Microwave Spectroscopy of terpenoids non-covalently bonded to hydrogen sulfide

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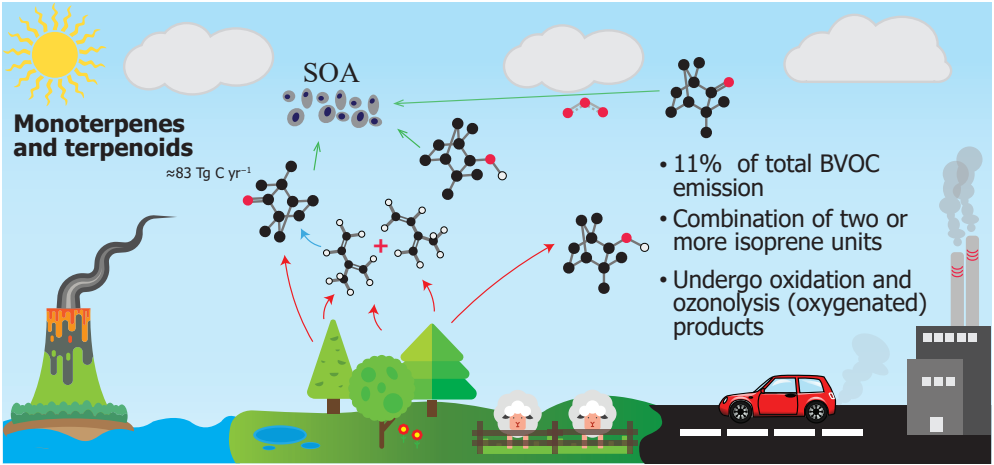
Monoterpenes and terpenoids



K. Sindelarova et al., , 2014, pp. 9317–9341

Micro-solvation of terpernoids

The presence of oxygenated functional group in terpenoids widens the chemical possibilities

- It is well known that they can form water complexes
- The literature contains several studies of micro-hydrated BVOCs

The hydrogen bond

Intermediate range interaction

donor

X—H ----- Y

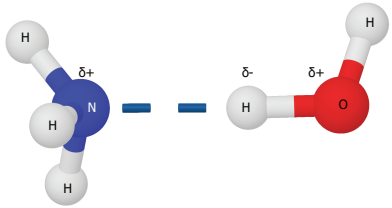
acceptor

X and Y more electronegative than H

F, O, N, S

Acceptor should be high electron density region:

- lone pair of electrons
- Π-bonded pair of electrons in a double or triple bond



The hydrogen bond

Intermediate range interaction

donor

X—H ----- Y

acceptor

X and Y more electronegative than H

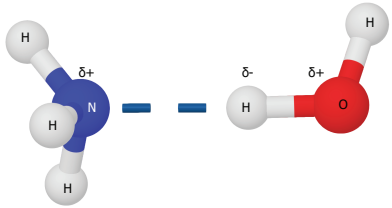
F, O, N, S

It is an important interaction that stabilizes vital systems[1]

It is the main contributor to the foramtion of atmospheric relevant species[2]

Acceptor should be high electron density region:

- lone pair of electrons
- Π-bonded pair of electrons in a double or triple bond



[1] G. R. Desiraju and T. Steiner,2001
[2] H. Zhao et al., Int J Mol Sci, 2016, p.4

Structure

Gas phase molecular structure

- Influences the inter and intramolecular interactions
- Dictates the physical and chemical properties of the system
- Give an idea about the reaction pathways and complexes formation

→ Important to get information of the gas-phase structure

How to determine the gas phase structure?

Pure rotational spectroscopy

- Employs state-of-the-art instruments
- High resolution pure rotational spectra are obtained
- Rotational constants that correspond to a unique geometry are extracted

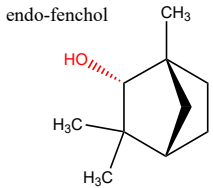
$$A = \frac{\hbar^2}{2I_a}, \quad B = \frac{\hbar^2}{2I_b}, \quad C = \frac{\hbar^2}{2I_c}$$

Micro-solvation of terpernoids

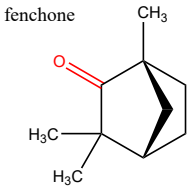
- Only few studies of organic molecules with sulfur containing species
- Complexes with Sulfur containing species??
- Similar or different to micro-hydration?

