaard. "The Effect of Fluorine Substitution in Alcohol-Amine Complexes". *Phys. Chem. Chem. Phys.*, **16**, 22882-22891 (2014).