Structure & dynamics of hydrogen bonded liquids

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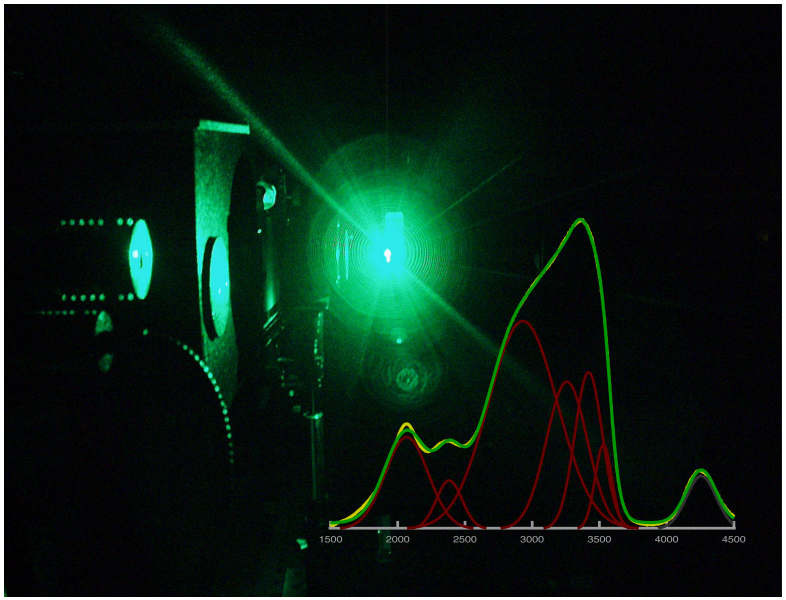
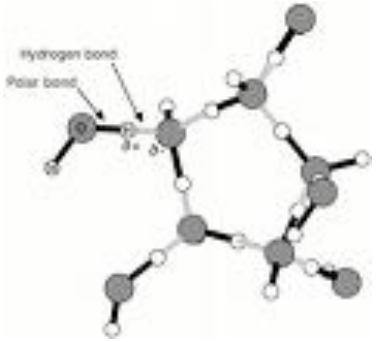


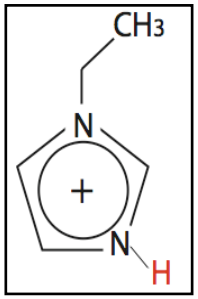
Co-workers:
Per Sillrén, Johan Matsson & Itai Panas
Chalmers