Systems of interest

- endo-fenchol ($C_{10}H_{18}O$), fenchone ($C_{10}H_{16}O$) and their complexes with water have been studied with Fourier transform microwave (FTMW) spectroscopy[1,2,3,4]
- They possess same skeleton but different functional groups



1,3,3-trimethylbicyclo[2.2.1]heptan-2-ol



1,3,3-trimethylbicyclo[2.2.1]heptan-2-one

[1] E. M. Neeman and T. R. Huet, , 2018, pp. 24708–24715

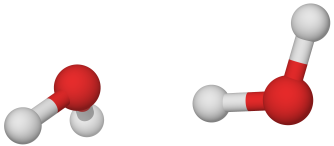
[2] E. M. Neeman and T. R. Huet, , 2021, pp. 2179–2185

[3] D. Loru, M. A. Bermúdez, and M. E. Sanz, , 2016, p. 074311

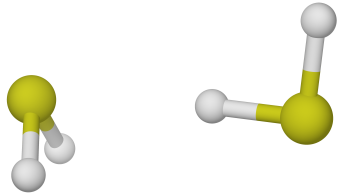
[4] M. Chrayteh et al., , 2021, pp. 20686–20694

Why H_2S

- H_2S is a trace gas in the atmosphere of natural and anthropogenic sources
- $(H_2S)_2$ and $(H_2O)_2$ have similar gas phase structure[1]
- This gives a solid basis for comparison



(a) H_2O dimer

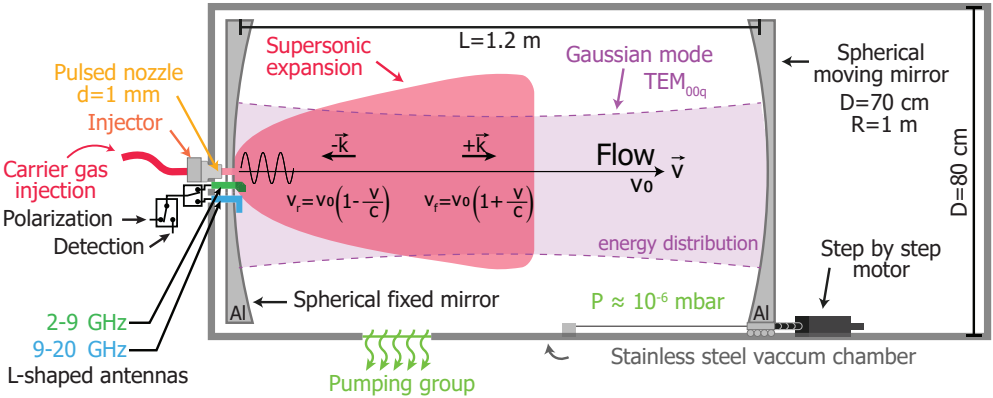


(b) H_2S dimer

[1] A. Das et al., , 2018, pp. 15199–15203

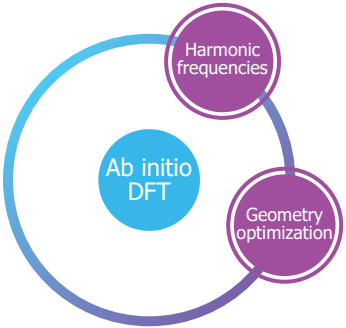
Spectrometers in PhLAM

- Two FTMW spectrometers operating from ≈ 1 to 20 GHz



Quantum chemical calculations

The synergic combination of computational methods and FTMW is a reliable approach for studying atmospheric molecules



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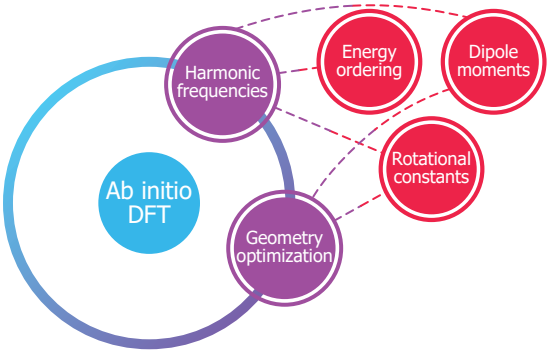

