新学術領域「コンピューティクスによる物質デザイン：複合相関と非平衡ダイナミクス」
16/Mar/’12

金表面に吸着されたチオール単分子層のコヒーレント振動の実時間計測

Real-time Measurement of Coherent Molecular Motion of Benzenethiol Monolayer Film on Gold Surface

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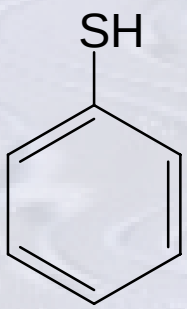
光誘起反応、光応答　　Laser, SR; cw反射分光

シリサイド/シィケート形成　　XPS, STS, STATE

STM誘起反応　　STM, VASP

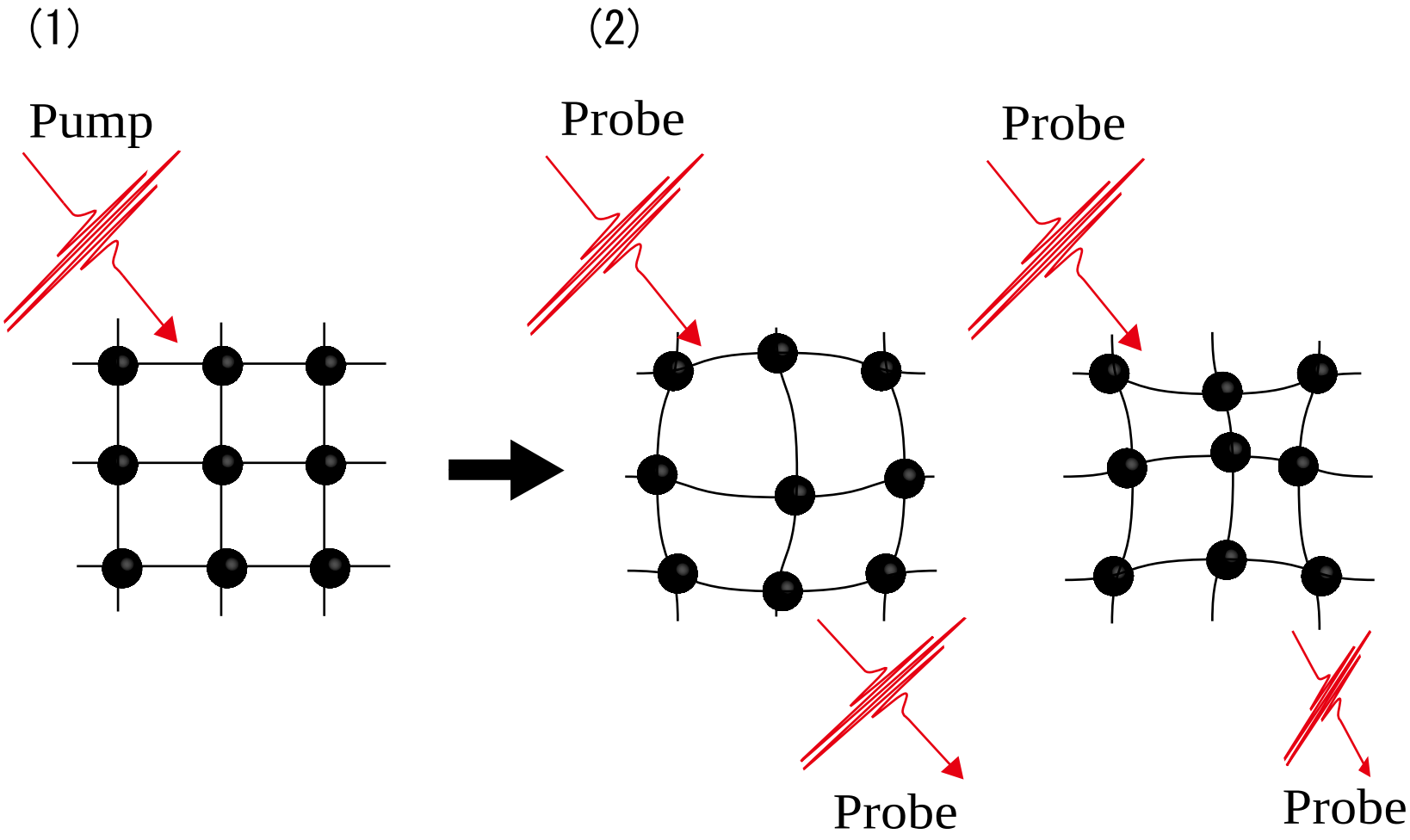
半導体上有機物　　UPS, 2PPES, Gaussian

超高速応答　　fs-laser



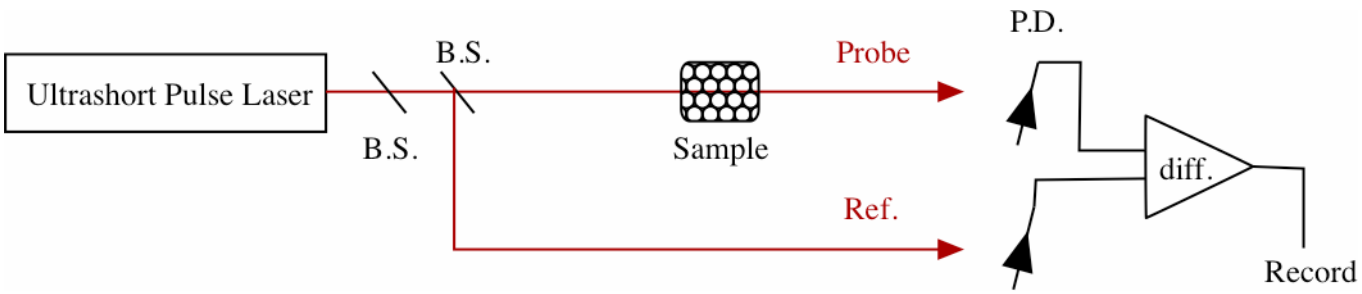
測定方法
液相
表面吸着相
干渉・変調

コヒーレント振動　-光応答-



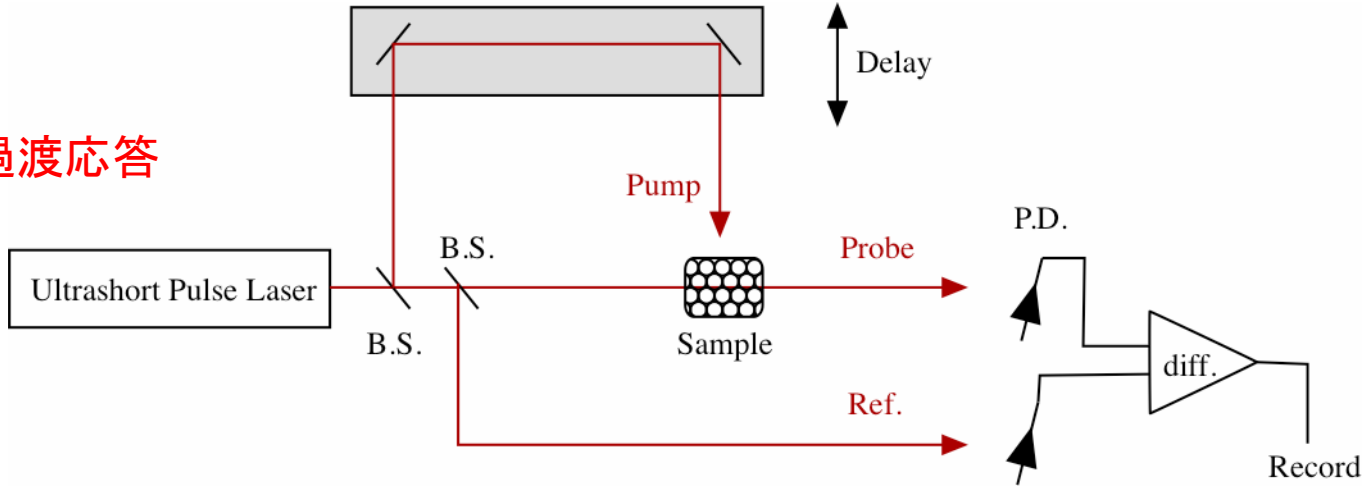
(1) ポンプ光で格子振動を励起
(2) 格子変形によってプローブ光の反射率変化を検出

