Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Spectroscopic evidence of special intermolecular interaction in iodomethane-ethanol mixtures: the cooperative effect of halogen bonding, hydrogen bonding, and solvent effect

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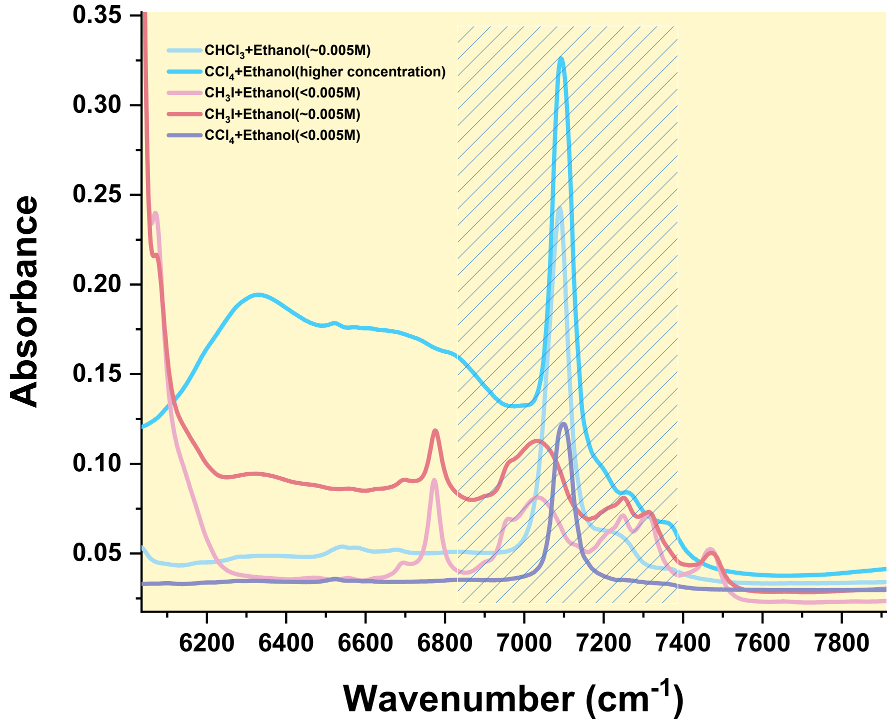

Figure S1. Binary mixtures of different halomethane and ethanol at low concentration.

As shown, the O-H band of ethanol locates at around 7095cm^{-1} in trichloromethane and carbon tetrachloride solution. In comparison, the low concentration ethanol dissolving in iodomethane always maintains a broader band at about 7030cm^{-1}. Increasing concentration of ethanol in carbon tetrachloride, the self-association occurs and the band shape is similar to the low concentration case. This suggests that there is only one interaction in the carbon tetrachloride-ethanol and trichloromethane-ethanol solution, while the ethanol in iodomethane should be more complicated. The NIRS of the ethanol and carbon tetrachloride-ethanol solution agrees the results of Krzysztof B. Bec′ , Yukihiro Ozaki and Mirosław Antoni Czarnecki.

Reference:

1. Czarnecki M A, Morisawa Y, Futami Y, et al. Advances in molecular structure and interaction studies using near-infrared spectroscopy. *Chem. Rev*, **2015**, 115(18): 9707-9744.
2. Beć K B, Grabska J, Huck C W, et al. Spectra–Structure Correlations in

Isotopomers of Ethanol (CX3CX2OX; X= H, D): Combined Near-Infrared and Anharmonic Computational Study. *Molecules*, **2019**, 24(11): 2189.

