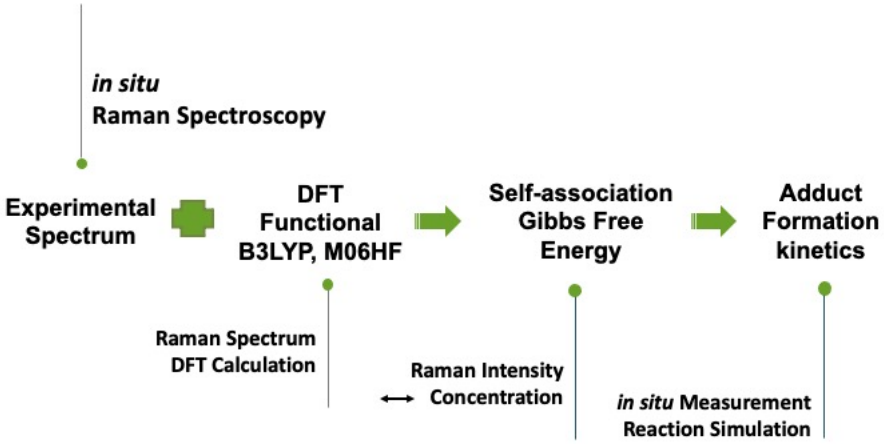
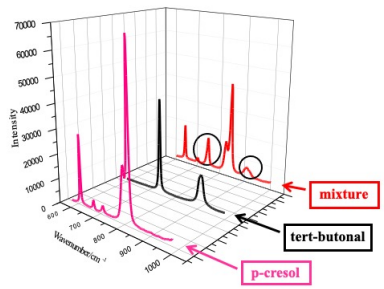
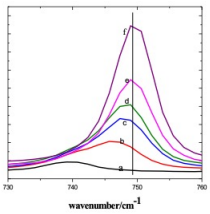
Approach



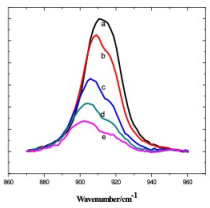
p-cresol-tert-butanol/CCl_4



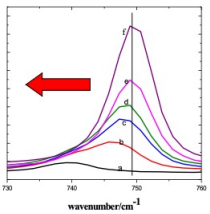
p-cresol-tert-butanol/CCl_4



changing in peak position



changing in line shape



Experimental data

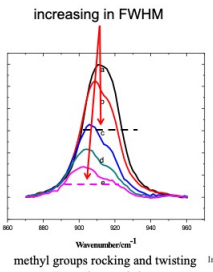
C_3C-O symmetric stretching

p-cresol-tert-butanol/CCl_4

peak position cm^{-1}		
C_3-C symmetric strtching	tert-butanol+CCl_4	adduct+CCl_4
	743.77	739.55

DFT calculation results of the ~750cm^{-1} band

increasing in FWHM

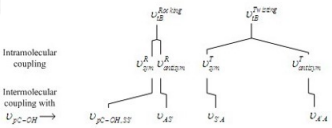


methyl groups rocking and twisting

Experimental data

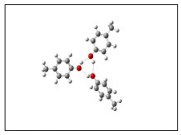
peak position cm^{-1}		
Vibration mode	tert-butanol+CCl_4	adduct+CCl_4
Symmetric rocking	908	895
Antisymmetric rocking	908	916
Symmetric twisting	923	928

DFT calculation results of the 915cm^{-1} band

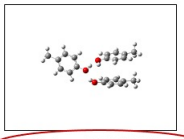


"Determining Stoichiometry in p-cresol/tert-butanol and p-cresol/piperazine Hydrogen Bond Complexes Using Raman Spectroscopy and DFT Calculation", Min Huang, Lin Cao and Jianghua Wu, presented at 2013 AIChE annual meeting, San Francisco, California, USA, Nov.5, 2013

p-Cresol self-Association



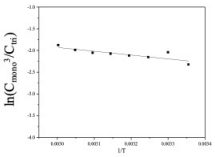
p-Cresol trimer, B3LYP/6-311++d p



p-Cresol trimer, M06HF/6-311++ d,p

Method	B3LYP/6-311++G		M06HF/6-311++G	
Species	Energy Ha	Peak Position cm^{-1}	Energy Ha	Peak Position cm^{-1}
Monomer	-346.79	656	-346.68	652(1.70)
Trimmer	-1040.35	657.5	-1040.03	648-651(4.59)
Gibbs	-6.67×10^{-3}		-3.33×10^{-3}	