光吸収率測定


Ultrashort Pulse Laser
B.S.
B.S.
Sample
Probe
Ref.
P.D.
diff.
Record

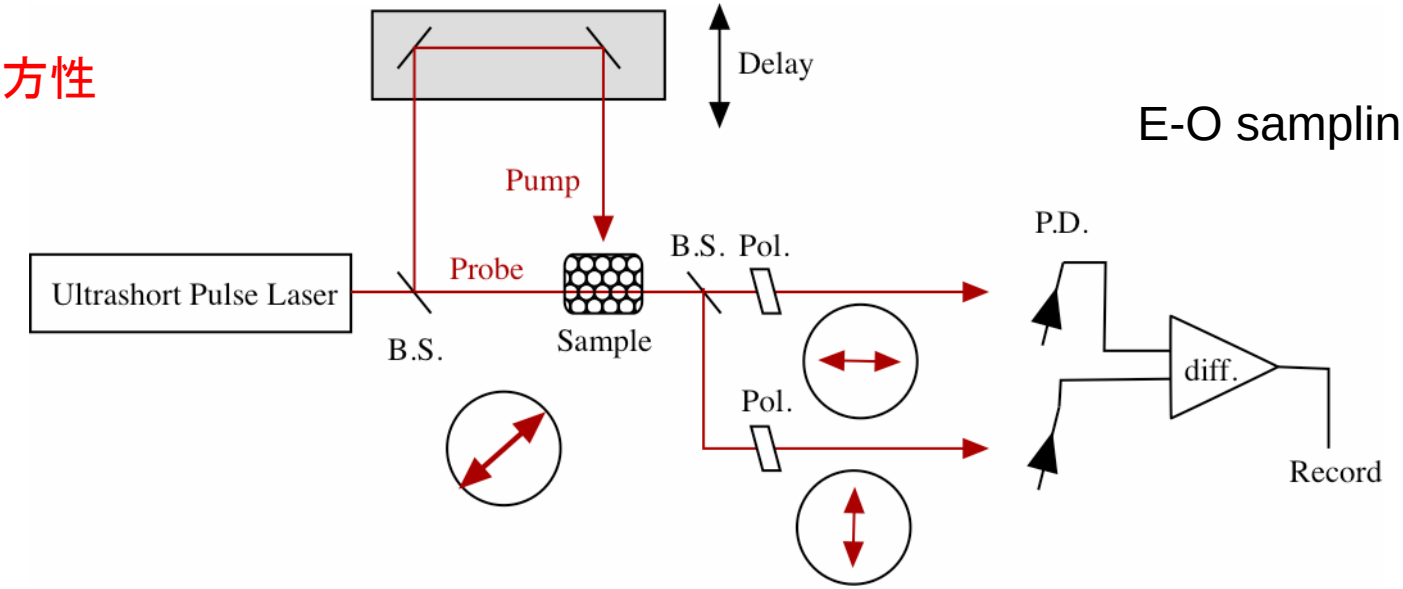
Pump-probe

吸収率過渡応答