Figure S2-S7 Raman spectra of some halomethane-ethanol mixtures

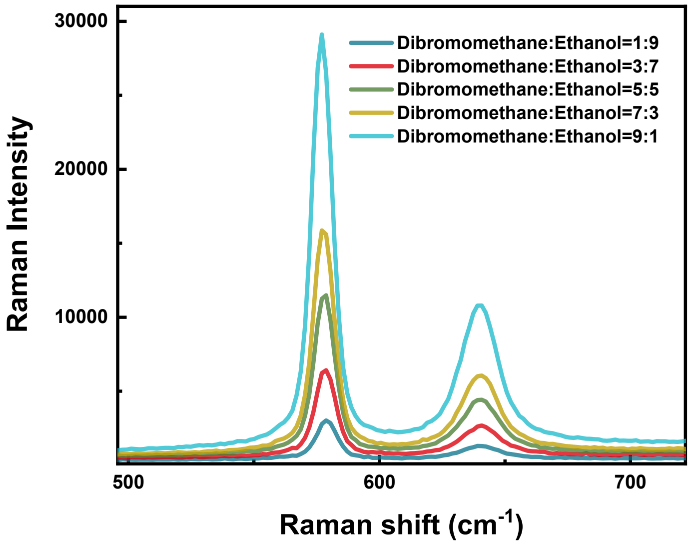

Figure S2. Raman spectra of dibromomethane-Ethanol mixtures in different volume ratio.

From Figure S2, the low wavenumber mode is assigned to symmetric C-Br stretching, while the high wavenumber mode is the asymmetric C-Br stretching. We can hardly observe the frequency shift of the both band because they shift only ~1cm^{-1} to the blue side.

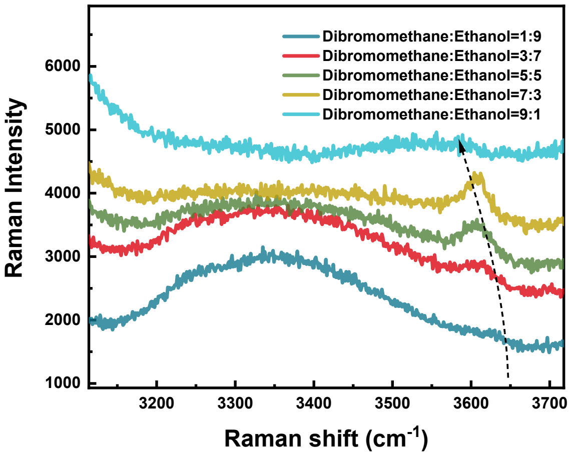

Figure S3. The O-H fundamental band of Dibromomethane-Ethanol mixtures.

The O-H fundamental region is interesting. In the medium solvation, the sharp peak **appears** at around 3600cm^{-1} and **disappears** with further dilution.

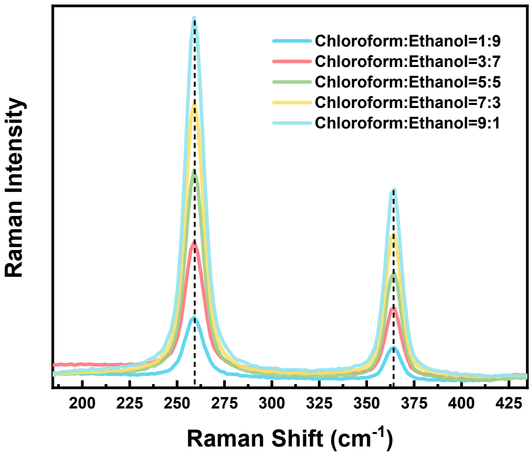

Figure S4. Raman spectra of Chloroform-Ethanol mixtures in different volume ratio.

In the Chloroform-Ethanol system, the C-Cl bands exhibit nearly no shift and we could not able to tell which direction these bands move.

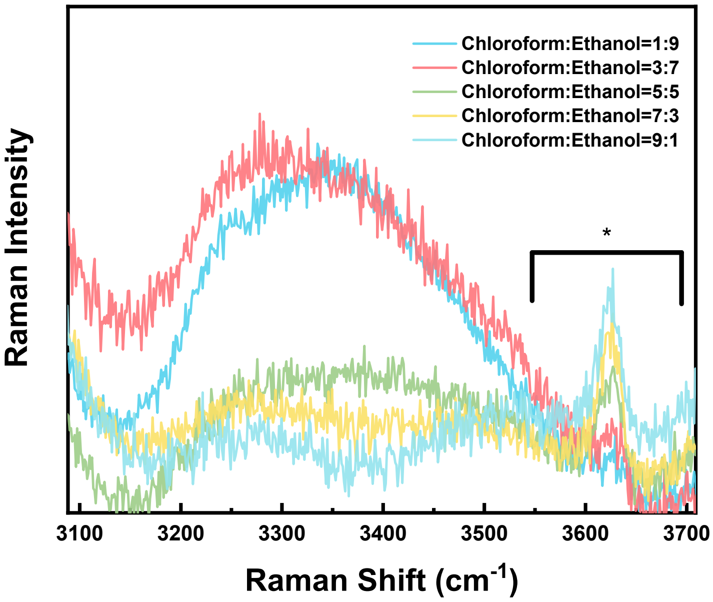

Figure S5. The O-H fundamental band of Chloroform-Ethanol mixtures.

