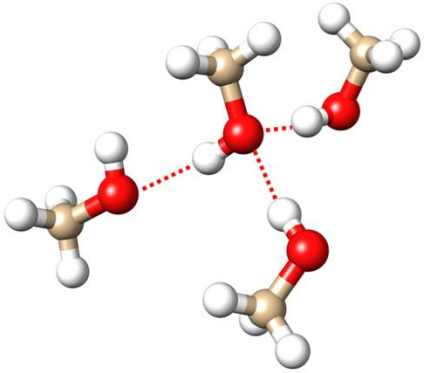
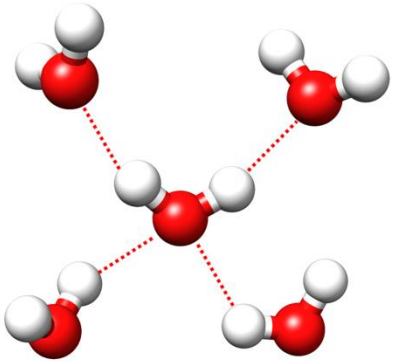
Dielectric Study of Alcohols using Broadband Terahertz-Time Domain Spectroscopy (THz-TDS)

Sohini Sarkar, D.Saha, S. Banerjee, A. Mukherjee, and P. Mandal
Department of Chemistry, IISER, Pune
sohinis@students.iiserpune.ac.in

Alcohols

➢ Alcohols differ from water in a number of ways:





• ampiphilic with both polar hydroxyl hydrophilic part and non polar alkyl hydrophobic part.

• miscible with myriads of polar and non polar solvents

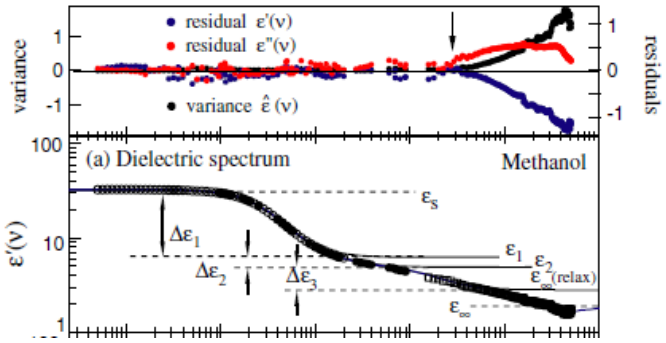
➢Insights from dielectric spectroscopy:

• slow relaxation process, ~ 50 ps
• intermediate relaxation, ~ 8 ps
•very fast process, ~ 1 ps

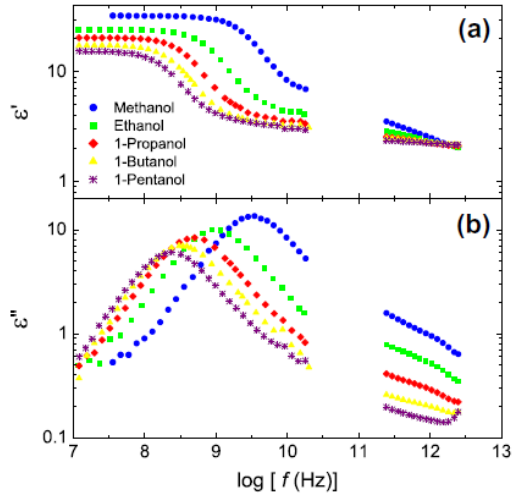
Previous Studies

Kindt et al. studied complex permittivity of alcohols in 0.01-1 THz; multiple Debye behaviour exhibited by alcohols.

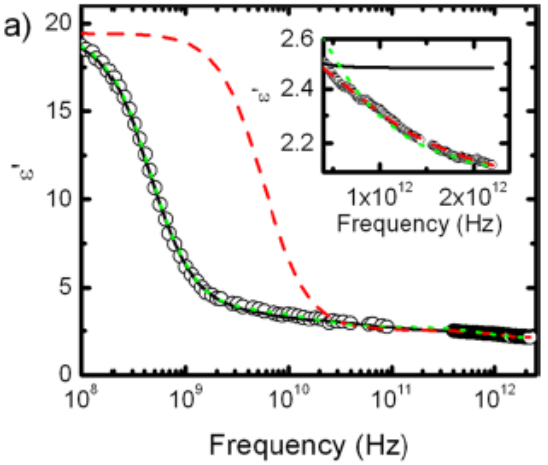
J. Phys. Chem. 1996, **100**, 10373-10379