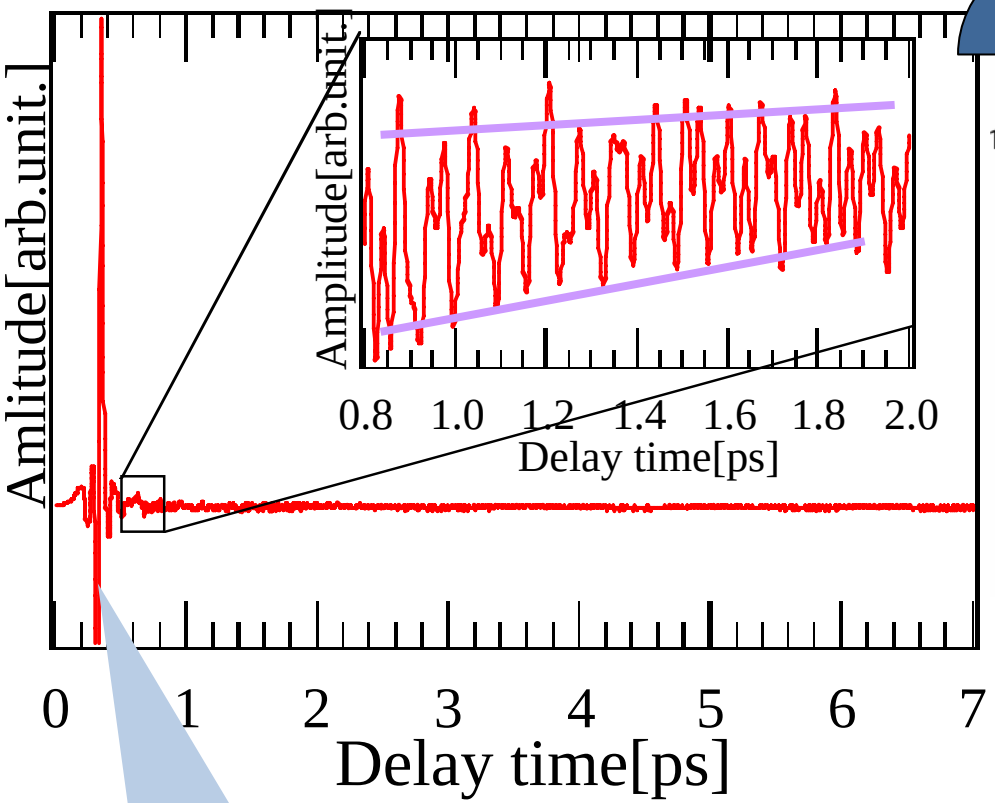
吸収率異方性

E-O sampling

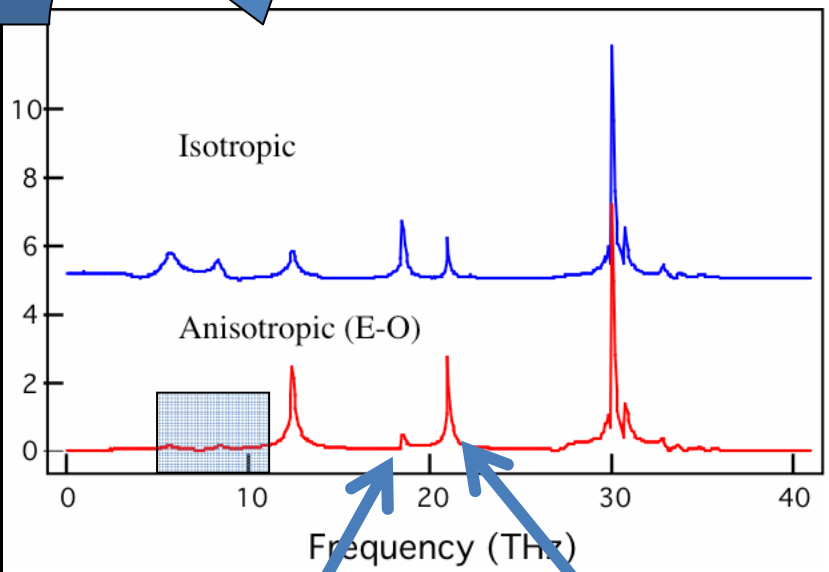


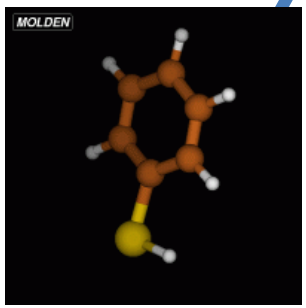
液層ベンゼンチオール(BT)