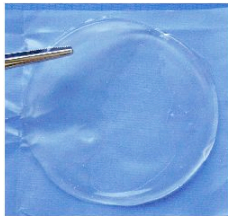


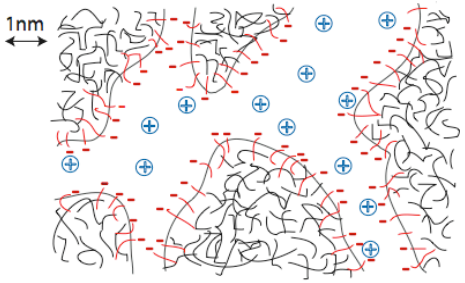
Hydrogen bonding



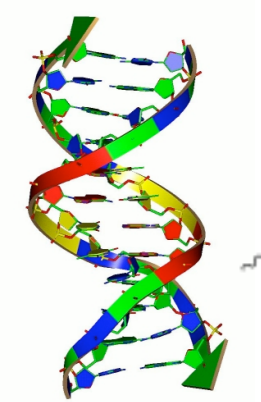
Protic ILs

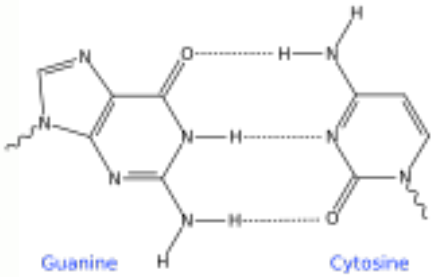




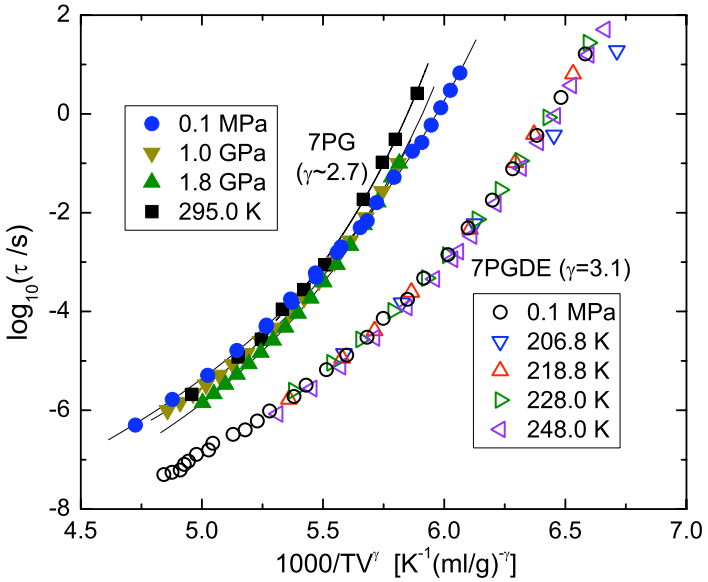


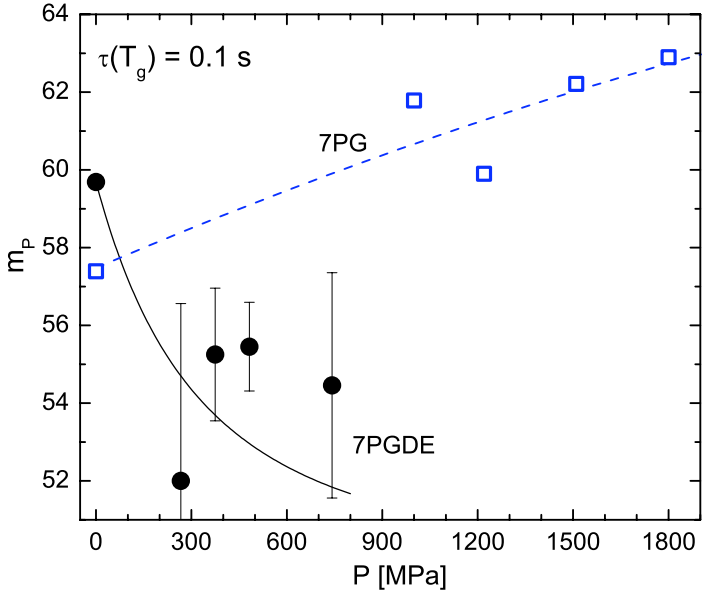
Fully hydrated Nafion®





Hydrogen bonded glass-forming liquids





7PGDE

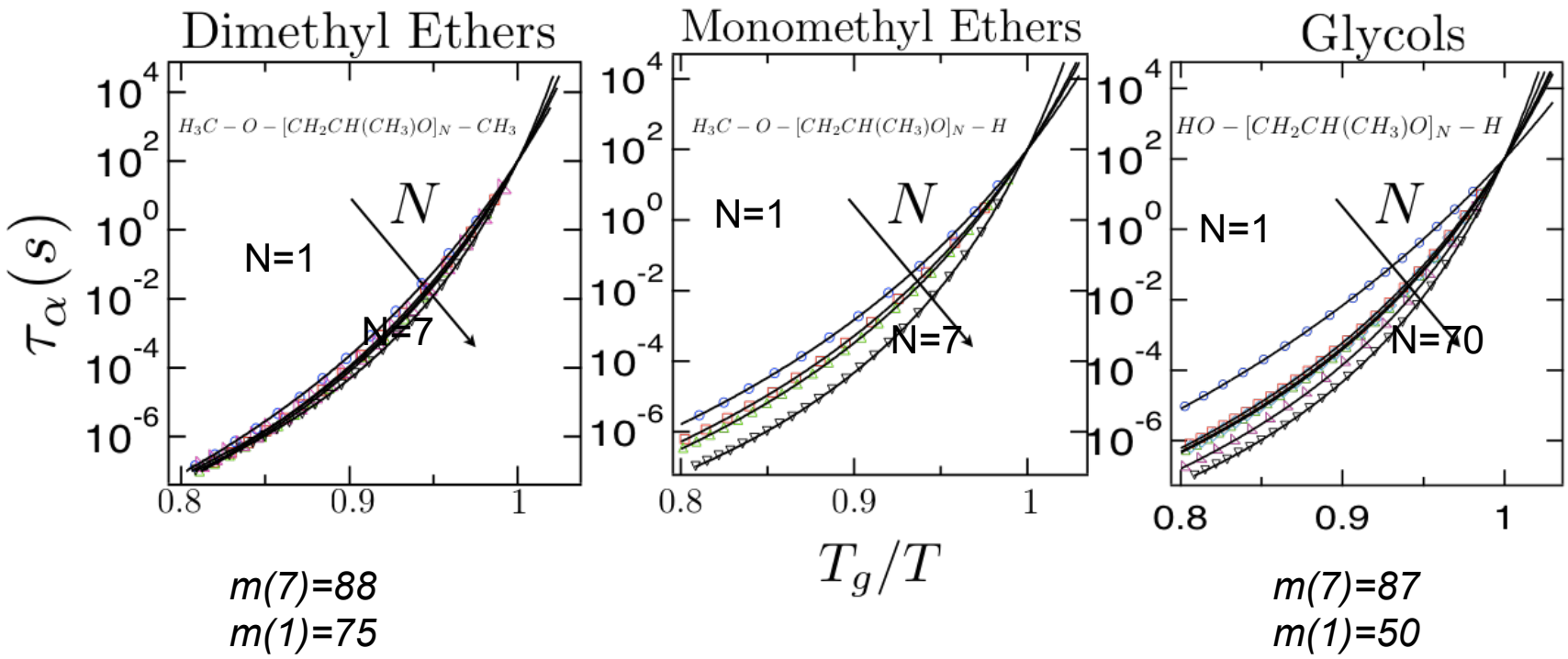
$H_3C\text{-}O\text{-}[CH_2CH(CH_2)O]_7\text{-}CH_3$

7PG

$HO\text{-}[CH_2CH(CH_2)O]_7\text{-}H$

Roland, Cassalini, Bergman, Mattsson, PRB 77, 012201 (2008)

Hydrogen bonded glass-forming liquids

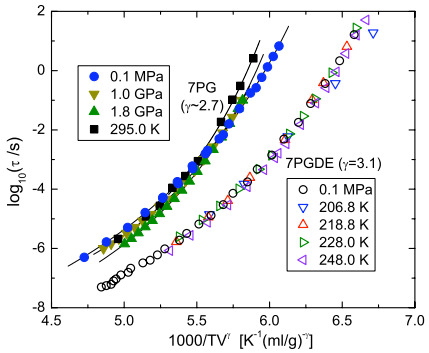


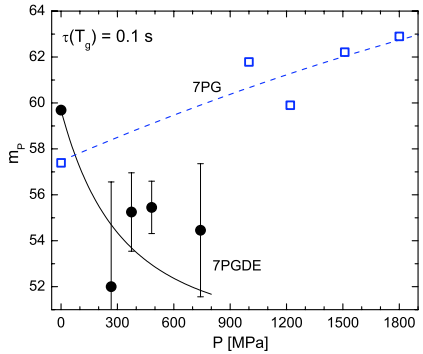
m(7)=88
m(1)=75

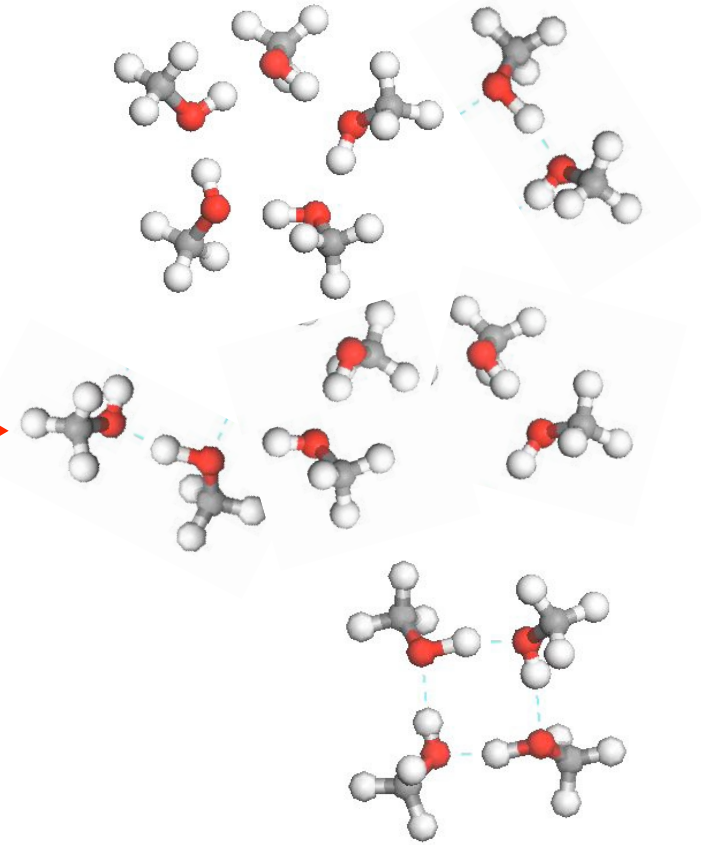
m(7)=87
m(1)=50

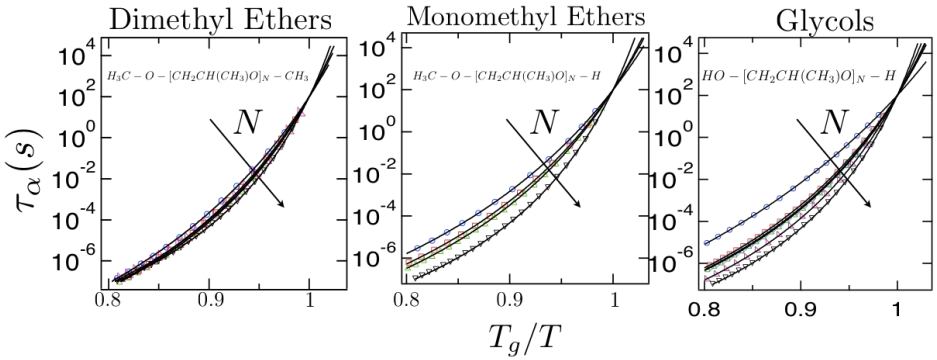
Strong dependence of the dynamics on H-bond density

Hydrogen bonding: dynamics vs. structure









(How) does the hydrogen-bond network change as a function of temperature?

Hydrogen bonding

…part of ongoing work…

Physica Scripta. Vol. 35, 000–000, 1987.

Structural Relaxation Behaviour in Polymers; A Molecular Weight Dependence in the Hypersonic Properties of Low Molecular Weight Poly(Propylene Glycol)

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Received July 10, 1986; accepted September 22, 1986

Abstract

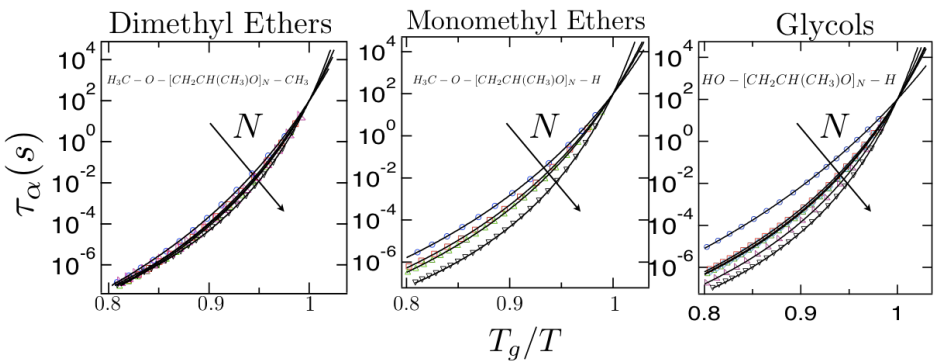
A molecular weight dependence in the hypersonic properties of low molecular weight poly(propylene glycol) (PPG) (400–4000) has been measured. Results for PPG 2000 are emphasized. Sound velocity increases with decreasing molecular weight and the maximum of the hypersonic loss peak shifts to higher temperatures. We ascribe this effect to a decrease in the flexibility of the polymer chain backbone as the molecular weight decreases. Hydrogen bonding involving the "OH" terminating groups causes an increase in the gauche/trans ratio and stiffens the chain.