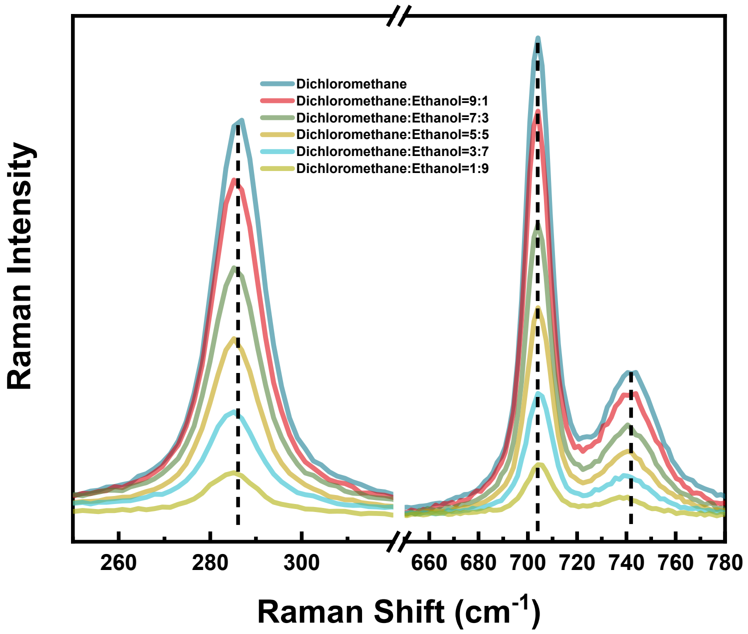

Figure S6. Raman spectra of Dichloromethane-Ethanol mixtures in different volume ratio.

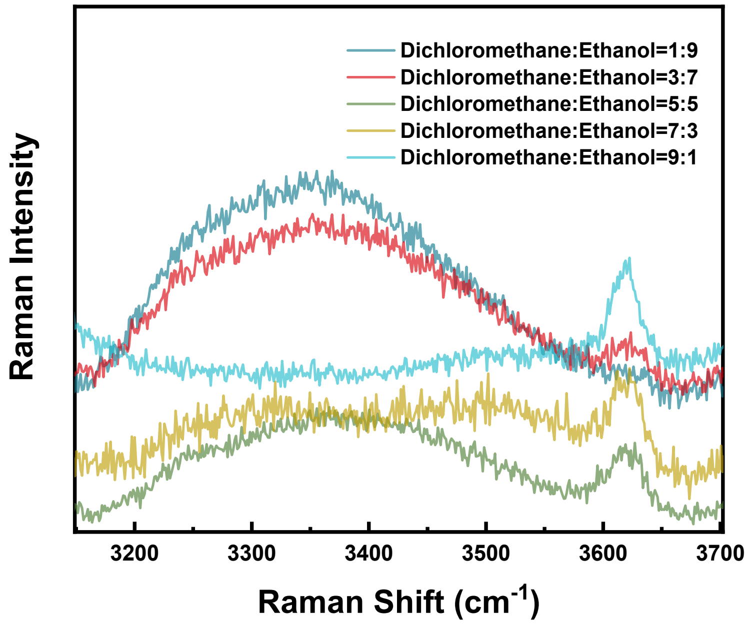

Figure S7. The O-H fundamental band of Dichloromethane-Ethanol mixtures.

In contrast, the O-H bands of Dichloromethane-Ethanol mixtures show very different behavior creating the sharp feature peak at all volume ratio. This result is consist with the previous researches on CCl_4 and Ethanol mixtures [3].