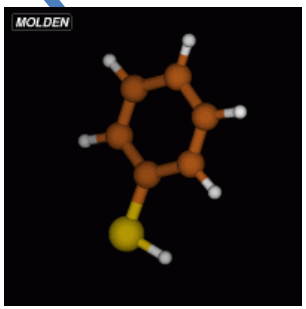
吸収過渡応答（光透過計測）



フーリエ変換





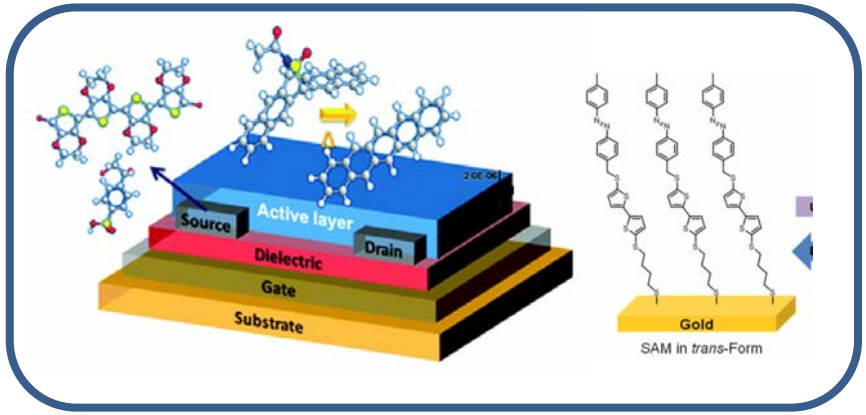


Electronic Response

概ねラマンと対応----->振動
等方、非等方で強度が異なる

Organic Thin Films

Organic-molecular devices



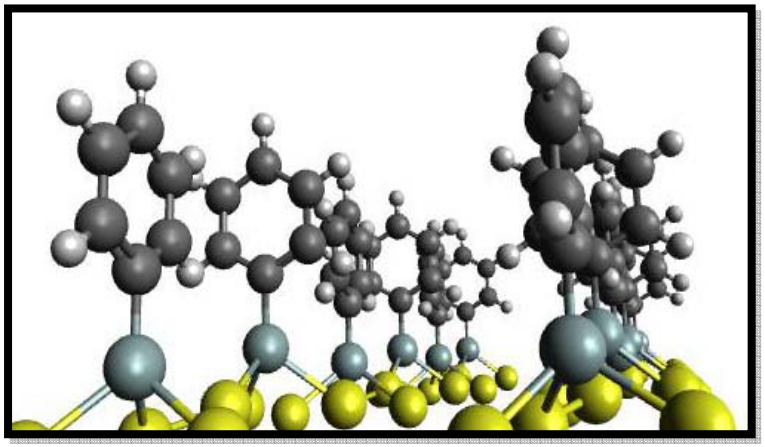
- Discreet Electronic States
- Response to External Field

e.g. Distortion by Gas

Photochromic Material

(1) *Chem. Mater.*, **23** , 1061–1069 (2011).
(2) J. *Am. Chem. Soc.*, **131**, 865-870 (2009).