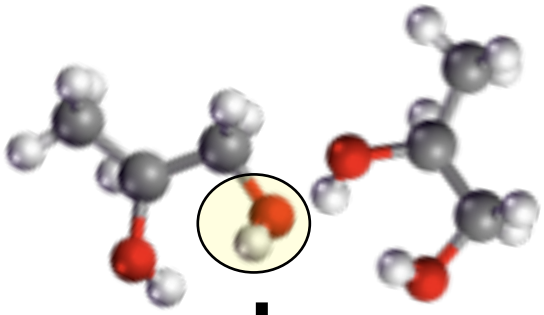
cular weight dependence for the hypersonic velocity and attenuation coefficient. No such dependence was found previously [2, 3]. In this paper we report the results of this work emphasizing those for PPG 2000.

In Brillouin scattering investigations any observed relaxation phenomenon is structural in character (including shear effects) and in the short time region ($\sim 10^{-11}$ s). Through this technique the hypersonic properties of the scattering medium are probed at high frequencies (~ 10 GHz).

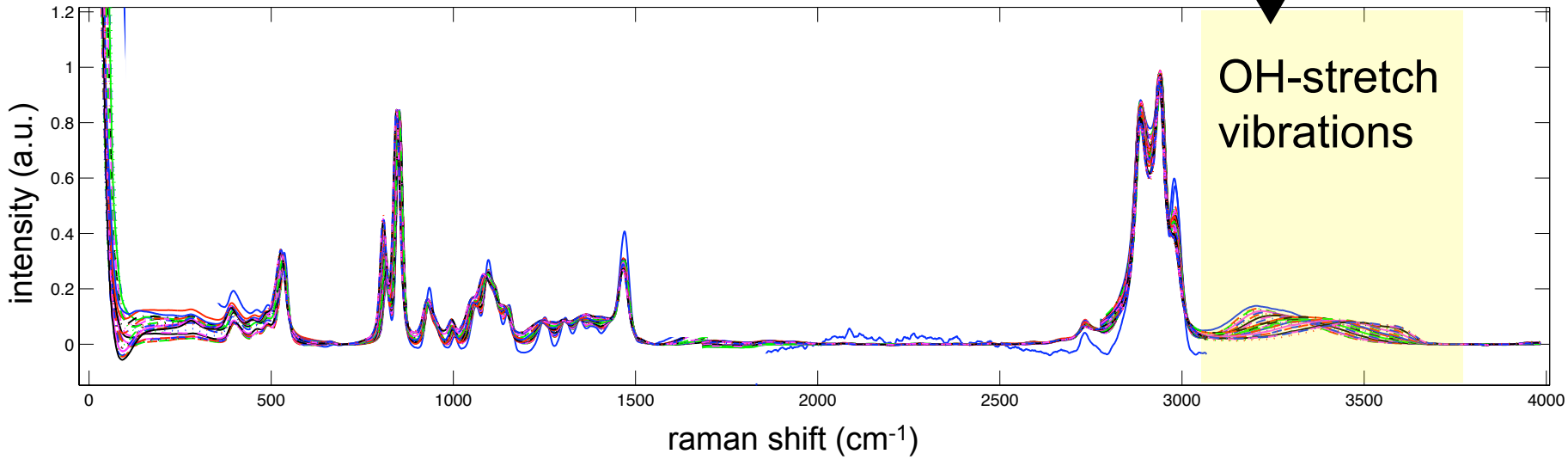
For an isotropic medium the frequency shift of the Brill-

Probing the H-bond network through vibrational spectroscopy



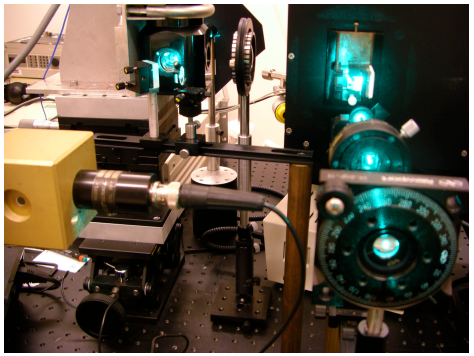


Raman spectra for propylene glycole



(How) does the hydrogen-bond network change as a function of temperature?

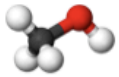
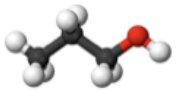
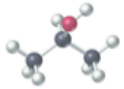
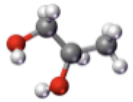
Raman experiments



Polarized and depolarized spectra $T_b \Rightarrow T_g$

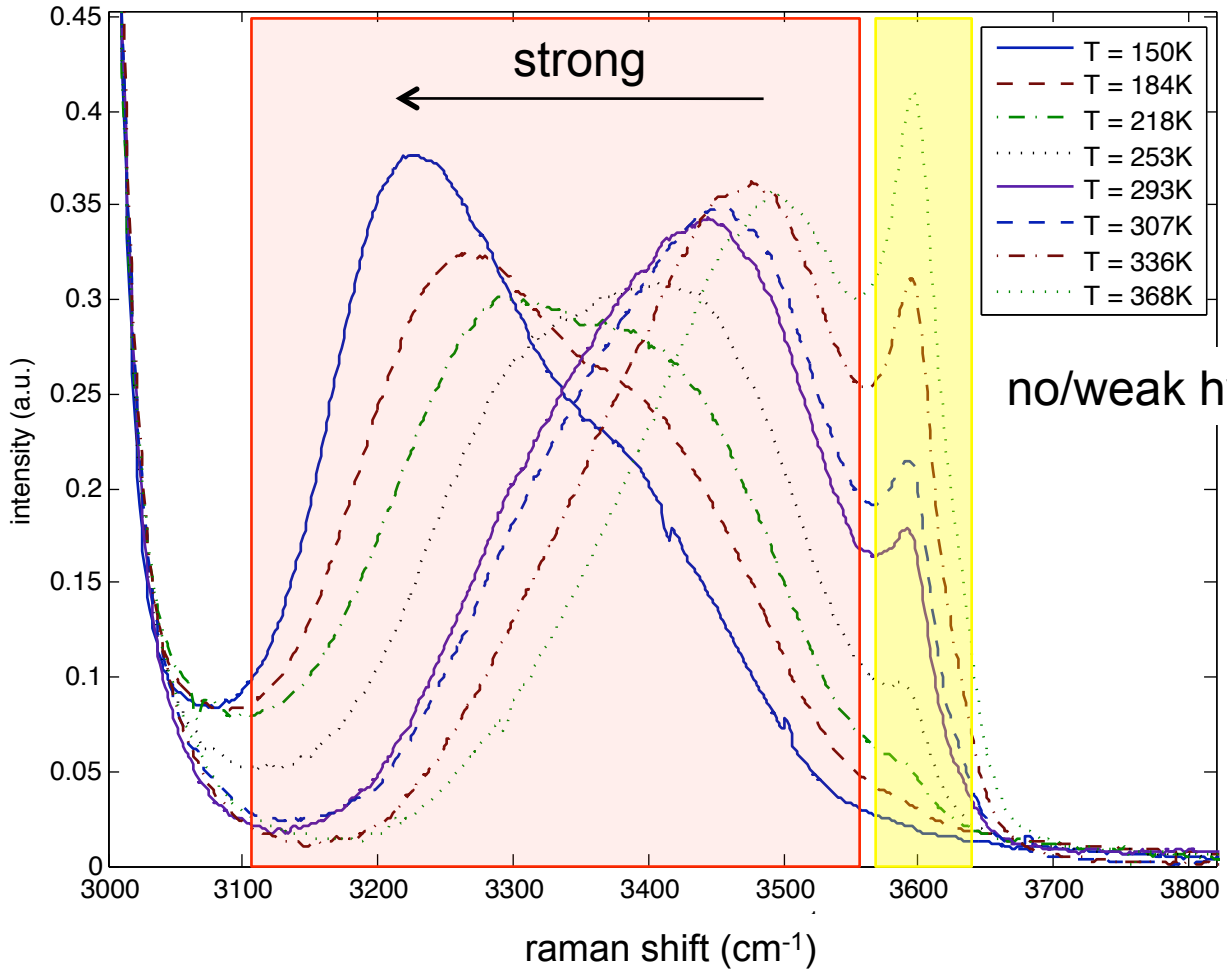
$$\alpha'^2 \propto I_P - 4/3 \times I_{DP} \quad \text{isotropic}$$

