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

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Alcohols differ from water in a number of ways:

- Alcohols are amphiphilic with both polar hydroxyl hydrophilic part and non-polar alkyl hydrophobic part.
- They are miscible with myriads of polar and non-polar solvents.

Insights from dielectric spectroscopy:

- Slow relaxation process, $\sim 50$ ps
- Intermediate relaxation, $\sim 8$ ps
- Very fast process, $\sim 1$ ps
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*


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

- **Current pre-amplifier**
- **Lock-in amplifier 1**
- **Lock-in amplifier 2**
- **PMT**
- **Bias**
- **Sample**
- **Optical Parametric Amplifier**
- **Mirrors**
- **Beam splitters**
- **Plano convex lens**
- **BBO**
- **Silicon filter**
- **Parabolic Mirror**
- **Chopper**
- **Plasma**
- **Dichroic mirrors**
- **400 nm bandpass filter**
- **Retro-reflector**
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.

\[
\frac{\tilde{E}_{sam}(t)}{\tilde{E}_{cell}(t)} = \frac{\tilde{E}_{sam}(\omega)}{\tilde{E}_{cell}(\omega)} = \sqrt{T(\omega)} \exp(i\phi(\omega))
\]
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

3.8 THz (~ 127 cm\(^{-1}\))

~ 8 THz

~ 4-5 THz

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.

Frequency \( \sim 4 \) THz
Debye Model & Damped Harmonic Oscillator Model

**Debye Model**

\[
\hat{\mathcal{E}}(\omega) = \varepsilon_\infty + \sum_{j=1}^{n} \frac{\Delta \varepsilon_j}{(1 + i \omega \tau_j)}
\]

- 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**

\[
\hat{\mathcal{E}}(\omega) = \varepsilon_\infty + \sum_{j=1}^{n} \frac{\Delta \varepsilon_j}{1 + i \omega \tau_j} + \sum_{l=1}^{k} \frac{A_j}{\omega^2 - \omega^2 + i \omega \gamma_l}
\]

**Single Debye and Double Damped Oscillator Model**

\[
\hat{\mathcal{E}}(\omega) = \varepsilon_\infty + \frac{\Delta \varepsilon}{1 + i \omega \tau} + \frac{A_1}{\omega_1^2 - \omega^2 - i \omega \gamma_1} + \frac{A_2}{\omega_2^2 - \omega^2 - i \omega \gamma_2}
\]
a) methanol, b) ethanol, c) 1-propanol, d) 2-propanol, e) 1-butanol, and f) 1-octanol.
### Debye and Oscillator parameters

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>$\tau$ (fs)</th>
<th>$\omega_1$ (THz)</th>
<th>$\omega_2$ (THz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>120</td>
<td>1.0</td>
<td>3.9</td>
</tr>
<tr>
<td>Ethanol</td>
<td>80</td>
<td>4.7</td>
<td>11.9</td>
</tr>
<tr>
<td>1-propanol</td>
<td>107</td>
<td>4.4</td>
<td>8.9</td>
</tr>
<tr>
<td>2-propanol</td>
<td>98</td>
<td>6.2</td>
<td>11.4</td>
</tr>
<tr>
<td>1-butanol</td>
<td>88</td>
<td>4.4</td>
<td>10.5</td>
</tr>
<tr>
<td>1-octanol</td>
<td>196</td>
<td>4.0</td>
<td>9.2</td>
</tr>
</tbody>
</table>

- **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

400 - 700 molecules

Energy Minimization

Heating up to 300 K

Equilibration at NPT for 5 ns

Production run at NVT for 5 ns
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

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Modes</th>
<th>Force Const. (kcal.mol(^{-1}\text{Å}^2))</th>
<th>Freq (THz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>O...H</td>
<td>6222.2</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>C...C</td>
<td>487.4</td>
<td>1.8</td>
</tr>
<tr>
<td>Ethanol</td>
<td>O...H</td>
<td>6309.5</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>C...C</td>
<td>282.3</td>
<td>1.1</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>O...H</td>
<td>6276.3</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>C...C</td>
<td>214.0</td>
<td>0.9</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>O...H</td>
<td>5985.9</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>C...C</td>
<td>286.9</td>
<td>1.0</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>O...H</td>
<td>6364.7</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>C...C</td>
<td>9.8</td>
<td>0.2</td>
</tr>
<tr>
<td>1-Octanol</td>
<td>O...H</td>
<td>6436.4</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>C...C</td>
<td>204.9</td>
<td>0.6</td>
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MP2/aug-cc-pVDZ method
## Comparing Experimental & Computed Results