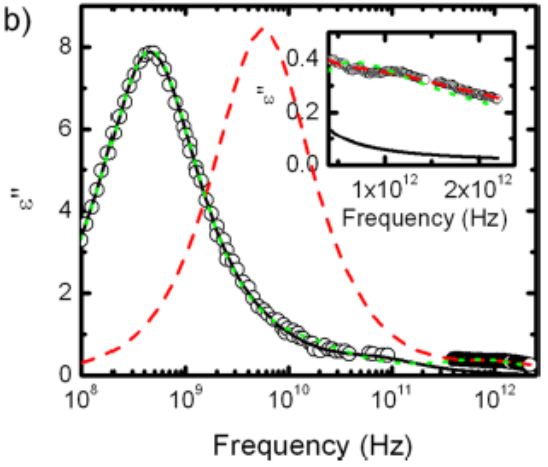


Phys. Rev. Lett., 2005, **95**, 197802



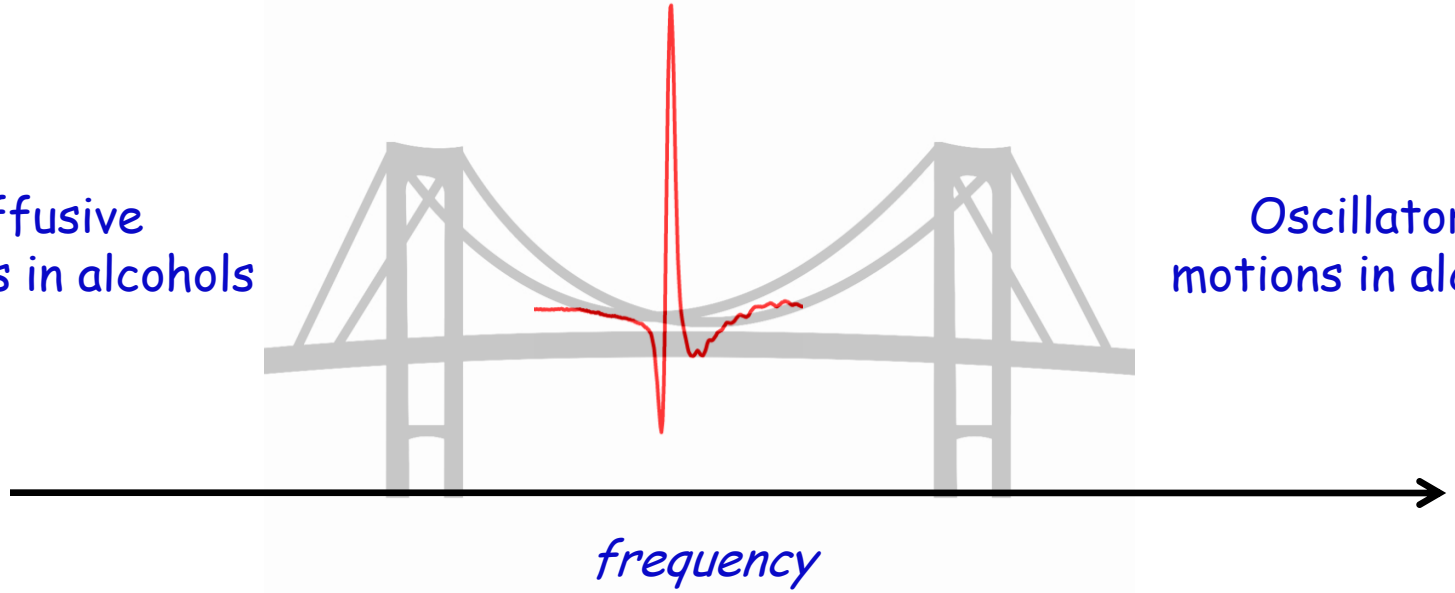
J. Mol. Struct., 2010, **981**, 173-178.





J. Phys. Chem. B 2014, **118**, 10156–10166

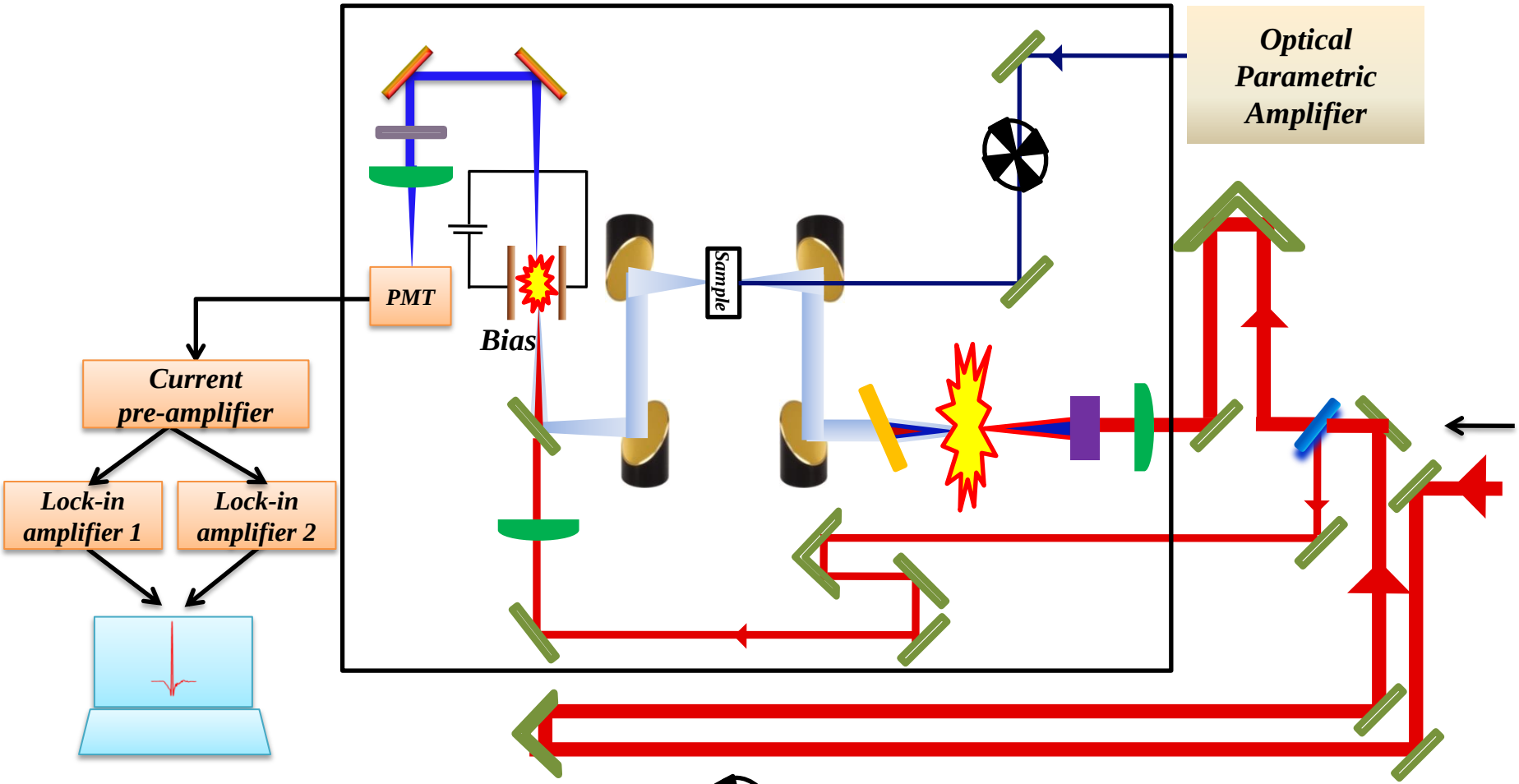
Why THz-TDS ?