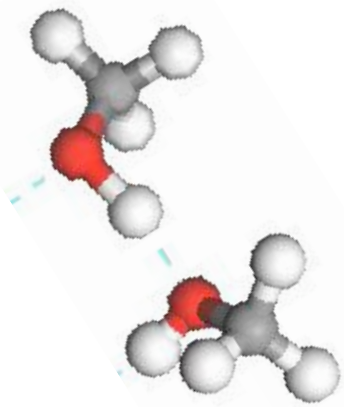
$$\gamma'^2 \propto 15 \times I_{DP}. \quad \text{anisotropic}$$

Liquid	T_g	T_m	T_b	m (if known)
Methanol 	100K	176K	337K	
Propanol 	96K	146K	370K	35 [3]
Isopropanol 	96K	185K	355K	
Propylene glycol 	168K	214K	455K	50
Propylene glycol monomethyl ether	143K	176K	392K	63
Water	124K-170K	273K	373K	

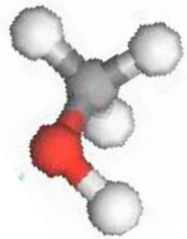
Vibrational spectra – OH-stretch vs. temperature

propylene glycole monomethylether (PGME)

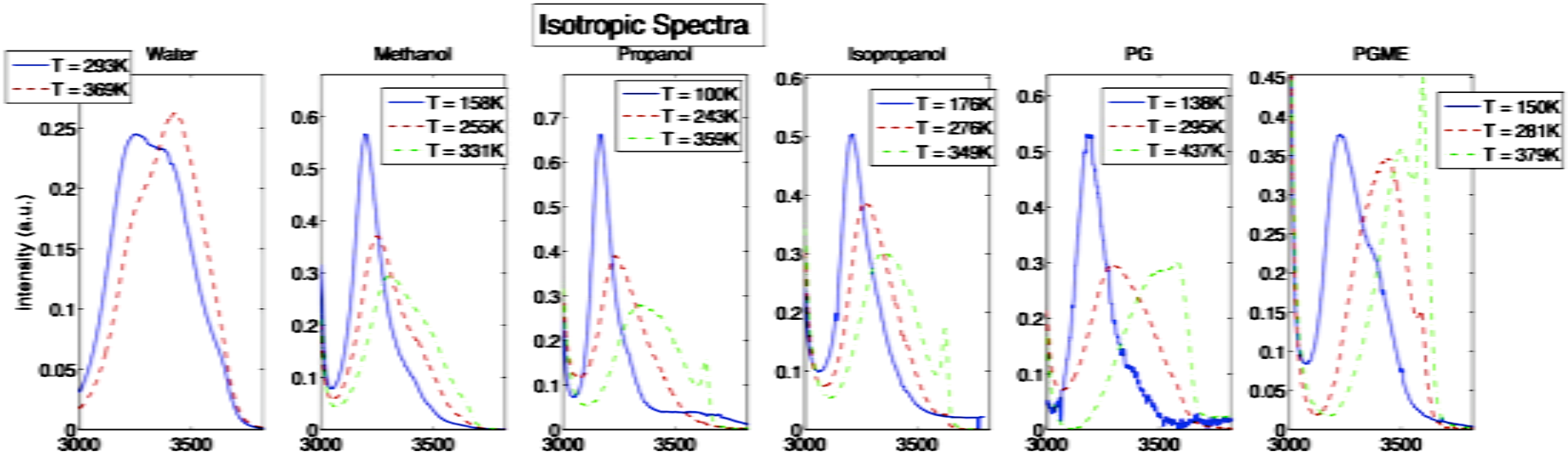




no/weak hydrogen bonding



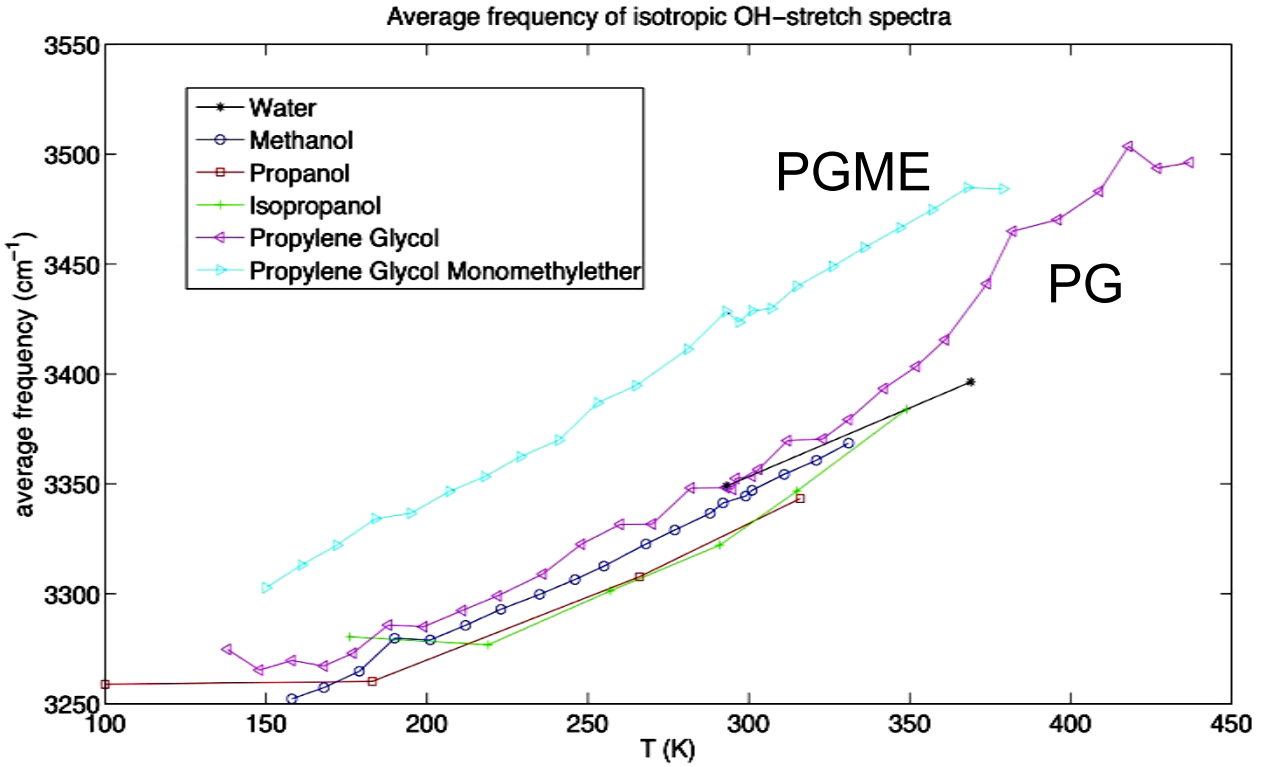
Vibrational spectra – OH-stretch vs. temperature