Self-assembled monolayer



- Easy to build
- Orientation Preference
- Interaction?

molecule-molecule
molecule-substrate

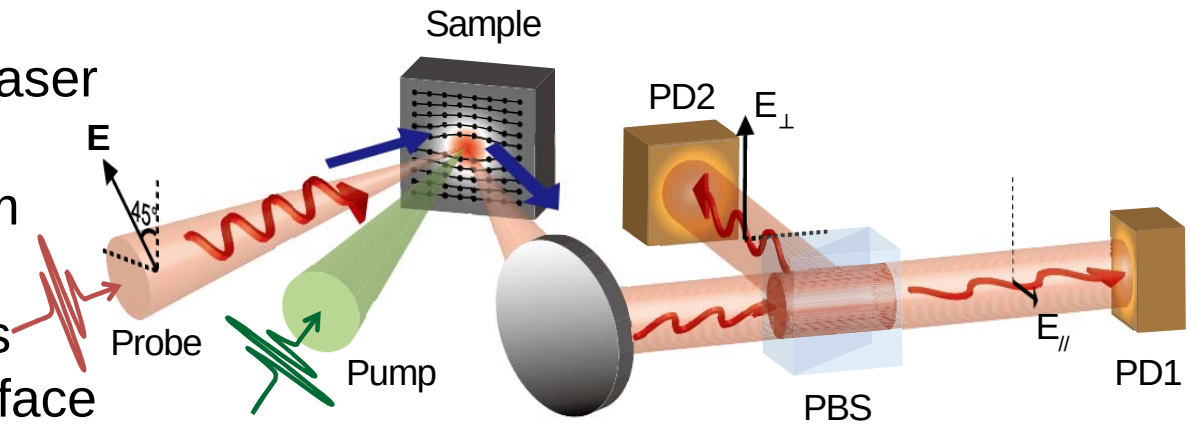
Coherent Motion by Electronic Excitation → Ultrafast dynamics!

Experimental

Optics

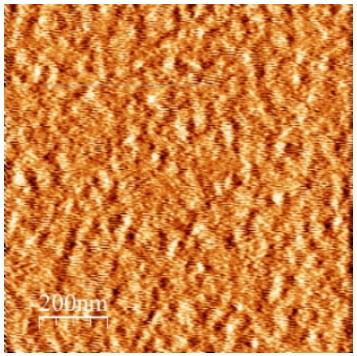
Pulsed Ti:Saphaire laser
Duration : 7.5 fs
Wavelength : 800 nm

Pump-probe process
EO sampling for Surface



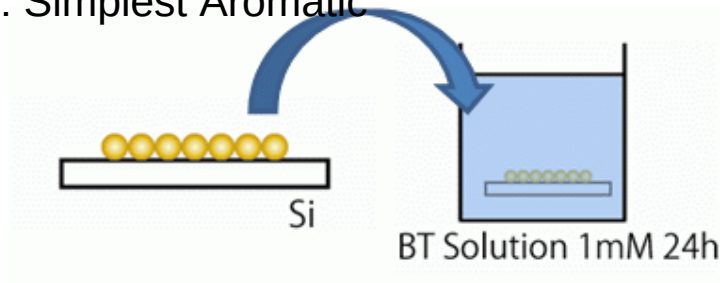
Specimen

Au deposition on Si(001)
(Plasma sputter in vacuum)



(1 μ × 1 μ)