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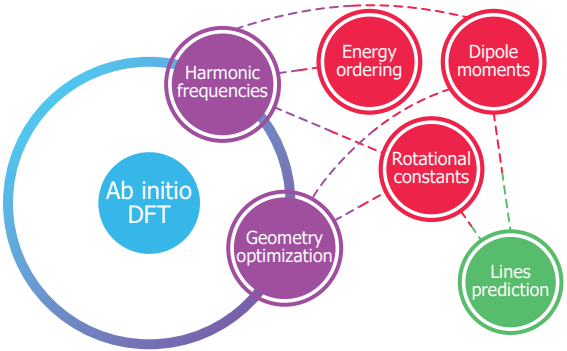

Quantum chemical calculations

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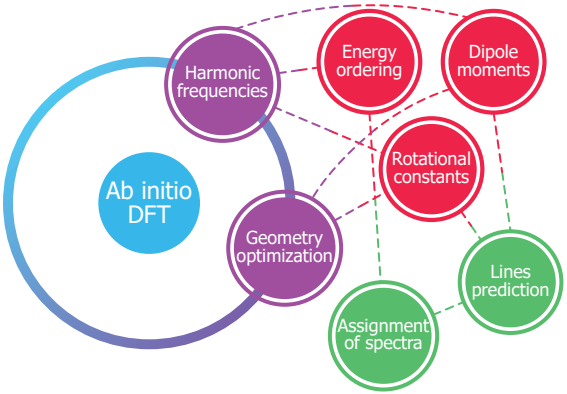


Complexes with H_2S

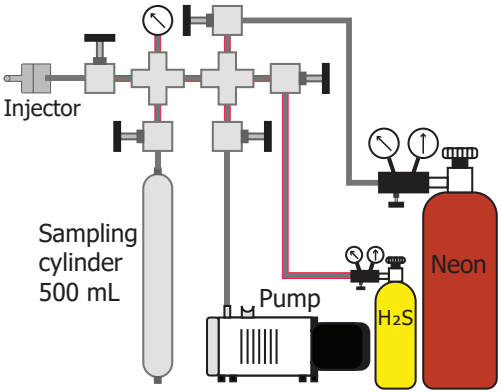
All calculations were performed using Gaussian 16

	Method	Basis set	Type
ab initio	MP2	6-311++G(d,p)	opt, freq, NBO, wfx
DFT	B3LYP	def2TZVP	opt,freq
	ωB97X-D	6-311++G(d,p)	

Experimental conditions

A premixture was required to handle H_2S

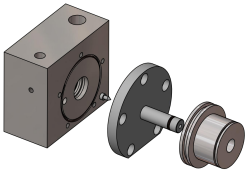
Carrier gas	Neon
P_{H_2S}	$\approx 1.5\,\%$ (50 mbar)



Experimental conditions

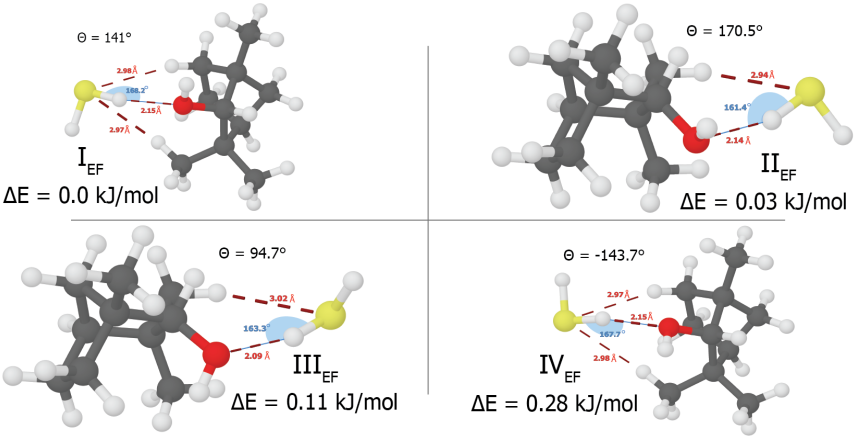
	P (bar)	T (K)	State
Fenchol	3.5	348	solid
Fenchone	3	348	liquid

Carrier gas premixture



Endo-fenchol$\cdots H_2S$

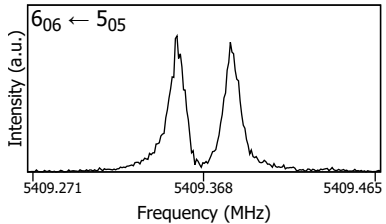
Four stable conformers are predicted with MP2, very close in energy