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>$\tau$ (fs)</th>
<th>$\omega_1$ (THz)</th>
<th>$\omega_2$ (THz)</th>
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<th>C....C</th>
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<td>5.4</td>
<td>1.1</td>
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<td>0.9</td>
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<td>10.5</td>
<td>4.3</td>
<td>0.2</td>
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<tr>
<td>1-octanol</td>
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<td>4.0</td>
<td>9.2</td>
<td>3.2</td>
<td>0.6</td>
</tr>
</tbody>
</table>
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

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PI: Dr Pankaj Mandal

Collaborators: Dr Arnab Mukherjee, Debasis Saha

Labmates: Sneha, Avinash, Reddy

Thank You
<table>
<thead>
<tr>
<th>Sample</th>
<th>$\varepsilon_0$</th>
<th>$\varepsilon_1$</th>
<th>$\tau_1$ (ps)</th>
<th>$A_1/(2\pi)^2$ [THz$^2$]</th>
<th>$\omega_1/2\pi$ [THz]</th>
<th>$\gamma_1/2\pi$ [THz]</th>
<th>$A_2/(2\pi)^2$ [THz$^2$]</th>
<th>$\omega_2/2\pi$ [THz]</th>
<th>$\gamma_2/2\pi$ [THz]</th>
<th>$\chi^2$</th>
<th>Correlation Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>1.83±0.11</td>
<td>0.27±0.01</td>
<td>0.12±0.02</td>
<td>0.64±0.10</td>
<td>1.0±0.05</td>
<td>1.3±0.2</td>
<td>7.35±0.4</td>
<td>3.89±0.1</td>
<td>6.38±0.2</td>
<td>5.5e-04</td>
<td>0.999</td>
</tr>
<tr>
<td>EtOH</td>
<td>1.86</td>
<td>0.1±0.04</td>
<td>0.08</td>
<td>8.8±0.1</td>
<td>4.7±0.1</td>
<td>18.4±0.3</td>
<td>3.9±0.2</td>
<td>11.9±0.1</td>
<td>0.7±0.1</td>
<td>3.8e-05</td>
<td>0.9999</td>
</tr>
<tr>
<td>1-propanol</td>
<td>2.04</td>
<td>0.05</td>
<td>0.1±0.01</td>
<td>0.23±0.05</td>
<td>4.43±0.05</td>
<td>2.6±0.4</td>
<td>12.6±8</td>
<td>8.8±3</td>
<td>50.3±35</td>
<td>1.2e-05</td>
<td>0.9999</td>
</tr>
<tr>
<td>2-propanol</td>
<td>1.93±0.11</td>
<td>0.08</td>
<td>0.09±0.01</td>
<td>9.5±2.8</td>
<td>6.3±0.8</td>
<td>31.8±8.8</td>
<td>1.84±0.5</td>
<td>11.3±0.3</td>
<td>0.15±0.1</td>
<td>1.33e-05</td>
<td>0.9999</td>
</tr>
<tr>
<td>1-butanol</td>
<td>2.07</td>
<td>0.03</td>
<td>0.08±0.01</td>
<td>0.38±0.05</td>
<td>4.4±0.03</td>
<td>3.5±0.2</td>
<td>12.6±0.3</td>
<td>10.4</td>
<td>79±3.7</td>
<td>6.7e-06</td>
<td>0.9999</td>
</tr>
<tr>
<td>1-octanol</td>
<td>2.06</td>
<td>0.2</td>
<td>0.18±0.01</td>
<td>3.8±0.45</td>
<td>4</td>
<td>25.7±3.4</td>
<td>5.06±4</td>
<td>9.2</td>
<td>26.8±1.7</td>
<td>5e-06</td>
<td>1</td>
</tr>
</tbody>
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