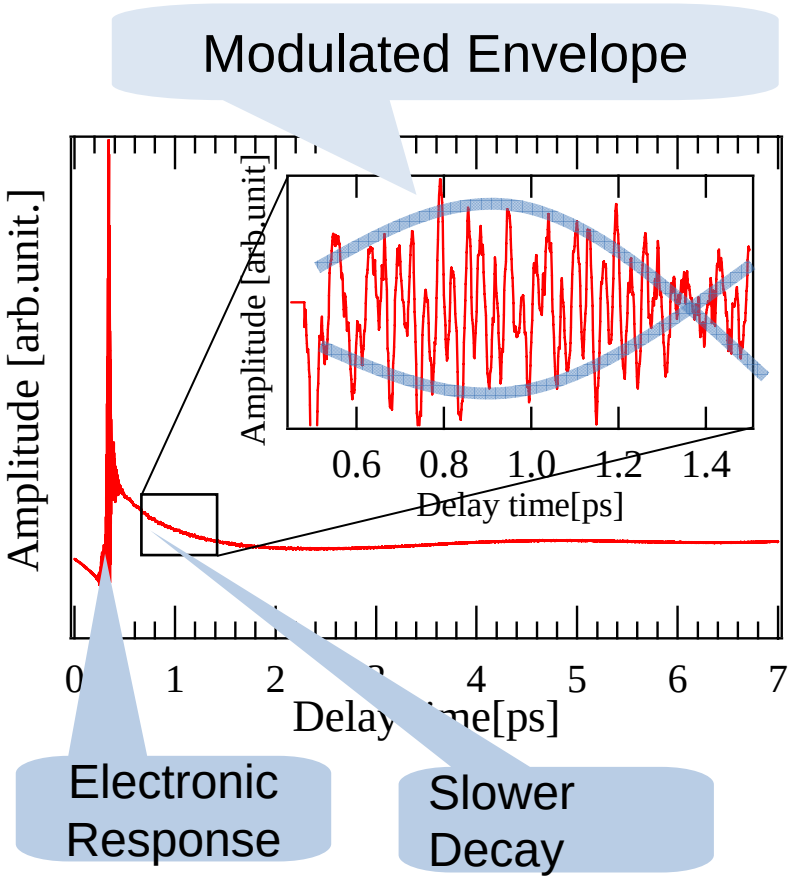
Benzenethiol (B.T.) on Au
Tiol: Typical SAM,
Benzene: Simplest Aromatic



Soaked into BT (in Me-OH)
c.f. Liquid BT (pure >98%)

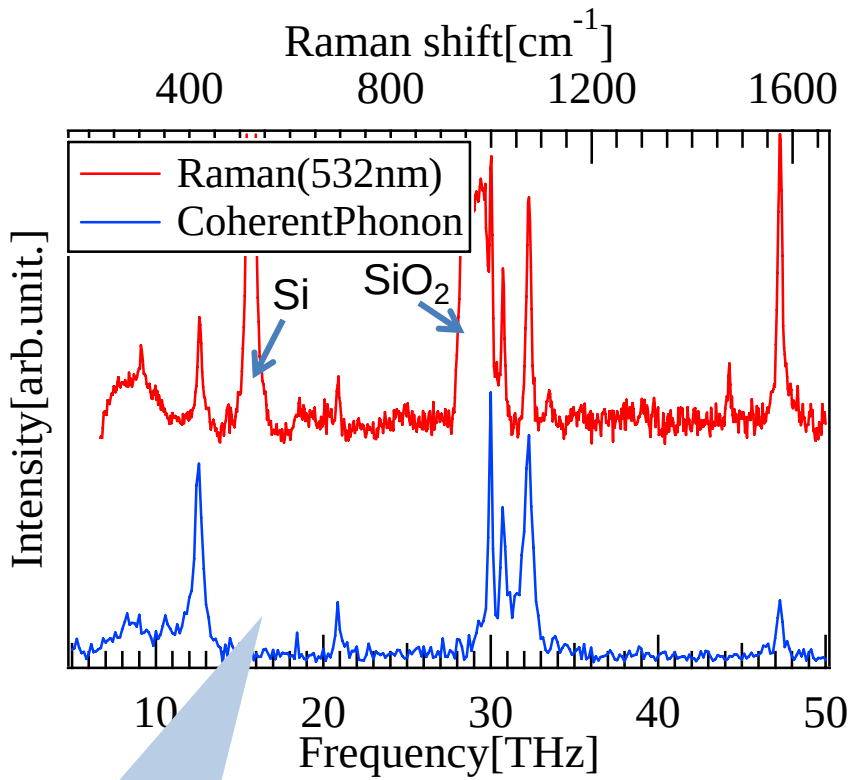
Adsorbed Benzenethiol on Au-film

Asymmetry in Reflectance



Fourie Trans.