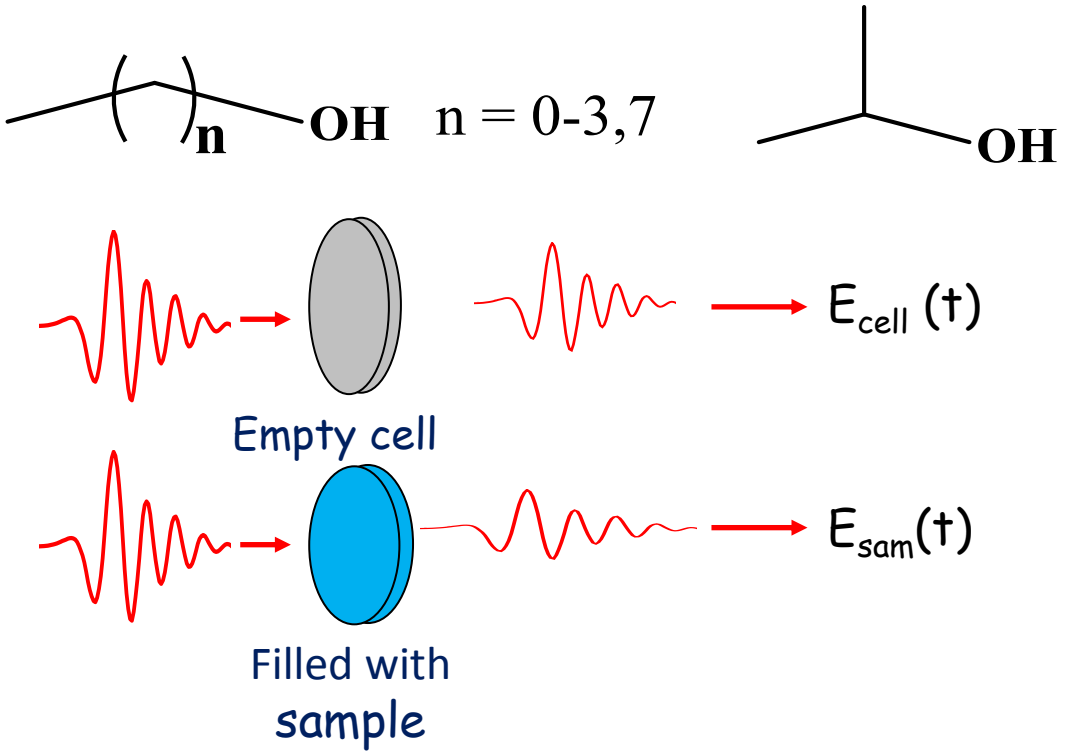
- 1 THz = 33.33 cm^{-1} = 4 meV, frequency range: 0.1 to 15 THz
- We can measure both the absorption and dispersion of the sample, from which complex valued permittivity $\hat{\varepsilon}(\omega)$ can be determined.
- $\hat{\varepsilon}(\omega)$ of alcohols at frequencies higher than 5 THz is not reported.
- Broadband THz-TDS (1-10 THz) has been utilized to study the dielectric properties of alcohols.

THz-TDS Experimental Setup

Optical Source: 50 fs, 4 mJ, 800 nm, 1 KHz from Spitfire



Experimental Details

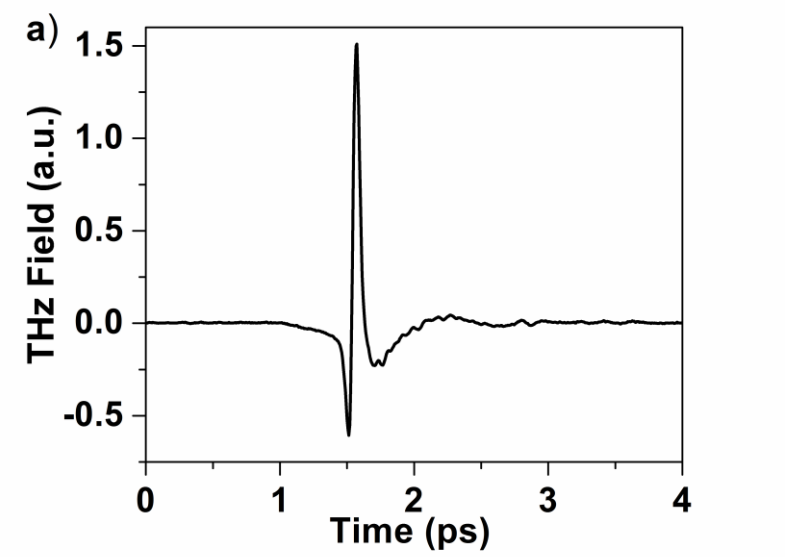


- 2 high resistivity silicon windows (2 mm thickness, 1 inch diameter) separated by PTFE spacer of 150 μm thickness.

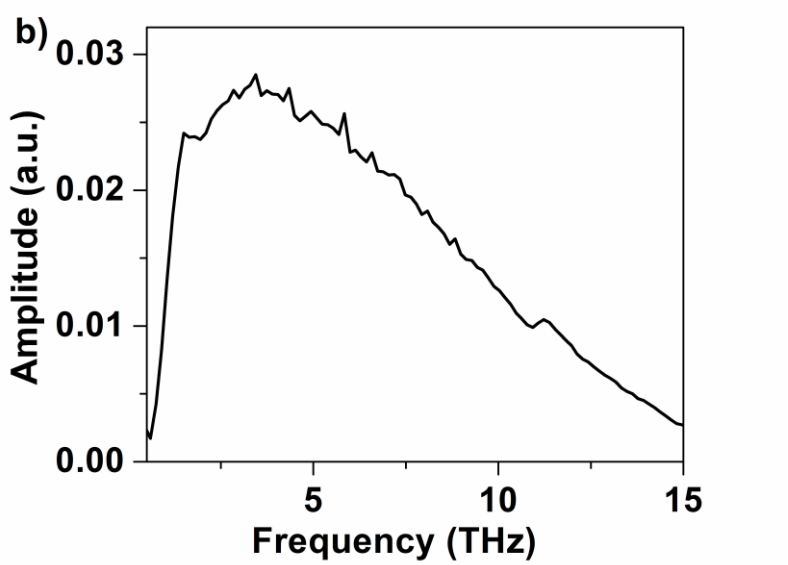
- To obtain a satisfactory S/N ratio, several measurements normally 30-50 are averaged.

$$\frac{\Im E_{sam}(t)}{\Im E_{cell}(t)} = \frac{\tilde{E}_{sam}(\omega)}{\tilde{E}_{cell}(\omega)} = \sqrt{T(\omega)}\exp(i\phi(\omega))$$