General trends

- Down shift of OH-stretch band with decreasing temperature
- More non-bonded OH-groups in liquids with low OH-bond density
- Non-bonded OH-groups decrease ⇒ connectivity increases

Average spectral frequency 3100-3800 cm^{-1}

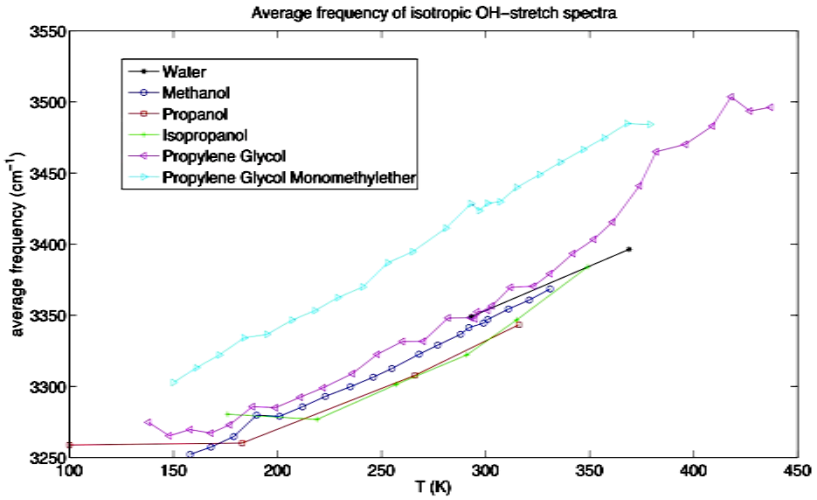


⇒ Remarkably similar temperature dependence, $\Delta\omega$~ 0.7 cm^{-1}/K

⇒ No evident anomalies/discontinuities in the super-cooled state

⇒ PGME has a higher average frequency.

Average spectral frequency 3100-3800 cm^{-1}



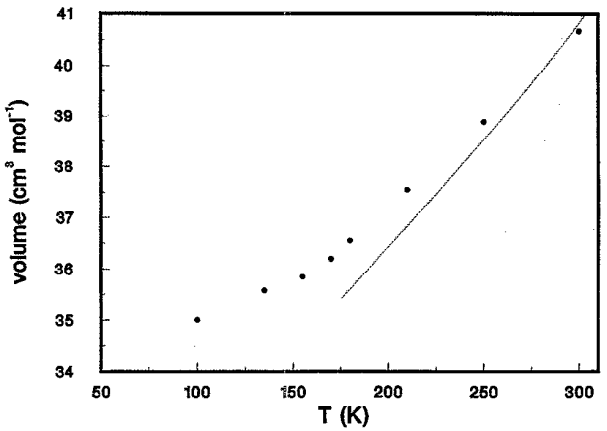
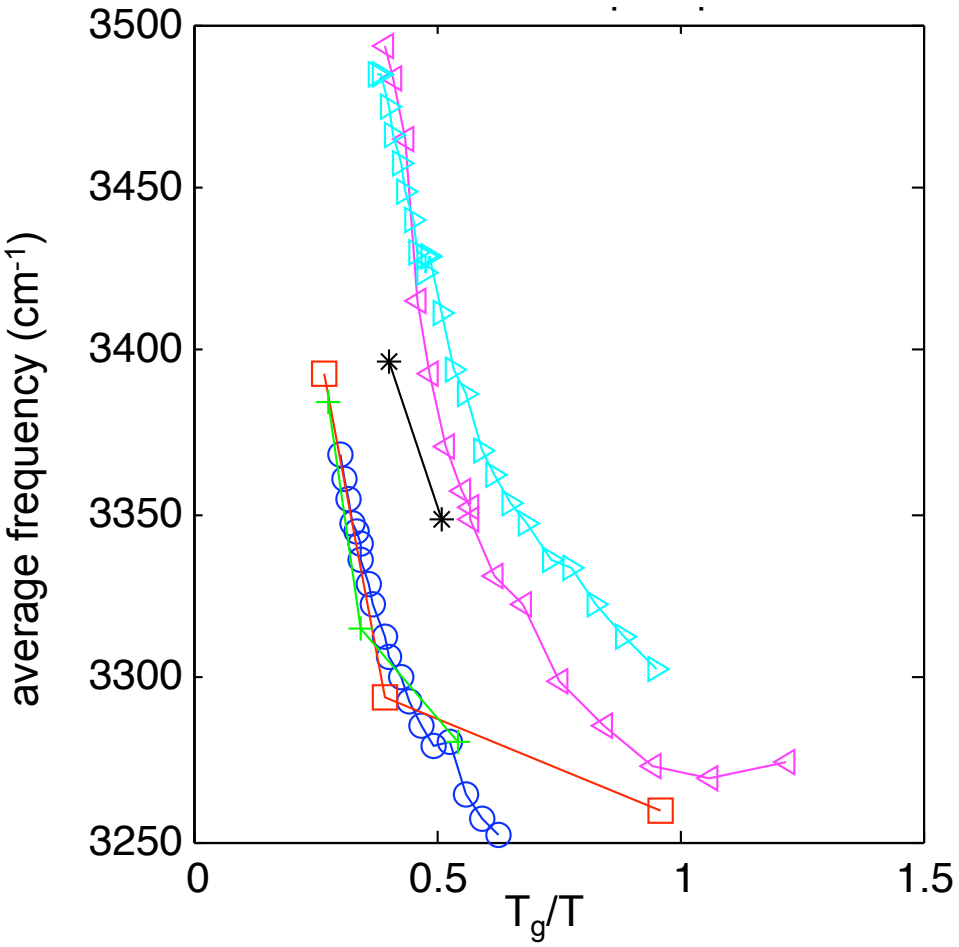


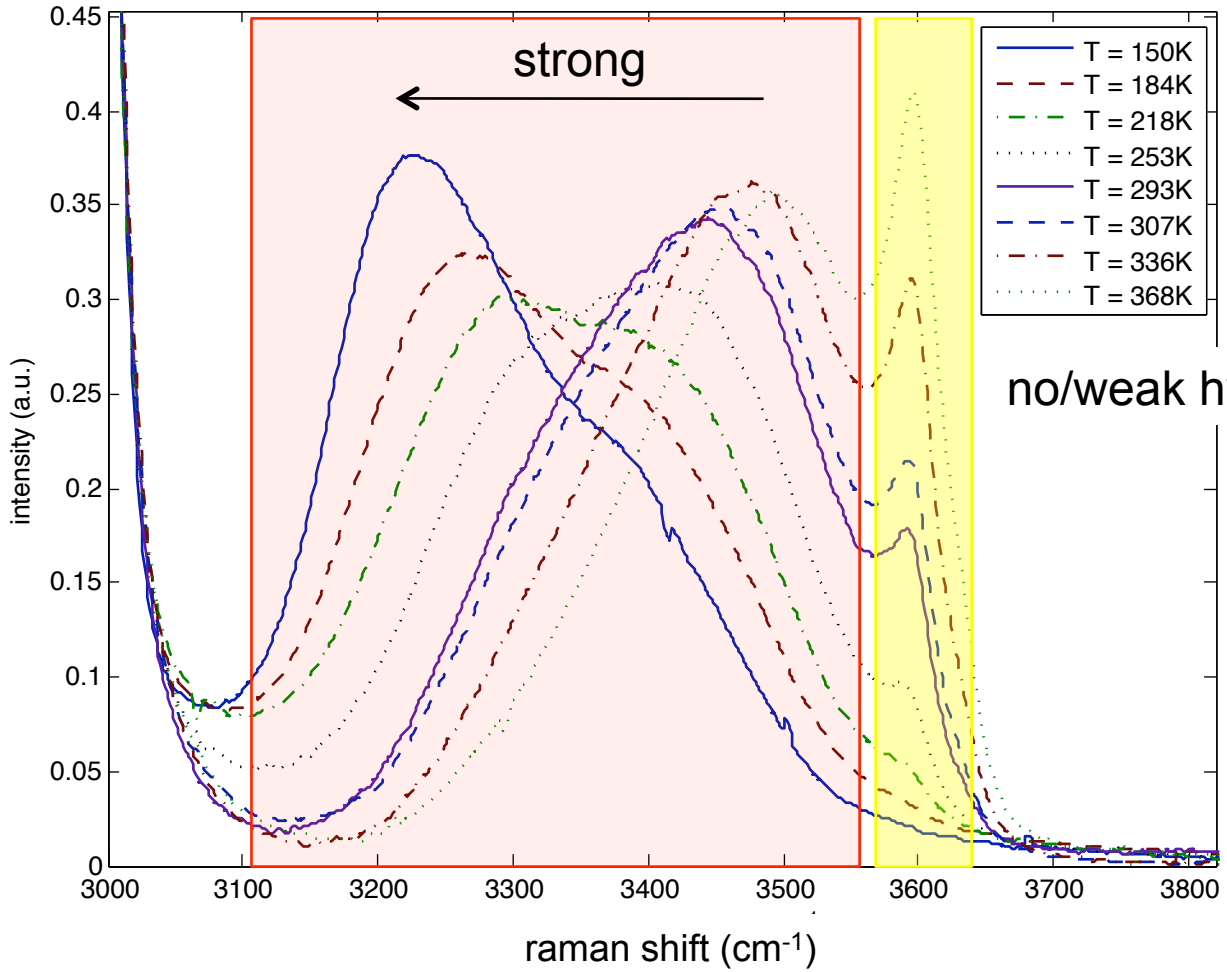
FIG. 1. Temperature dependence of the molar volume of methanol. The solid curve is the experimental data taken from Ref. 14, and the dots are the present molecular dynamics results.