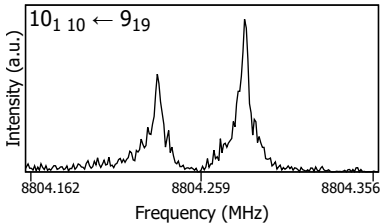


Bond distance in Å; ∠(OHS) in °; Θ: D(OHSH) in °

Experimental transitions

- Correction factors were applied to the rotational constants to facilitate the search
- 56 lines were recorded at high resolution





Semi rigid Hamiltonian

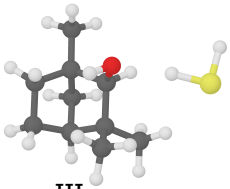
Transitions were fitted to Watson Hamiltonian in the A-reduction

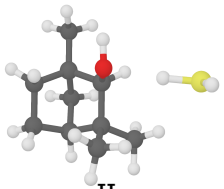
$$\begin{aligned}\hat{H}^{sr}_{rot} =& \frac{1}{2}(B^{(A)} + C^{(A)})\hat{J} + \left[A^{(A)} - \frac{1}{2}(B^{(A)} + C^{(A)})\right]\hat{J}_z^2 \\ &+ \frac{1}{2}(B^{(A)} - C^{(A)})(\hat{J}_x^2 - \hat{J}_y^2) - \Delta_J \hat{J}^4 - \Delta_{JK}\hat{J}^2\hat{J}_z^2 - \Delta_K \hat{J}_z^4 \\ &- 2\delta_J \hat{J}^2(\hat{J}_x^2 - \hat{J}_y^2) + \delta_K\left[\hat{J}_z^2(\hat{J}_x^2 - \hat{J}_y^2) + (\hat{J}_x^2 - \hat{J}_y^2)\hat{J}_z^2\right] \\ &+ \dots\end{aligned}$$

Fit

	Exp.	III_{EF}	II_{EF}
		MP2	MP2
A (MHz)	1161.23470(480)	1182.5	1187.5
B (MHz)	494.214373(162)	505.8	510.2
C (MHz)	430.006742(129)	439.6	445.3
E (+ZPE)	(kJ mol^{-1})	0.11	0.03

Two conformers can be assigned to these constants





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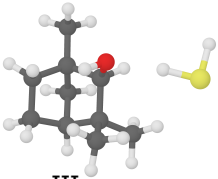
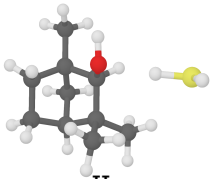
C (MHz)	430.006742(129)	439.6	445.3
μ_a (D)	observed	2.7	1.6
μ_b (D)	not observed	0.02	0.8
μ_c (D)	not observed	0.1	0.2



III_{EF}

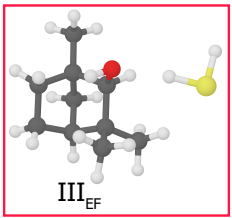


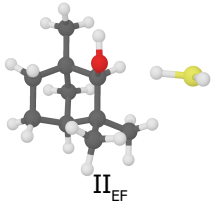
II_{EF}

Fit

Only a-type transitions were observed

	Exp.	III_{EF}	II_{EF}
		MP2	MP2
A (MHz)	1161.23470(480)	1182.5	1187.5
B (MHz)	494.214373(162)	505.8	510.2
C (MHz)	430.006742(129)	439.6	445.3
μ_a (D)	observed	2.7	1.6
μ_b (D)	not observed	0.02	0.8
μ_c (D)	not observed	0.1	0.2





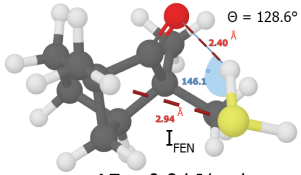
Experiment vs. Theory

Good agreement between calculations (III_{EF}) and fitted constants

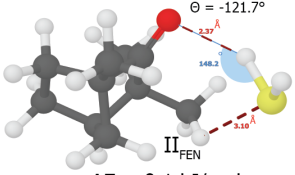
Constants	Experimental	MP2	ωB97X-D	B3LYP
A (MHz)	1161.23470(480)	1182.5	1187.5	1192.7
B (MHz)	494.214373(162)	505.8	498.4	497.4
C (MHz)	430.006742(129)	439.6	434.8	434.9
N	56			
RMS (kHz)	1.46			
J_{max}	13			
$K_{a_{max}}$	4			