Calculations:

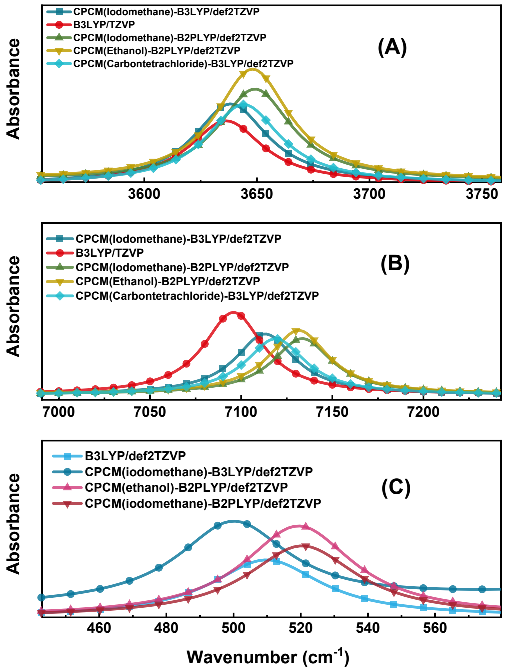

Figure S8. The calculated infrared spectra of using different methods at ethanol O-H fundamental region (A), ethanol O-H overtone region (B), and iodomethane C-I fundamental region (C) with and without CPCM solvent effect.

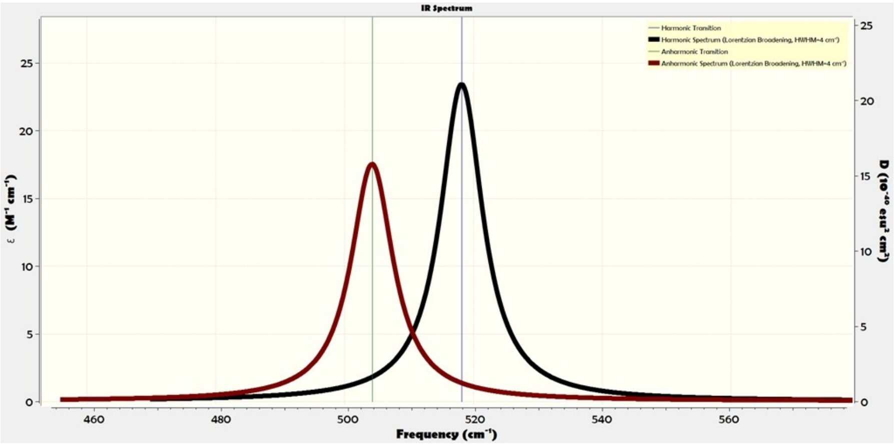

Figure S9. The predicted harmonic and anharmonic IR spectra of CH_3I under CPCM(iodomethane)-B3LYP-GD3BJ/def2TZVP level.

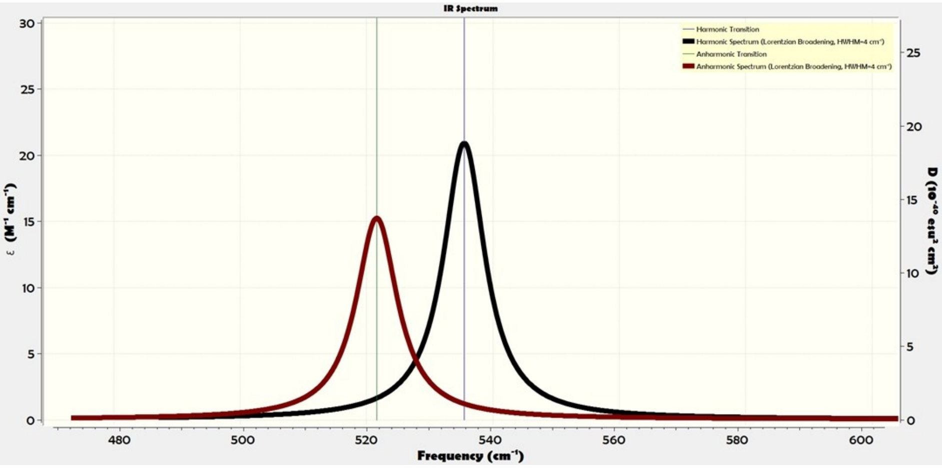

Figure S10. The predicted harmonic and anharmonic IR spectra of CH_3I under CPCM(iodomethane)-B2PLYP-GD3BJ/def2TZVP level.