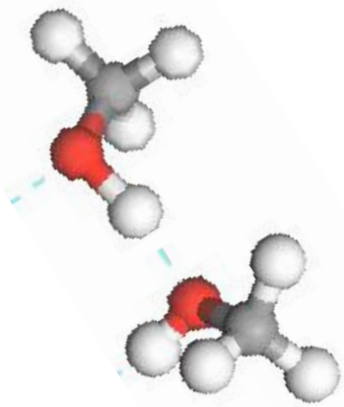


Sindzingre & Klein, *JCP 96, 4681 (1992)*

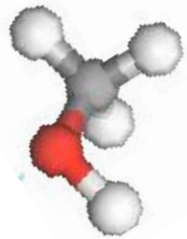
Vibrational spectra – OH-stretch vs. temperature

propylene glycole monomethylether (PGME)



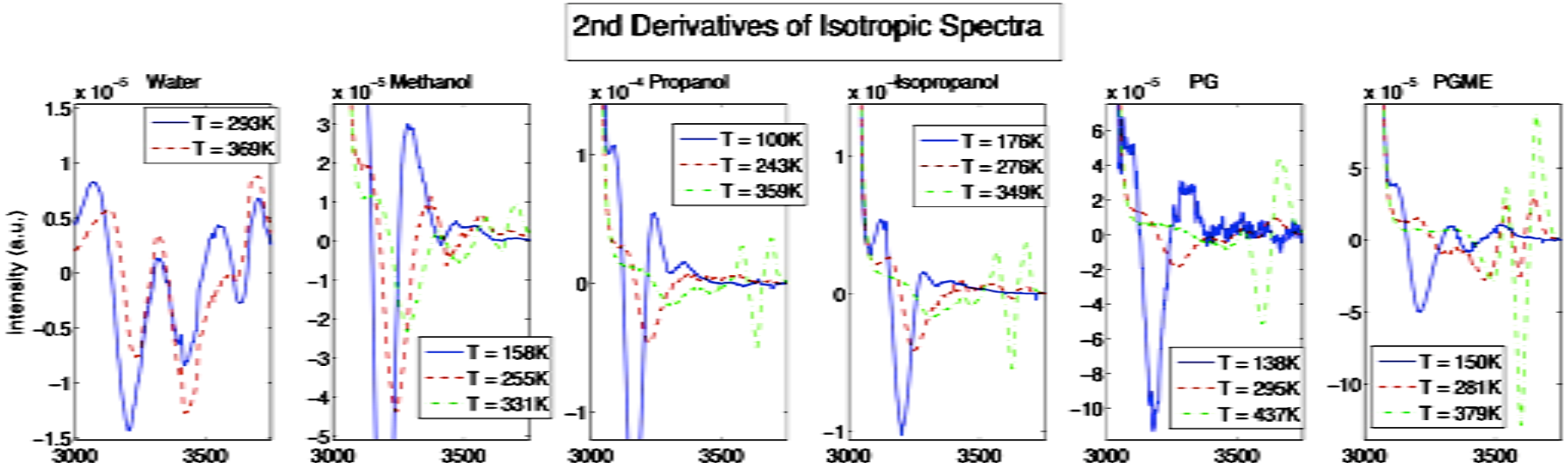


no/weak hydrogen bonding



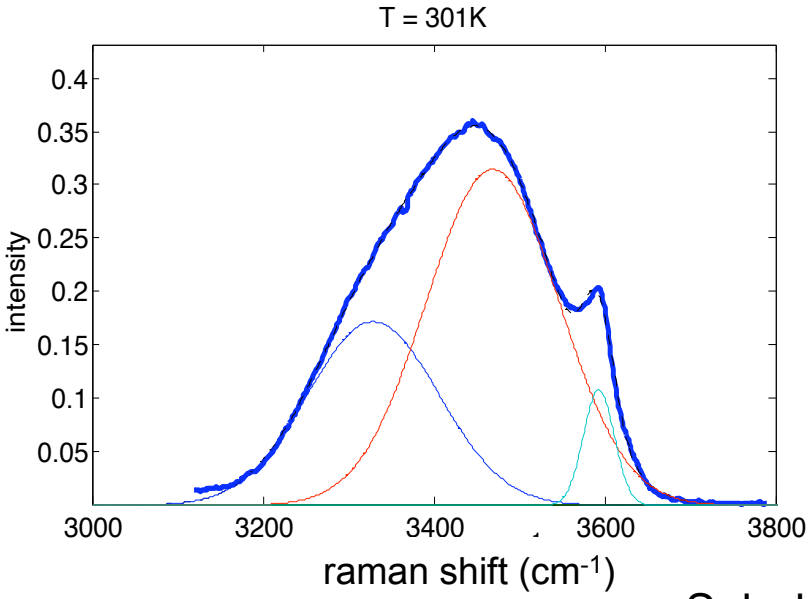
Band analysis – 2nd derivative to identify components

- In the 2nd derivative of the Raman spectra each sub-band corresponds to a minimum
- 3 minima found in the isotropic spectra