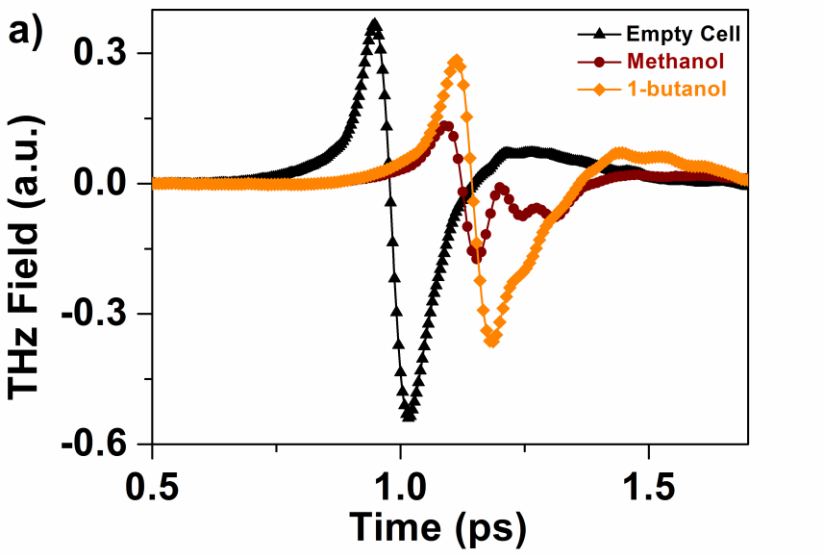
Terahertz Data of Alcohols



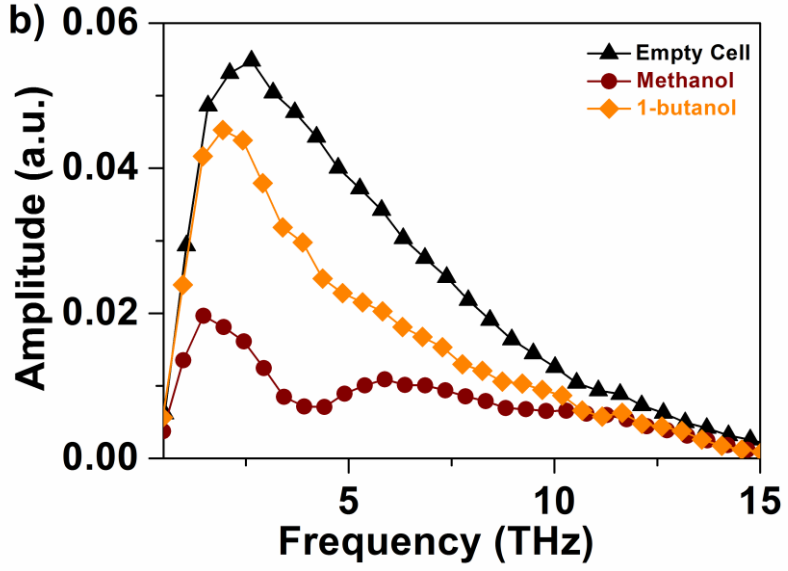
THz Time domain spectrum (THz-TDS)