Fenchone$\cdots H_2S$

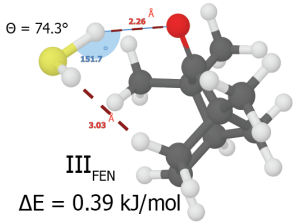
Six stable conformers were predicted with MP2



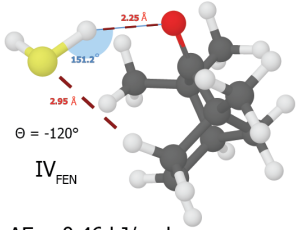
ΔE = 0.0 kJ/mol



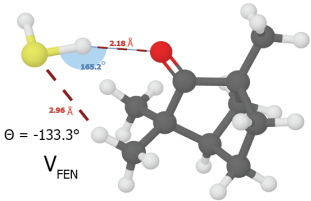
ΔE = 0.1 kJ/mol



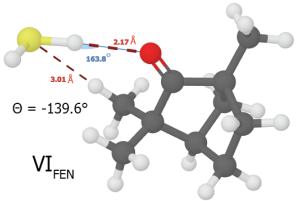
ΔE = 0.39 kJ/mol



ΔE = 0.46 kJ/mol



ΔE = 3.98 kJ/mol

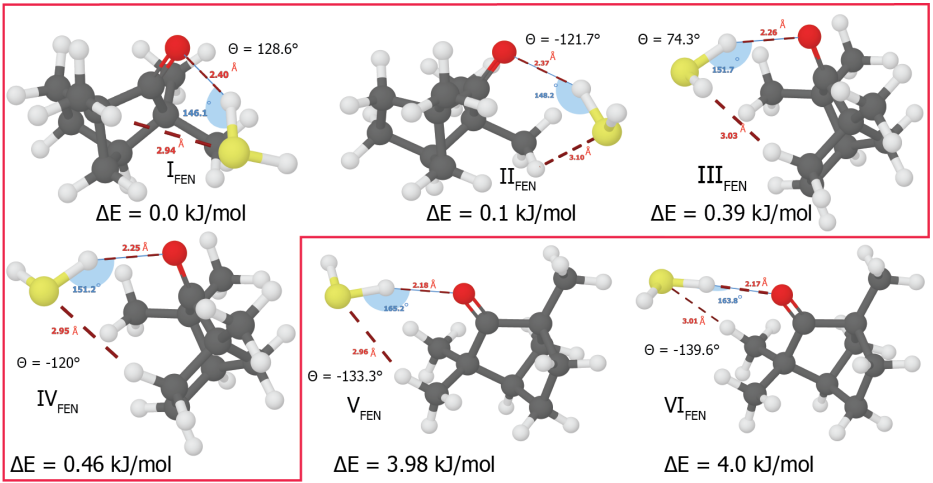


ΔE = 4.0 kJ/mol

Bond distance in Å; ∠(OHS) in °; Θ: D(OHSH) in °

Fenchone$\cdots H_2S$

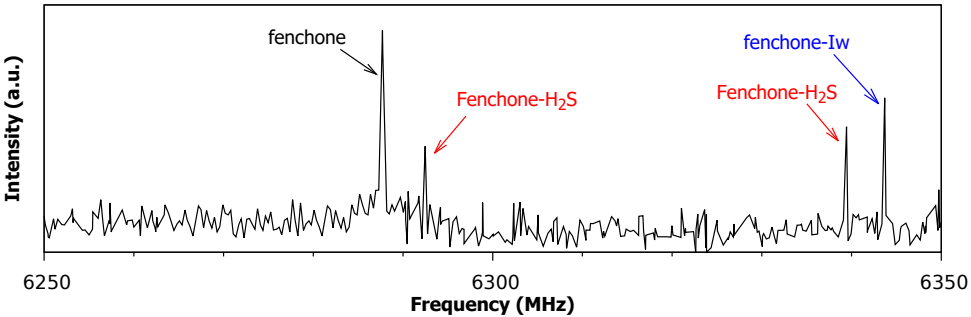
Six stable conformers were predicted with MP2