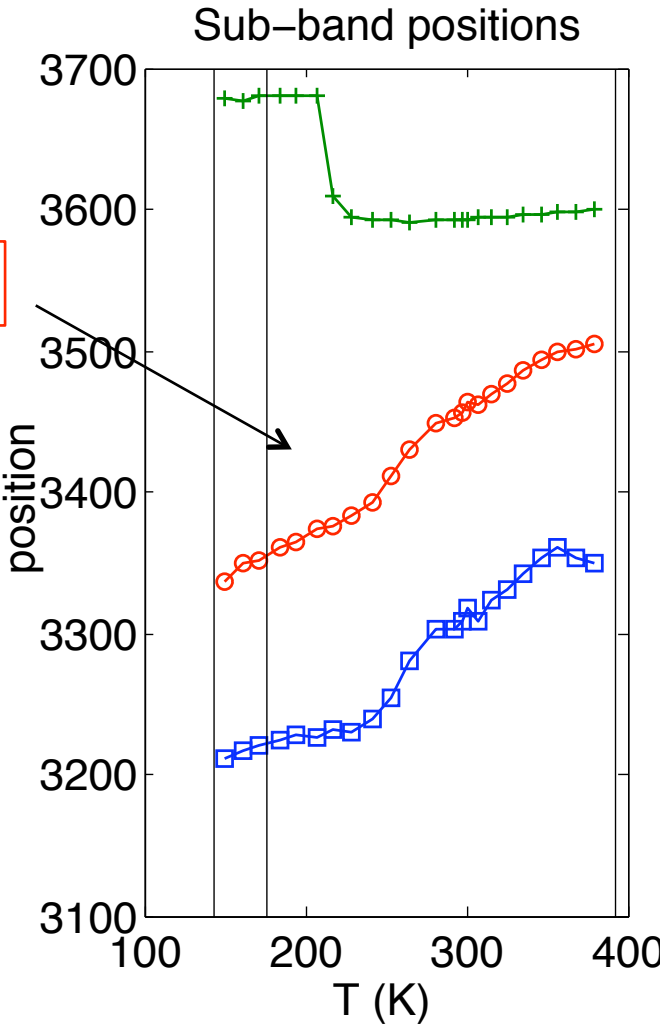


- Position of ~3600 cm^{-1} independent of temperature, intensity decreases
- ~3300 cm^{-1}, ~3500 cm^{-1} shifts toward lower frequencies with decreasing temperature, strengths of the bands vary with temperature

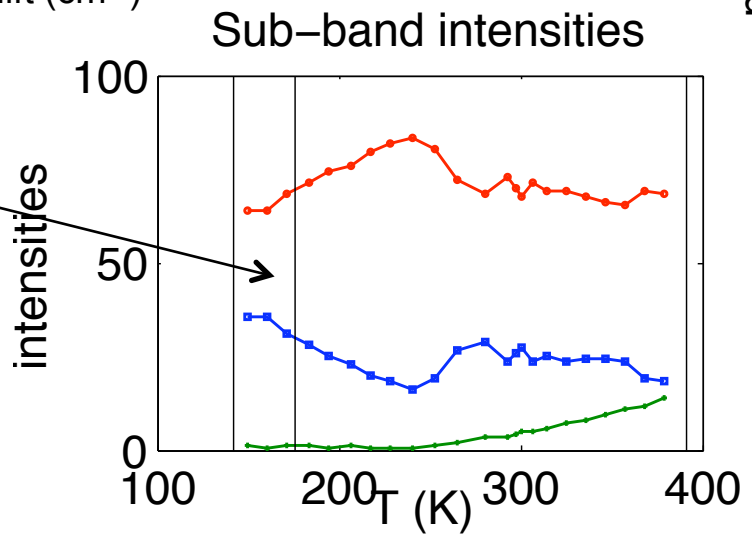
Band analysis – fitting PGME with 3 gaussian functions