THz frequency domain amplitude spectrum

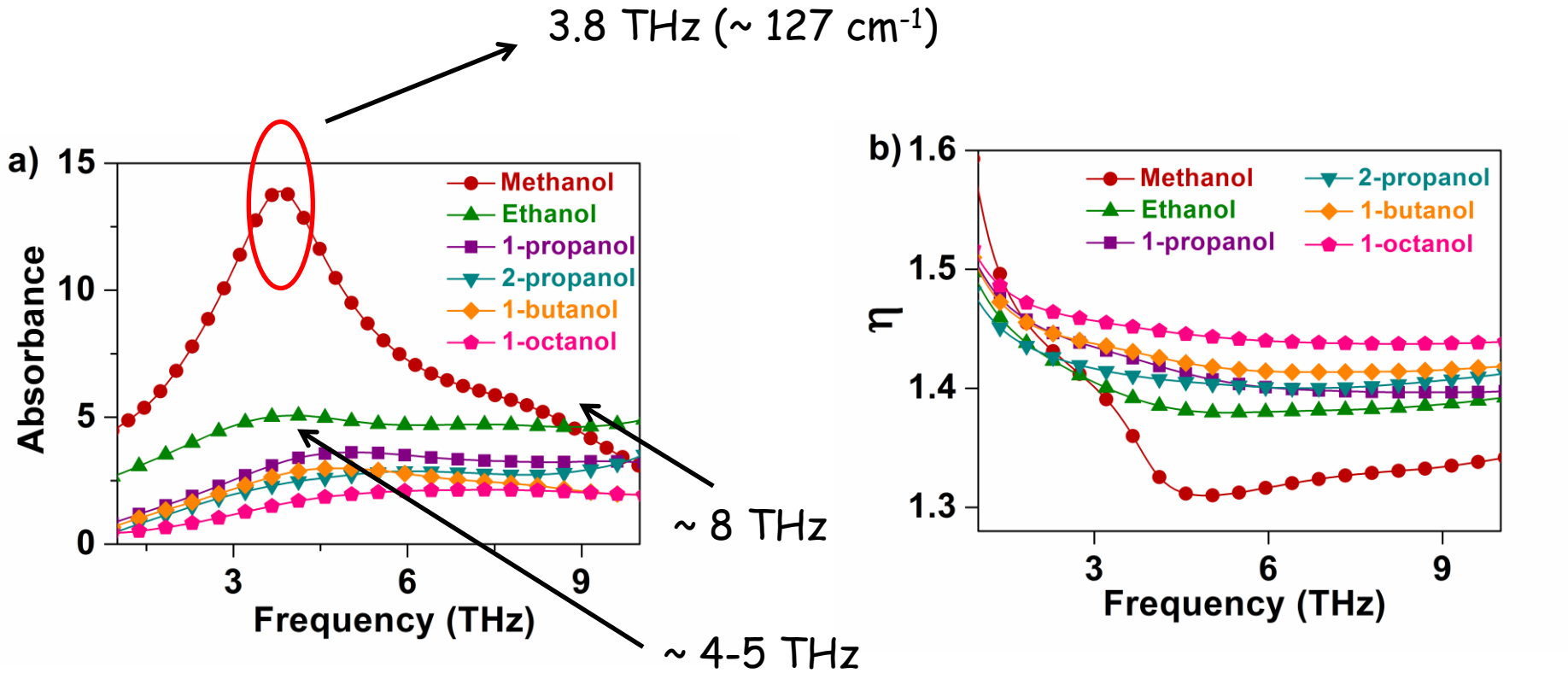


THz-TDS of alcohols



THz frequency domain amplitude spectrum

Absorbance & Refractive Index

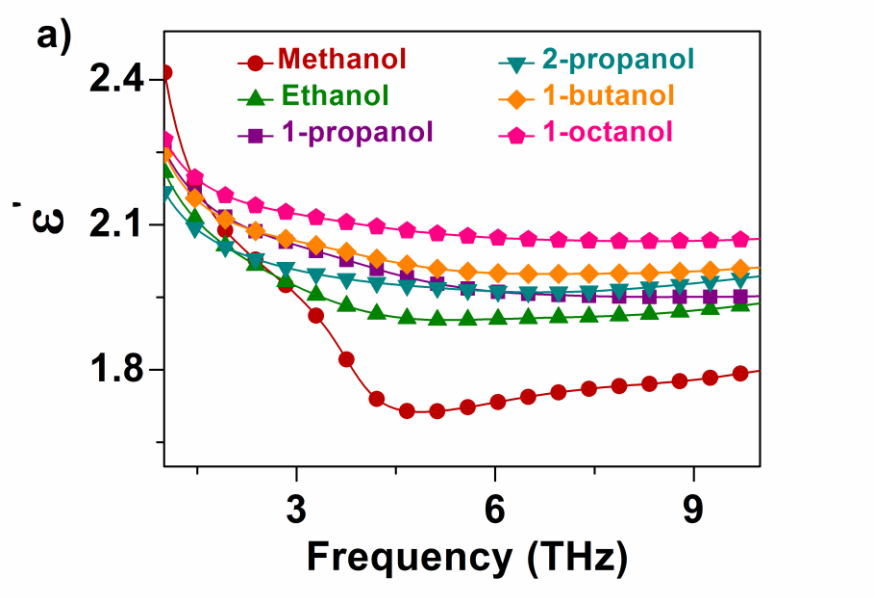


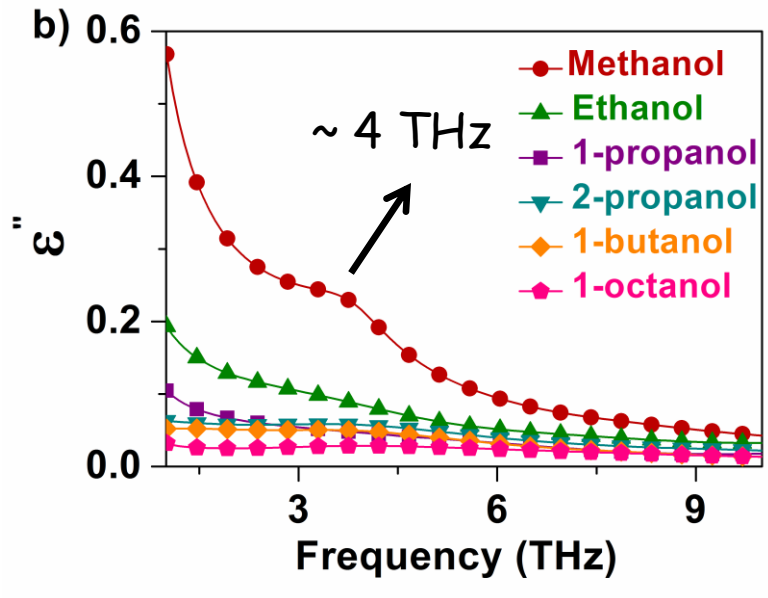
Frequency dependent a) absorbance and b) refractive index of monohydric alcohols

Dielectric Study

$$\hat{\varepsilon}(\omega) = \varepsilon^{'}(\omega) - i\varepsilon^{''}(\omega)$$

$$\varepsilon'(\omega) = \eta^2(\omega) - k^2(\omega), \varepsilon''(\omega) = 2\eta(\omega)k(\omega)$$





Frequency dependent a) real and b) imaginary components of dielectric function of different alcohols.

Debye Model & Damped Harmonic Oscillator Model

Debye Model

$$\hat{\varepsilon}(\omega) = \varepsilon_\infty + \sum_{j=1}^{n} \frac{\Delta\varepsilon_j}{(1+i\omega\tau_j)}$$

- At higher frequencies resonant or oscillatory motion of a molecule or group of molecules come into play.
- Only dielectric relaxation models become invalid.
- Damped harmonic oscillator model has to be used to understand the oscillatory motions of the molecules.

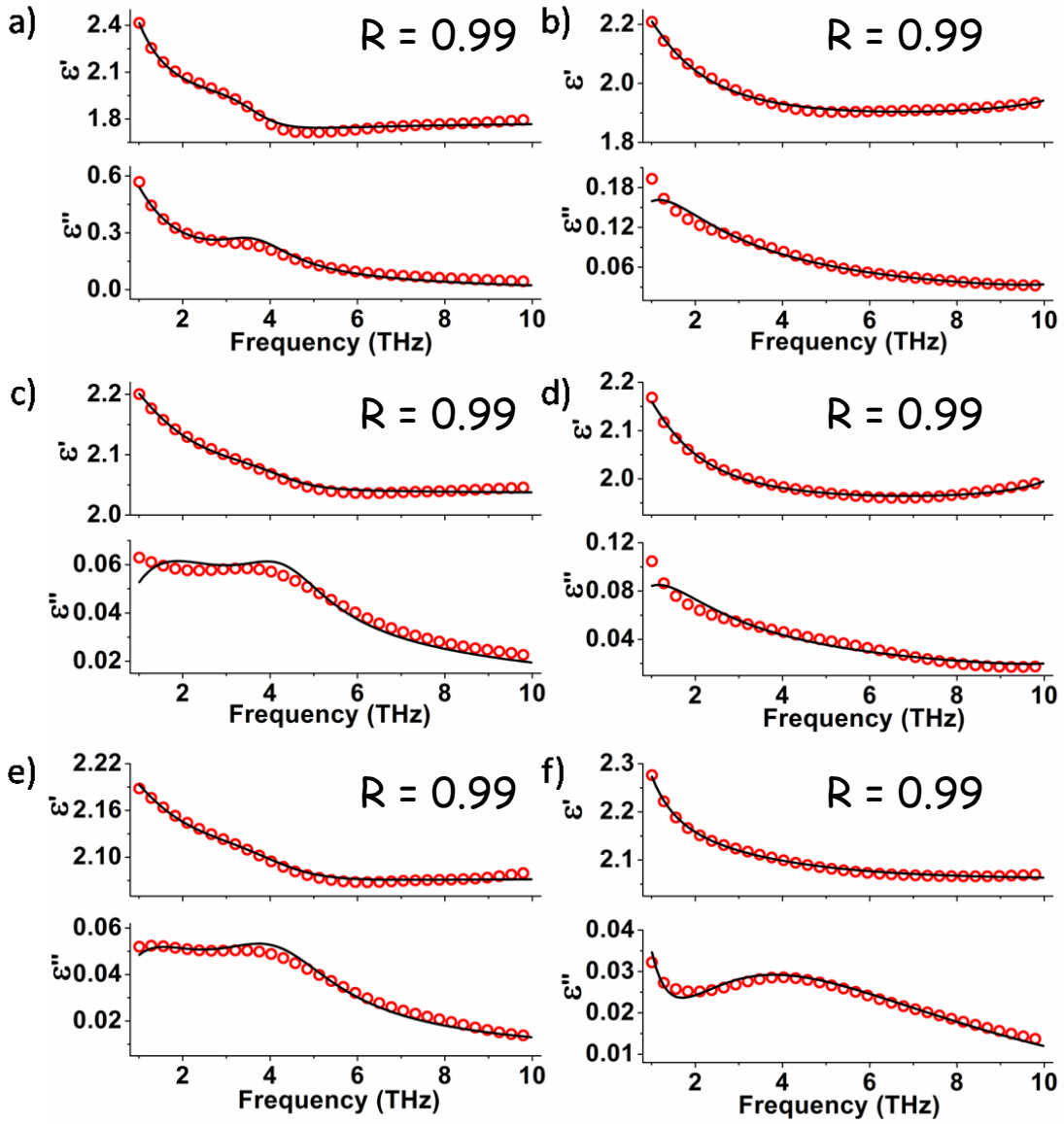
Debye + Damped Harmonic Oscillator Model

$$\hat{\varepsilon}(\omega) = \varepsilon_\infty + \sum_{j=1}^{n} \frac{\Delta\varepsilon_j}{1+i\omega\tau_k} + \sum_{l=1}^{k} \frac{A_j}{\omega_l^2 - \omega^2 + i\omega\gamma_l}$$