Bond distance in Å; ∠(OHS) in °; Θ: D(OHSH) in °

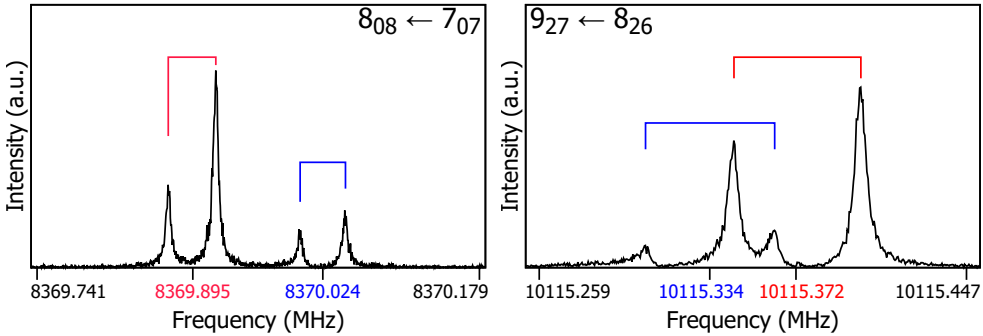
Rotational spectrum

- Rotational constants were corrected before predictions
- The first two assigned transitions were $6_{16} \leftarrow 5_{15}$ and $6_{06} \leftarrow 5_{05}$



Rotational spectrum

- At high resolution, the experimental lines showed splittings
- few up to 200 kHz
- Intensities of the lines were 3:1



→ Characteristic of large amplitude motion

Fit

- 169 lines were fitted into two separate states
- Strong state 0^- and weak state 0^+

	Experimental		III_{FEN}	IV_{FEN}
	0^+	0^-	MP2	MP2
A (MHz)	983.41497(21)	983.40341(13)	984.2	985.3
B (MHz)	582.232474(64)	582.241521(34)	597.2	599.0
C (MHz)	511.016389(44)	511.007220(30)	525.1	526.9

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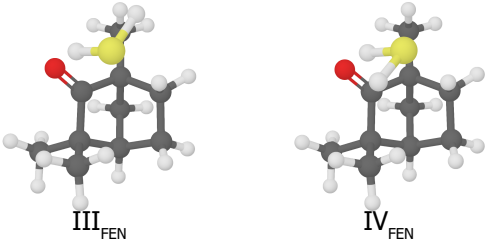
C (MHz)	511.016389(44)	511.007220(30)	525.1	526.9

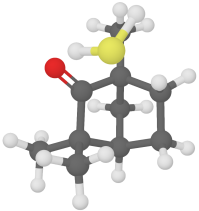
Two conformers can be assigned to the observed lines



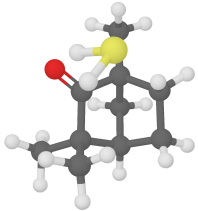
Fit

- a, b and c transitions are observed
- Both have observable components

	Experimental		III_{FEN}	IV_{FEN}
	0^+	0^-	MP2	MP2
A (MHz)	983.41497(21)	983.40341(13)	984.2	985.3
B (MHz)	582.232474(64)	582.241521(34)	597.2	599.0
C (MHz)	511.016389(44)	511.007220(30)	525.1	526.9
μ_a (D)	observed intense		2.7	2.5
μ_b (D)	observed weak		1.1	0.4
μ_c (D)	observed medium		1.3	1.5



III_{FEN}

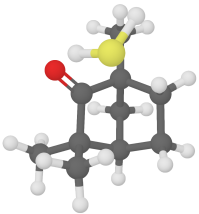


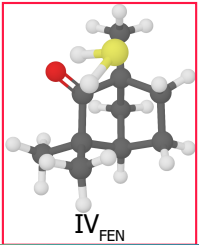
IV_{FEN}

Fit

- If we compare polarizing power used with dipole components
- Conformer IV_{FEN} is the one observed

	Experimental		III_{FEN}	IV_{FEN}
	0^+	0^-	MP2	MP2
A (MHz)	983.41497(21)	983.40341(13)	984.2	985.3
B (MHz)	582.232474(64)	582.241521(34)	597.2	599.0
C (MHz)	511.016389(44)	511.007220(30)	525.1	526.9
μ_a (D)	observed intense		2.7	2.5
μ_b (D)	observed weak		1.1	0.4
μ_c (D)	observed medium		1.3	1.5