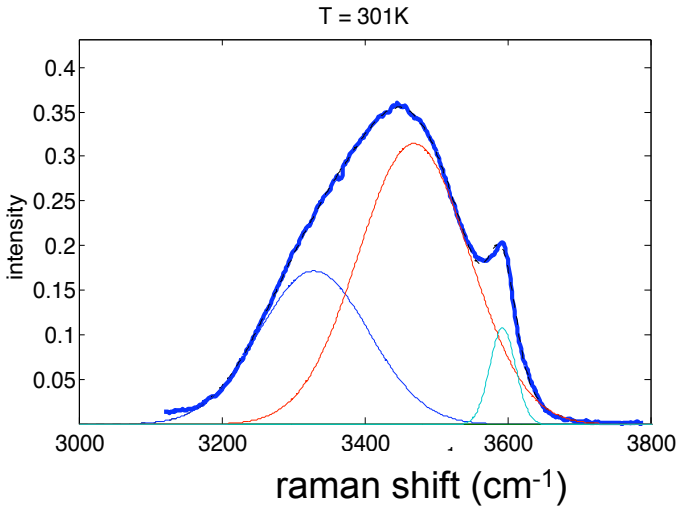
softening

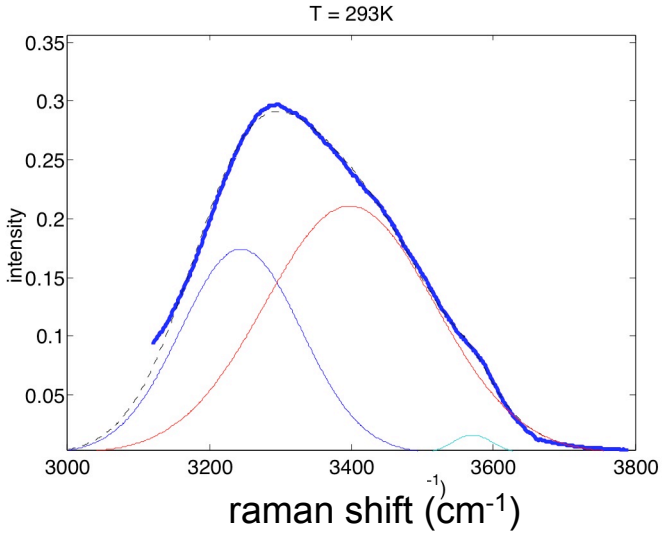


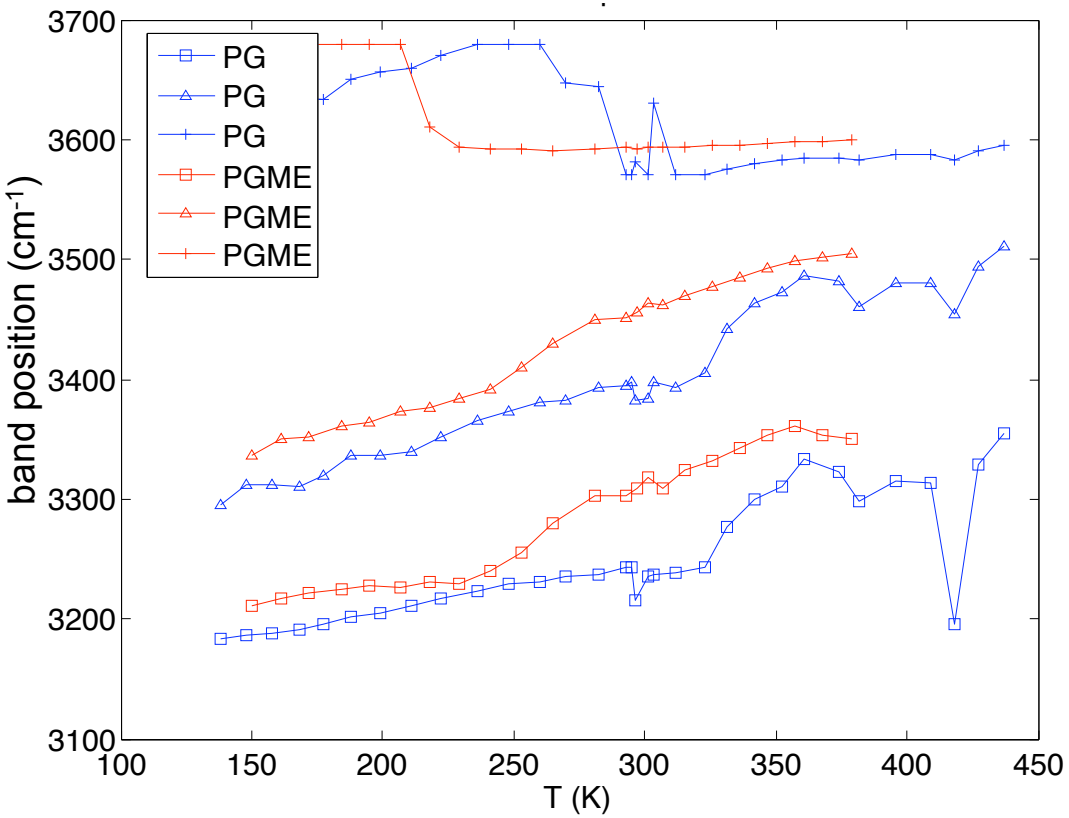
Intensity redistribution



Band analysis: PG vs. PGME

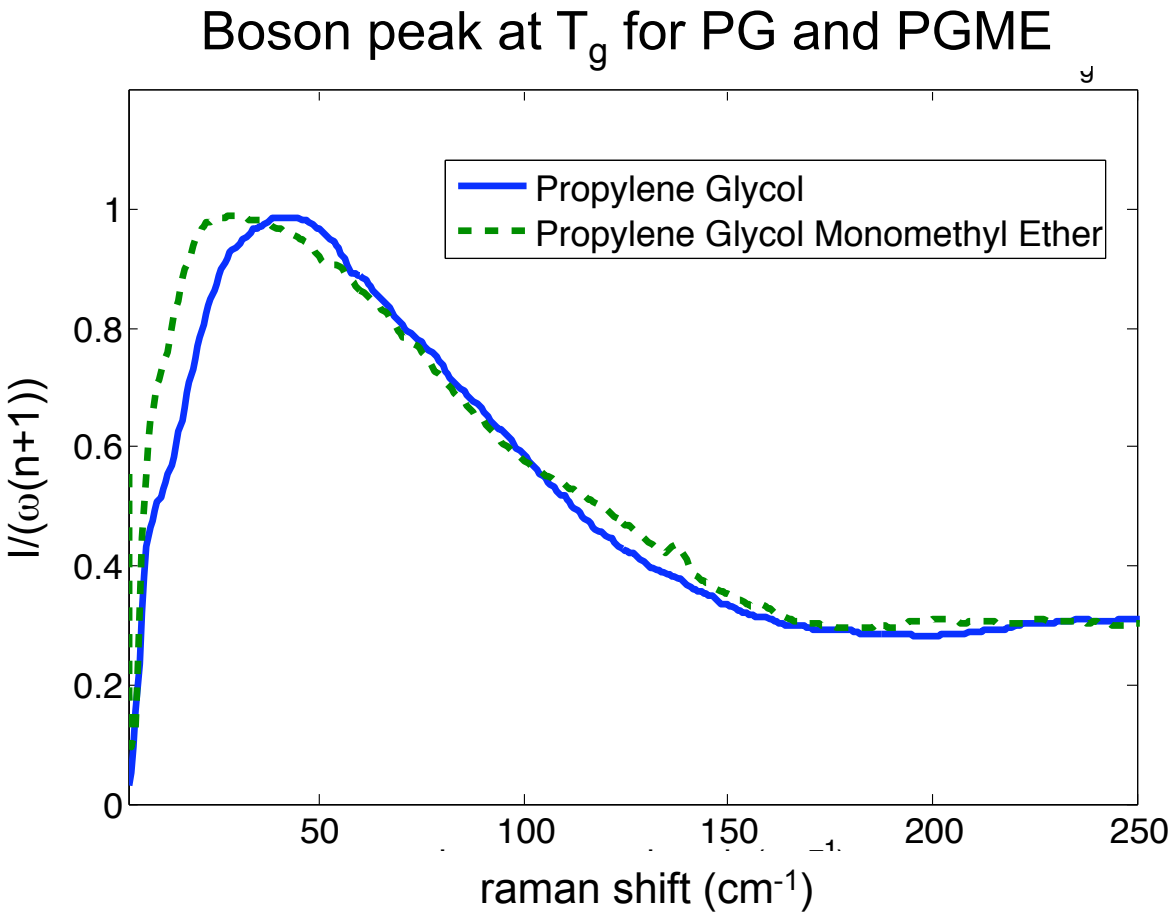






Main difference in weight of the two bands

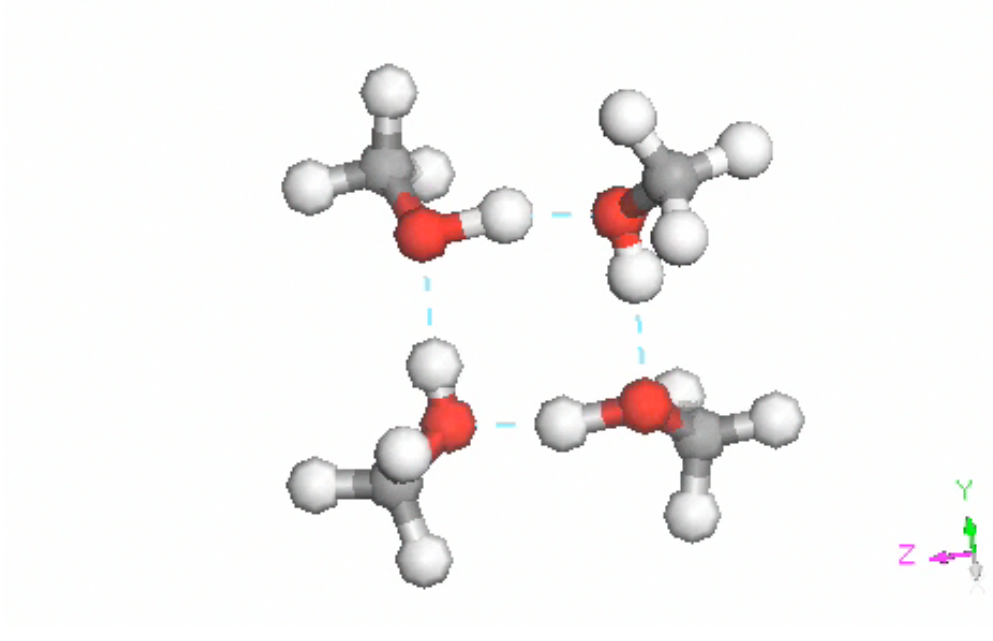
Vibrational spectra – Boson peak



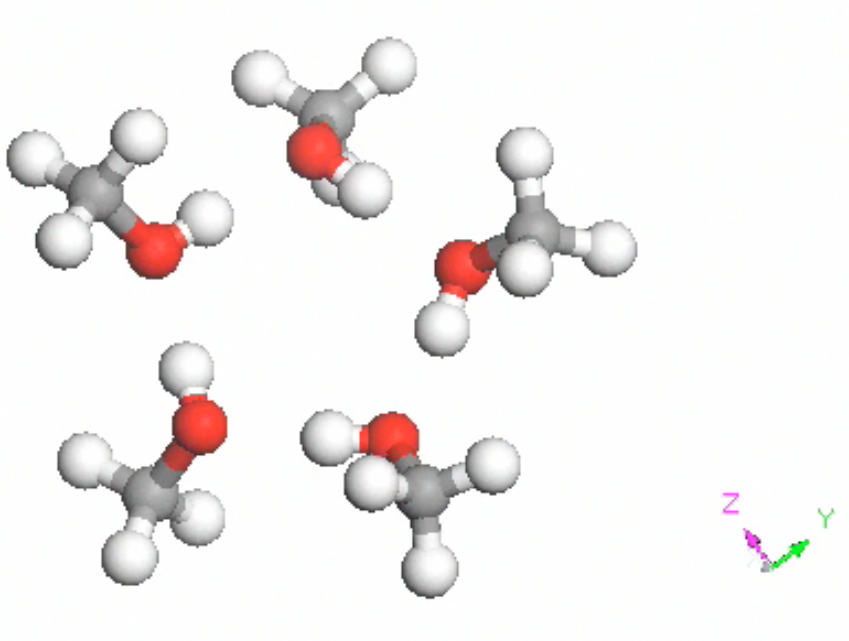
Stronger hydrogen bond network also reflected in a higher boson peak frequency

Vibrational spectra – modelling

Toy structures of methanol from ab-initio calculation



3170 cm^{-1}



2855 cm^{-1}

What did we learn?

⇒ Surprising similar temperature dependence of the OH-stretch band $\Delta\omega$=*0.7 cm^{-1}/K*. Similar structural rearrangement?

⇒ Soften of OH band combination of mode softening and redistribution of intensity

⇒ Liquids with low H-bond density “non H-bonded” molecules are present at high temperatures.
Low temperatures - incorporation in the H-bond network.