Single Debye and Double Damped Oscillator Model

$$\hat{\varepsilon}(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1+i\omega\tau} + \frac{A_1}{\omega_1^2 - \omega^2 - i\omega\gamma_1} + \frac{A_2}{\omega_2^2 - \omega^2 - i\omega\gamma_2}$$

Experimental Dielectric Functions and their Fits



a) methanol, b) ethanol, c) 1-propanol, d) 2-propanol, e) 1-butanol, and f) 1-octanol.

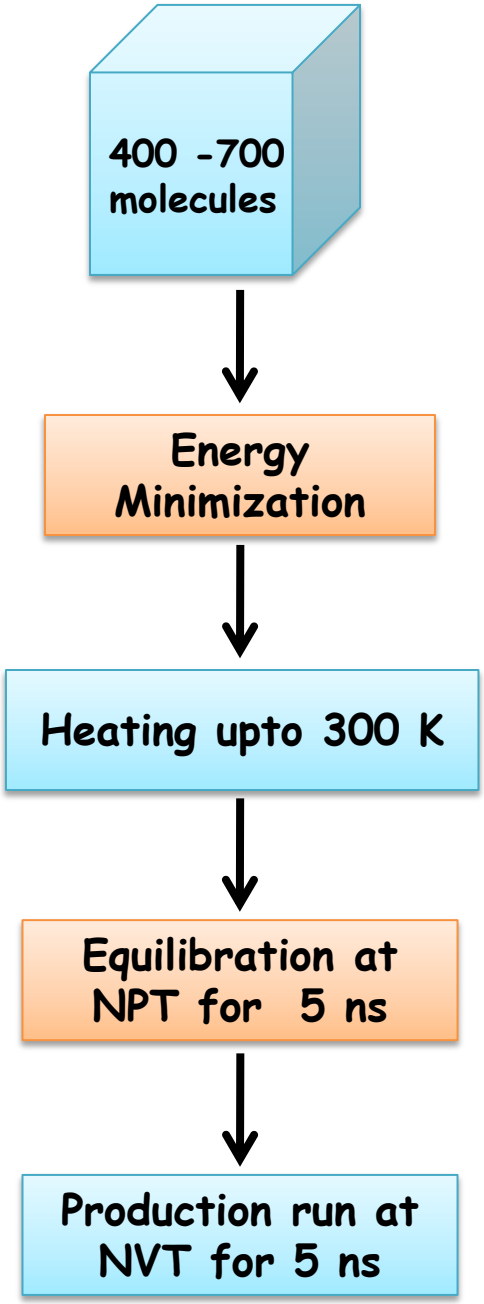
Debye and Oscillator parameters

Alcohol	τ (fs)	ω_1 (THz)	ω_2 (THz)
Methanol	120	1.0	3.9
Ethanol	80	4.7	11.9
1-propanol	107	4.4	8.9
2-propanol	98	6.2	11.4
1-butanol	88	4.4	10.5
1-octanol	196	4.0	9.2

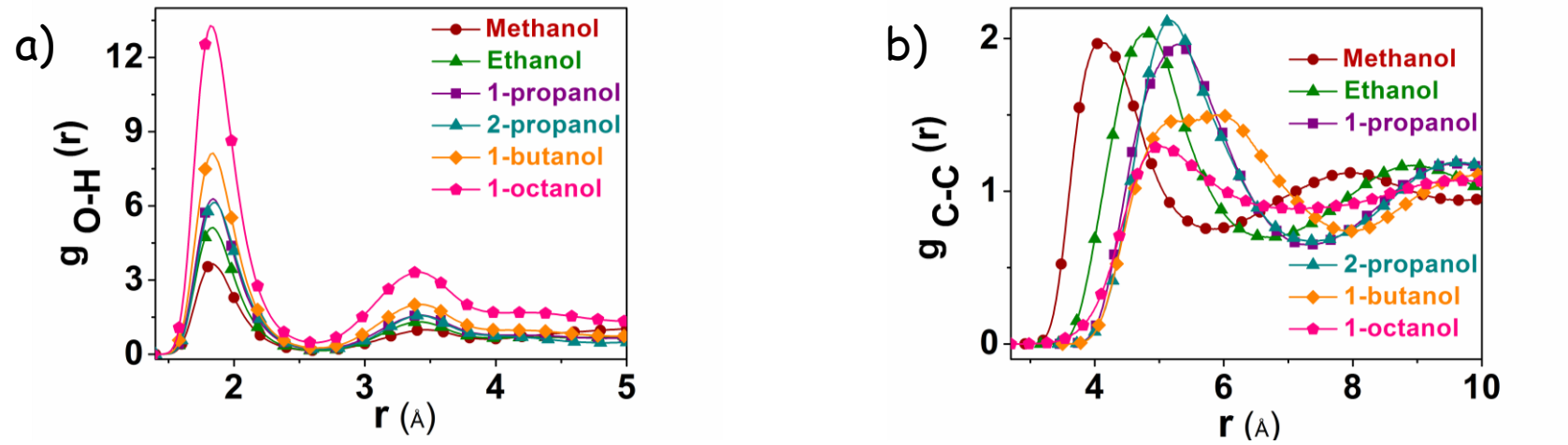
- Fast process ~ 100 – 200 fs: H-bond breaking and reforming dynamics.
- Except 2-propanol other alcohols show a peak at ~5 THz. The peak for 2 propanol is at ~6 THz.
- Ethanol and higher alcohols exhibit a peak at higher THz frequency (~9 – 12 THz).