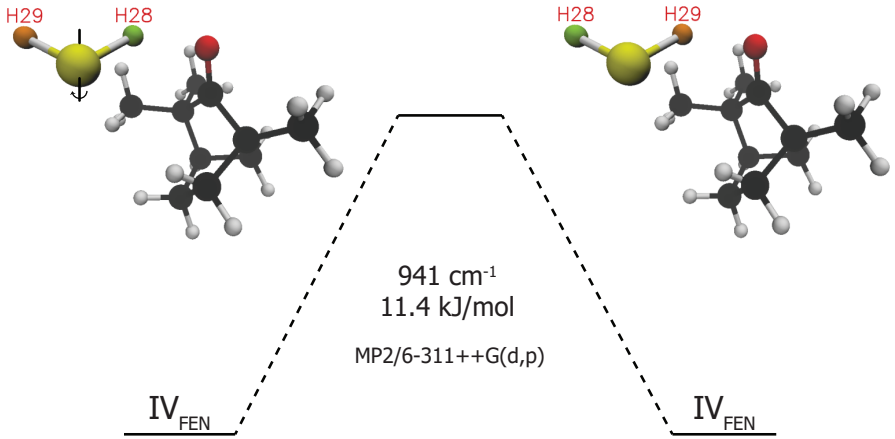
Experiment vs. Theory

Good agreement between calculations (IV_{FEN}) and fitted constants

Constants	Experimental		MP2	ωB97X-D	B3LYP
	0^+	0^-			
A (MHz)	983.41497(21)	983.40341(13)	985.3	987.8	978.0
B (MHz)	582.232474(64)	582.241521(34)	599.0	592.7	595.5
C (MHz)	511.016389(44)	511.007220(30)	526.9	520.0	522.8
N	70	99			
RMS (kHz)	1.72				
J_{max}	12				
$K_{a_{max}}$	4				

Large amplitude motion

- The only movement that can give iso-energetic structures is the proton exchange
- It can be achieved by the rotation around the C_2 axis of H_2S



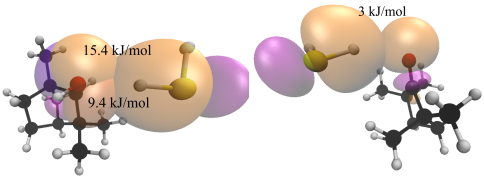
fenchol$\cdots H_2S$ vs. fenchone$\cdots H_2S$

In order to better understand the differences between the two complexes, different analyses were performed:

- Natural Bonding Orbitals (NBO)
  - Provides an intuitive framework to rationalize the transfer of electronic charge
- Non Covalent Interactions (NCI) plot
  - Analyzes the electron density and its derivatives

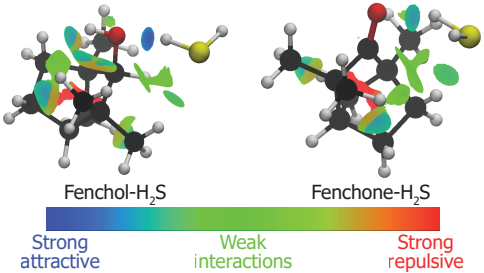
NBO and NCI analyses

Hydrogen bonding



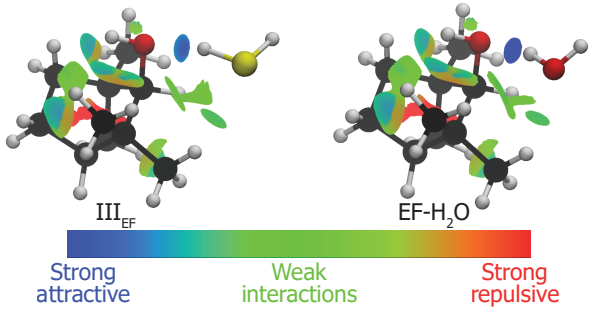
fenchol$\cdots H_2S$
LP(1), LP(2) and BD* (SH)

fenchone$\cdots H_2S$
LP(2) and BD* (SH)



- Hydrogen bond is stronger in fenchol$\cdots H_2S$ complex
- This might explain observing the splitting in fenchone$\cdots H_2S$