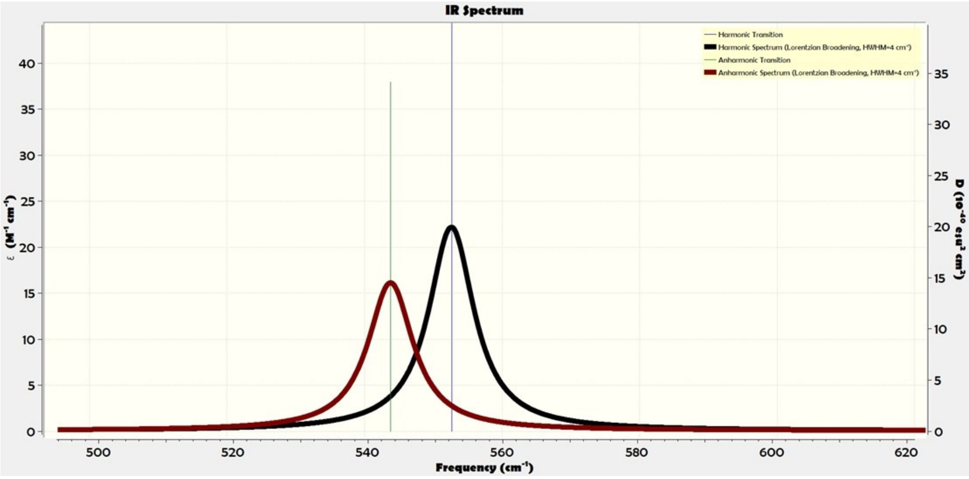

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Figure S11. The predicted harmonic and anharmonic IR spectra of CH_3I under CPCM(iodomethane)-M06-2X-GD3/def2TZVP

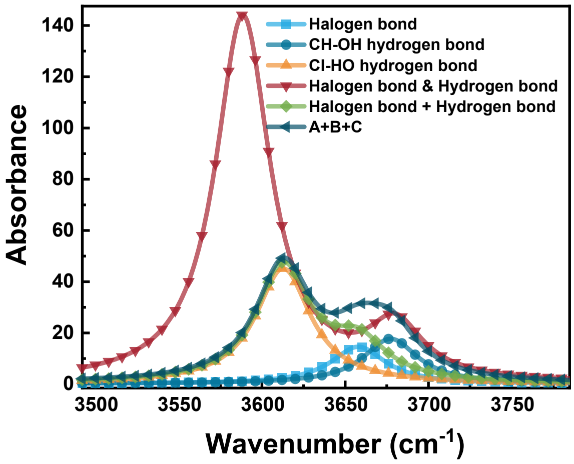

Figure S12. The computed O-H stretching fundamental bands of selected geometries under B3LYP-GD3BJ/def2-TZVP level without solvent effect. However, the counterpoise correction is employed when calculating the frequency.

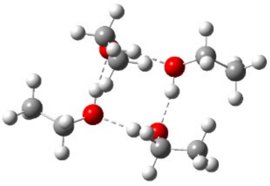

Figure S13. Optimized structure of water cluster.

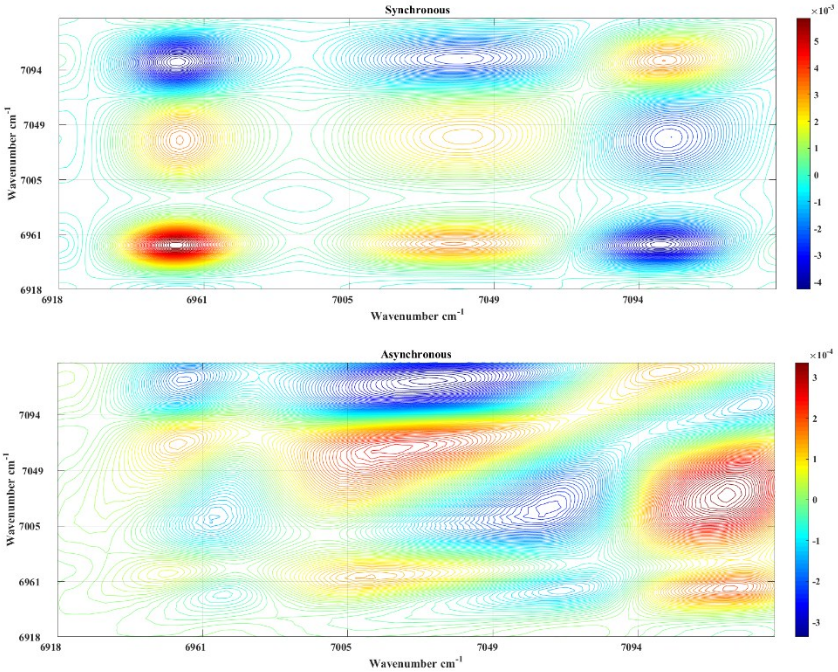

Figure S14. The 2D-NIR spectra of the ethanol-rich region.