J. Chem. Phys, 1964, **40**, 3249-3256
Phys. Chem. Chem. Phys., 2015, **17**, 30481

Simulation Details

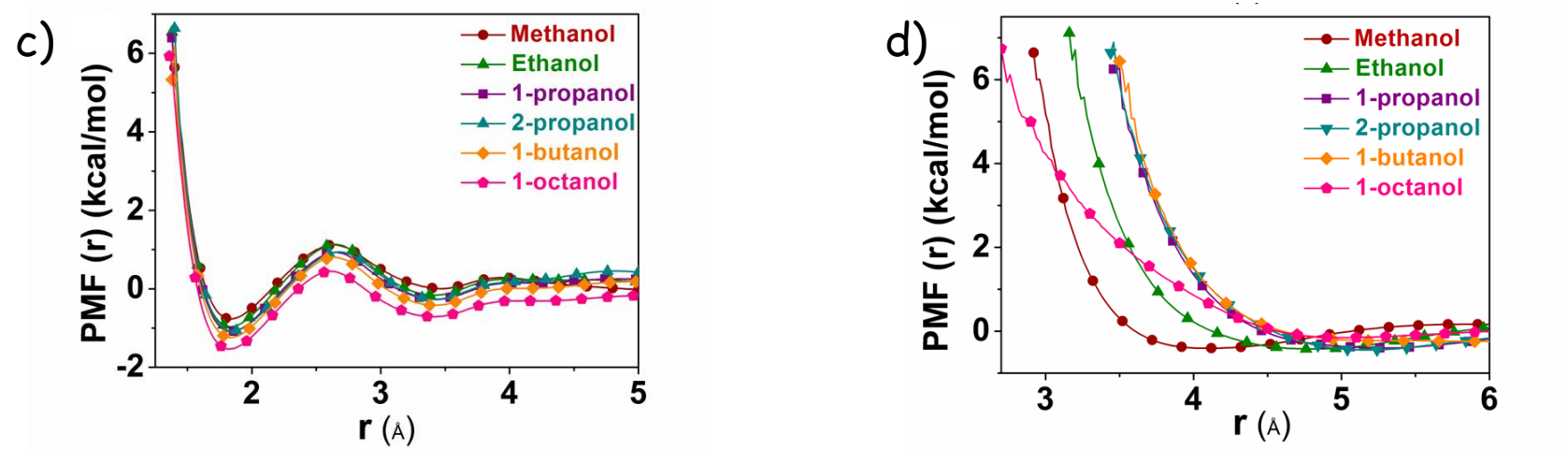


RDF and PMF plots for different alcohols



RDF plot between a) oxygen and hydroxyl hydrogen & b) carbon atoms of alkyl chains of different alcohols

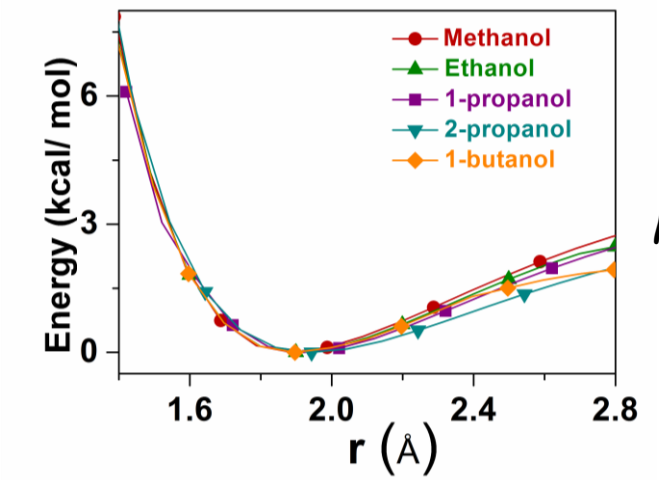
$$PMF(r) = -k_B T \ln RDF(r)$$



PMF plot between a) oxygen and hydroxyl hydrogen & b) carbon atoms of alkyl chains of different alcohols

Frequencies from fitting PMF Plots

Alcohol	Modes	Force Const.(kcal.mol^{-1}Å^2)	Freq. (THz)
Methanol	O...H	6222.2	6.4
	C...C	487.4	1.8
Ethanol	O...H	6309.5	5.4
	C...C	282.3	1.1
1-Propanol	O...H	6276.3	4.7
	C...C	214.0	0.9
2-Propanol	O...H	5985.9	4.6
	C...C	286.9	1.0
1-Butanol	O...H	6364.7	4.3
	C...C	9.8	0.2
1-Octanol	O...H	6436.4	3.2
	C...C	204.9	0.6