p-Cresol self-Association



$$\Delta G_{ex} = -1.8 kcal/mol$$

$$\Delta G_{M06} = -2.1 kcal/mol$$

$$M_3 \rightleftharpoons 3M$$

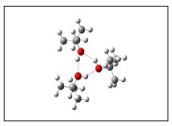
$$r_{mono} = -\frac{dC_{mono}}{dt} = k_+ C_{tri} - k_- C_{mono}^3$$

$$K_e = \frac{k_+}{k_-} = \frac{C_{mono}^3}{C_{tri}}$$

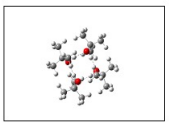
$$\ln K = \ln A + \frac{\Delta G_3}{RT} = \ln\left(\frac{C_{mono}^3}{C_{tri}}\right)$$

$$\frac{C_{mono}^3}{C_{tri}} = \frac{I_{mono}^3 / 2.7}{\left(I_{mono} + \frac{I_{tri}}{2.7}\alpha_{RR} - I_{RR}\right)^2}$$

tert-Butanol self-Association



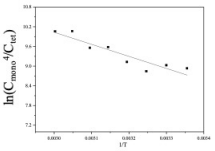
tert-Butanol trimer, M06HF/6-311++ d,p



tert-Butanol tetramer, M06HF/6-311++ d,p

Method	B3LYP/6-311++G		M06HF/6-311++G	
Species	Energy Ha	Peak Position cm^{-1}	Energy Ha	Peak Position cm^{-1}
Monomer	-233.65	743.8(16.8)	-233.55	765.9(21.8)
Trimmer	-700.65	764-784(72)	700.6	764-770(66)
Tetramer	-934.57	746.4(78.3)	-934.205	766-768(91.6)
Gibbs	-7.5×10^{-3}		-1.25×10^{-3}	

tert-Butanol self-Association



$$\Delta G_{ex} = -6.1 kcal/mol$$

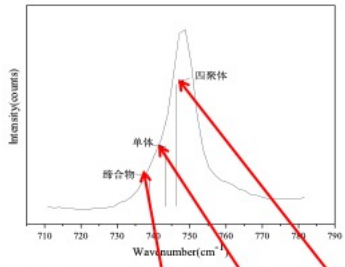
$$\Delta G_{B3LYP} = -4.71 kcal/mol$$

$$M_4 \rightleftharpoons 4M$$

$$\ln K = \ln A + \frac{\Delta G_4}{RT} = \ln\left(\frac{C_{mono}^4}{C_{tet}}\right)$$

$$\frac{C_{mono}^4}{C_{tet}} = \frac{I_{mono}^4 / 4.8}{\left(I_{mono} + \frac{I_{tet}}{4.8}\alpha_{RR} - I_{RR}\right)^3}$$

Raman Intensity of 750cm^{-1} band



DFT Calculated absolute Raman Cross-section

	adduct	monomer	tetramer
Peak position cm^{-1}	739.6	743.8	746.4
Cross-section	16.5	16.8	78.3

$$I_T = I_{add} + I_{tet} + I_{mono}$$

$$I_T = \alpha_{add} N_{add} + \alpha_{tet} N_{tet} + \alpha_{mono} N_{mono}$$

$$I_{add} = \alpha_{tert} N_{add}$$

$$I_{tet} = 4.7 \alpha_{tert} N_{tet}$$

$$I_T = \alpha_{tert} N_{add} + 4.7 \alpha_{tert} N_{tet} + \alpha_{tert} N_{mono}$$

$$N_{add} = C_{add} N$$

$$N_{tet} = C_{tet} N$$

$$N_{mono} = C_{mono} N$$

$$I_T = \alpha_{tet} N (C_{add} + 4.7 C_{tet} + C_{mono})$$

"Study of p-Cresol/Tert-Butanol Adduct Formation Using in Situ Raman Spectroscopy and DFT Calculation", Min Huang, Lin Cao, ZhiCao Yuan, 2014 AIChE annual meeting proceeding, Atlanta, Georgia, USA, Nov.18, 2014