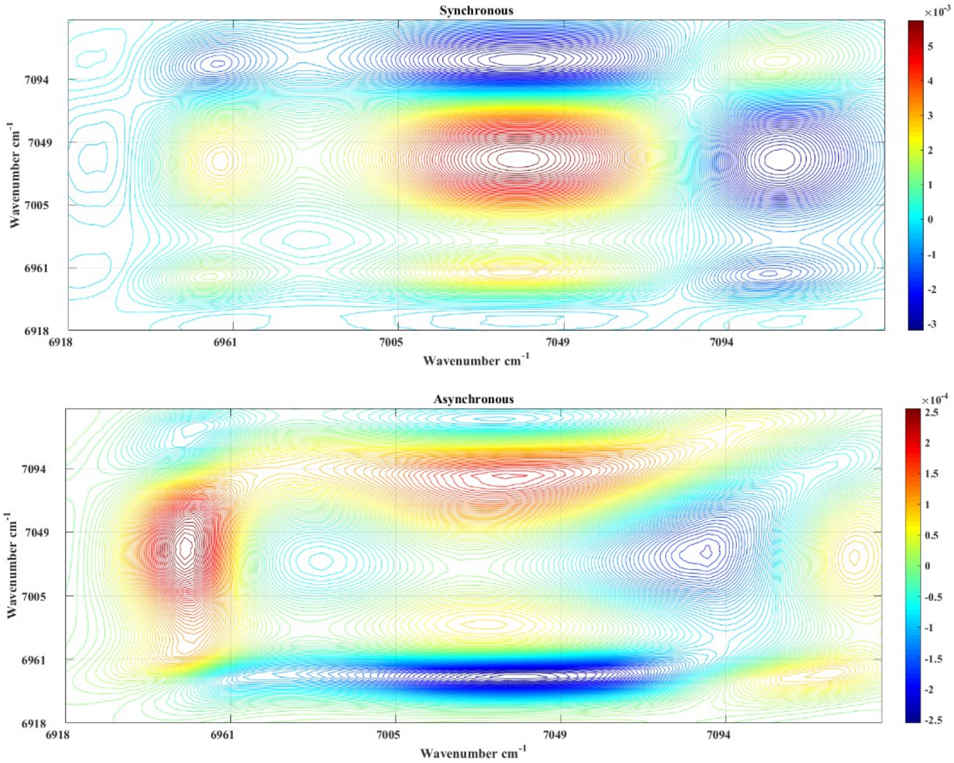

Figure S15. The 2D-NIR spectra of the iodomethane-rich region.

Table S1. Calculated frequencies of C-I and O-H mode using M06-2X-GD3 or B3LYP-D3 methods.

	M06-2X-GD3 (scaled by 0.975)	B3LYP-D3 (scaled by 0.975)	B2PLYP-CPCM-DVPT2
C-I stretching of monomer	543.62 cm^{-1}	518.50 cm^{-1}	520.41 cm^{-1}(CH_3I) 519.34 cm^{-1}(C_2H_6O)
C-I stretching of A	545.10 cm^{-1}	512.92 cm^{-1}	527.25 cm^{-1}(CH_3I)
C-I stretching of B		508.14 cm^{-1}	
C-I stretching of C		508.63 cm^{-1}	
C-I stretching of D		513.66 cm^{-1}	
O-H stretching of A	3769.04 cm^{-1}	3695.77 cm^{-1}	3627.11 cm^{-1}(CH_3I)
O-H stretching of B		3650.19 cm^{-1}	
O-H stretching of C		3715.42 cm^{-1}	
O-H stretching of D		3625.69 cm^{-1} 3718.24 cm^{-1}	
O-H stretching of tetramer		3300.76 cm^{-1} 3319.50 cm^{-1} 3348.81 cm^{-1}	