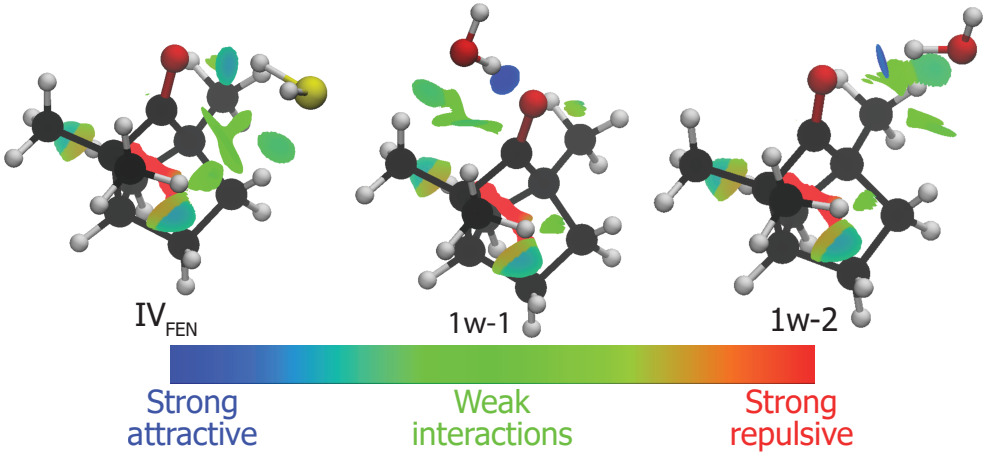
EF-H_2O vs. EF-H_2S



- H_2O form stronger hydrogen bond, which can be further validated from natural bonding analysis, by comparing stabilizing energy of the charge transfer ($\approx$15 kJ mol^{-1} vs. $\approx$40 kJ mol^{-1}[1])
- Difference is the orientation of H atom in H_2S

[1] E. M. Neeman and T. R. Huet, , 2021, pp. 2179–2185

FEN-H_2O vs. FEN-H_2S



- Different structure from the mono-hydrates
- H_2O form stronger H-bond

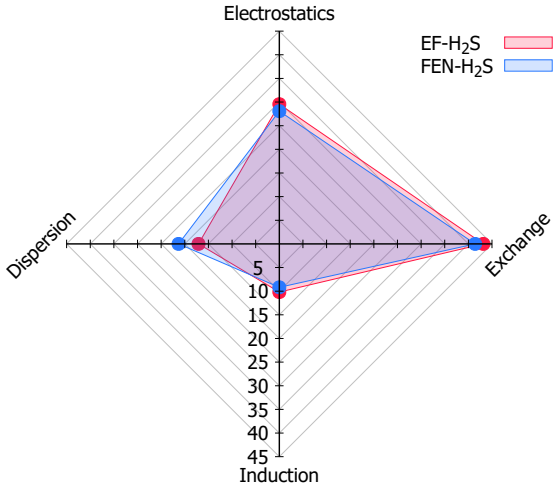
Symmetry Adapted Perturbation Theory

A tool for energy decomposition analysis; It decomposes the total intermolecular interaction energy into:

- Electrostatic:
  - Repulsive or attractive
  - Hydrogen bonding
- Exchange:
  - Repulsive
  - Pauli exclusion
- Induction:
  - Polarization of molecular orbitals
- Dispersion:
  - Attractive
  - London dispersive forces

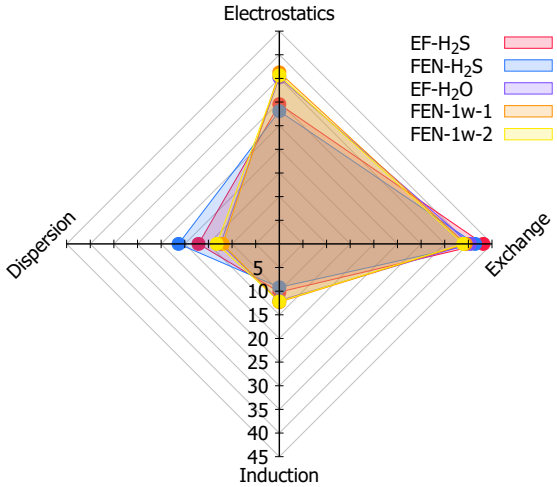
SAPT analysis

- H-bond in fenchol$\cdots H_2S$ stronger
- Dispersive forces in fenchone$\cdots H_2S$ are stronger



SAPT analysis

- H_2S form weaker H-bond
- Dispersive forces with H_2S are stronger



Conclusion

Summary

- Hydrogen-bonded complexes of two monoterpenoids (alcohol and ketone) with H_2S were observed using FP-FTMW spectrometers
- The complex of fenchone$\cdots H_2S$ showed splitting of its experimental lines due to proton exchange arising from H_2S internal rotation
- Non-covalent analyses were carried out to compare between the complexes and their water analogs

Future work

- Investigate more complexes with H_2S
  - Similar functional groups
  - Aldehydes and carboxylic acids
- Is it possible to form complexes with two or three H_2S molecule?

Thank You

Questions?