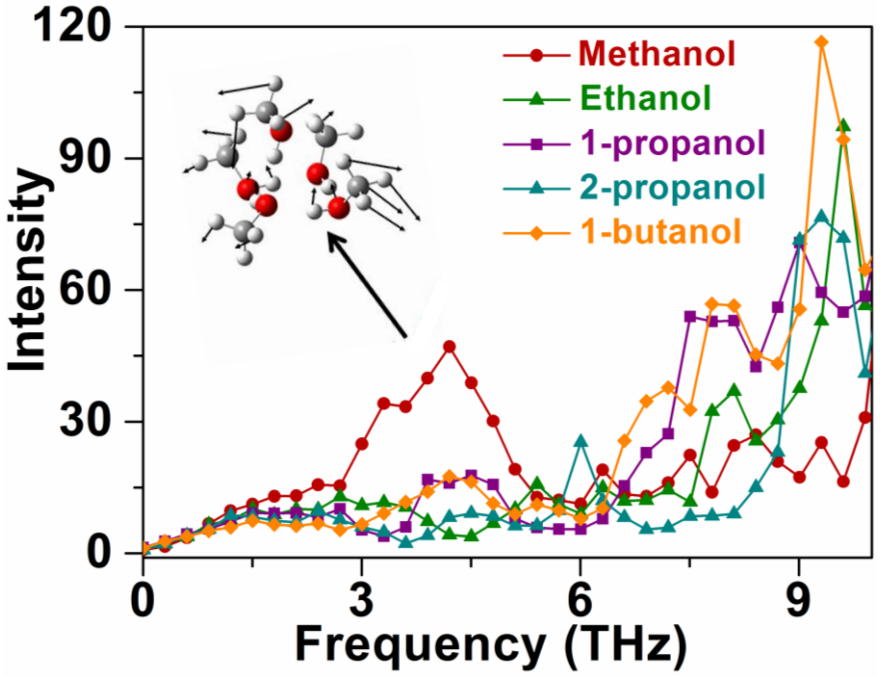


MP2/aug-cc-pVDZ method

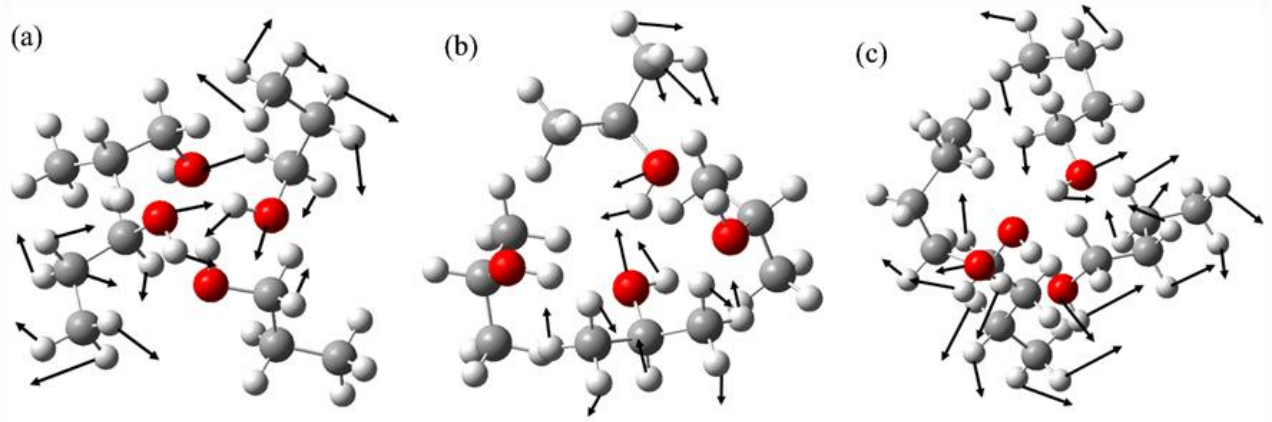
Comparing Experimental & Computed Results

	Fit to Experimental Data			Computed Frequencies (THz)	
Alcohol	**τ (fs)**	**ω_1 (THz)**	**ω_2 (THz)**	**O....H**	**C....C**
Methanol	120	1.0	3.9	6.4	1.8
Ethanol	80	4.7	11.9	5.4	1.1
1-propanol	107	4.4	8.9	4.7	0.9
2-propanol	98	6.2	11.4	4.6	1.0
1-butanol	88	4.4	10.5	4.3	0.2
1-octanol	196	4.0	9.2	3.2	0.6

Spectra from Quantum Calculations

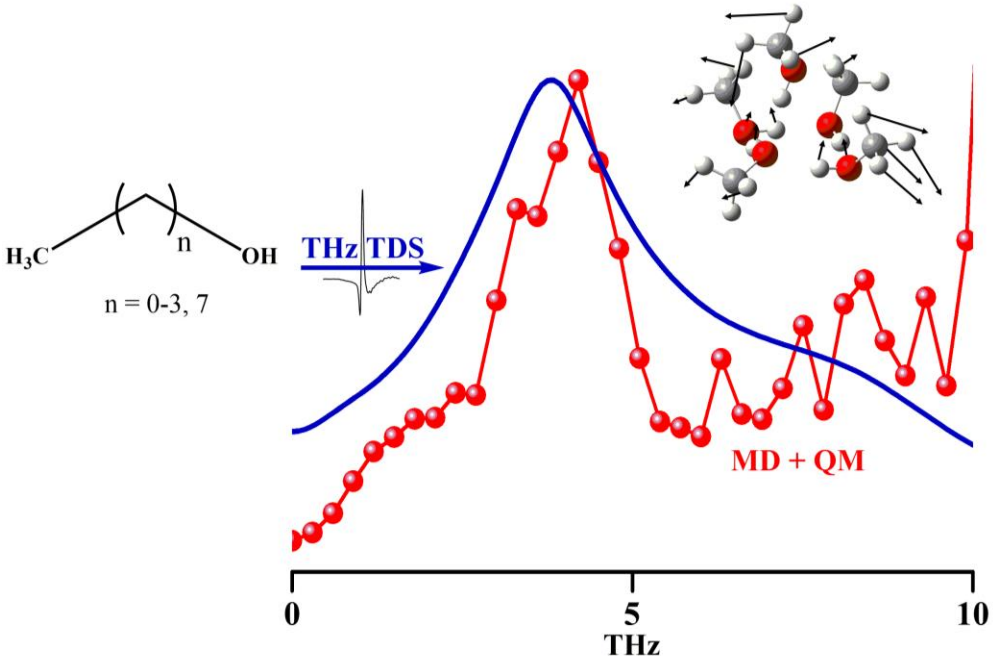


Average spectra from frequency calculation of 20 different configurations of each alcohol.



Motions involved around ~5 THz region for (a) 1-propanol, (b) 2-propanol and (c) 1-butanol.

Conclusion



- Single Debye and double damped harmonic oscillators, reproduces the experimental complex dielectric spectra
- Debye relaxation : ~ 100 – 200 fs, H bond rupture and reformation
- 3.9 and 6.2 THz : intermolecular H bond stretching
- ~ 9 THz : rattling of free –OH groups
- ~ 1THz and below : alkyl group interactions

Acknowledgement

Organizers: Dr Benjamin McCall, Birgit D McCall

PI: Dr Pankaj Mandal

Collaborators: Dr Arnab Mukherjee, Debasis Saha

Labmates: Sneha, Avinash, Reddy

Thank You

Sample	ε_0	ε_1	$\tau 1$ (ps)	$A_1/(2\pi)^2$ [THz^2]	$\omega_1/2\pi$ [THz]	$\gamma_1/2\pi$ [THz]	$A_2/(2\pi)^2$ [THz^2]	$\omega_2/2\pi$ [THz]	$\gamma_2/2\pi$ [THz]	χ^2	Correlation Coefficient
MeOH	1.83±.01	0.27±0.1	0.12±0.02	0.64±0.1	1.0±0.05	1.3±.2	7.35±0.4	3.89±0.1	6.38±0.2	5.5e-04	0.999
EtOH	1.86	0.1±.04	0.08	8.8±0.1	4.7±0.1	18.4±0.3	3.9±0.2	11.9±0.1	0.7±0.1	3.8e-05	0.9999
1-propanol	2.04	0.05	0.1±.01	0.23±.05	4.43±.05	2.6±0.4	12.6±8	8.8±3	50.3±35	1.2e-05	0.9999
2-propanol	1.93±.01	0.08	0.09±.01	9.5±2.8	6.3±0.8	31.8±8.8	1.84±0.5	11.3±0.3	0.15±.01	1.33e-05	0.9999
1-butanol	2.07	0.03	0.08±.01	0.38±.05	4.4±.03	3.5±0.2	12.6±0.3	10.4	79±3.7	6.7e-06	0.9999
1-octanol	2.06	0.2	0.18±.01	3.8±.45	4	25.7±3.4	5.06±.4	9.2	26.8±1.7	5e-06	1