Comparison of c.w.Raman



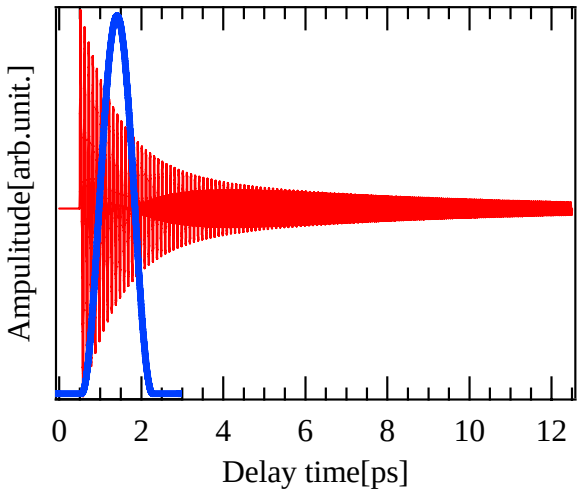
No signal from substrate

Shifted from Liquid

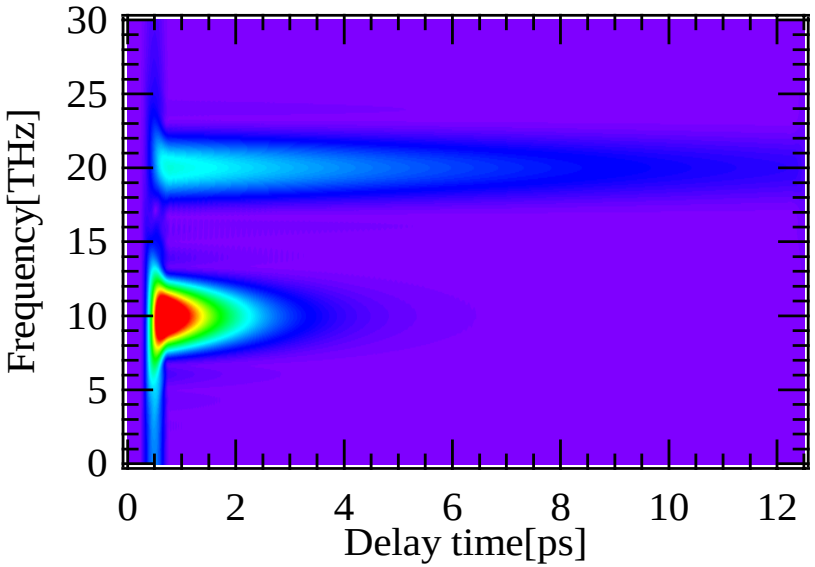
Detection Surface-sensitive to Monolayer Molecular Motion in Real-times

時間分解FFT–時間強度変化–

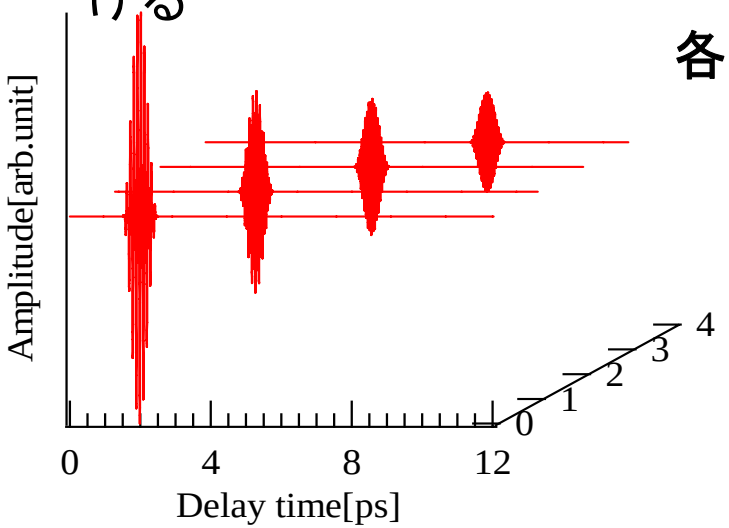
実時間波形



時間分解FFT

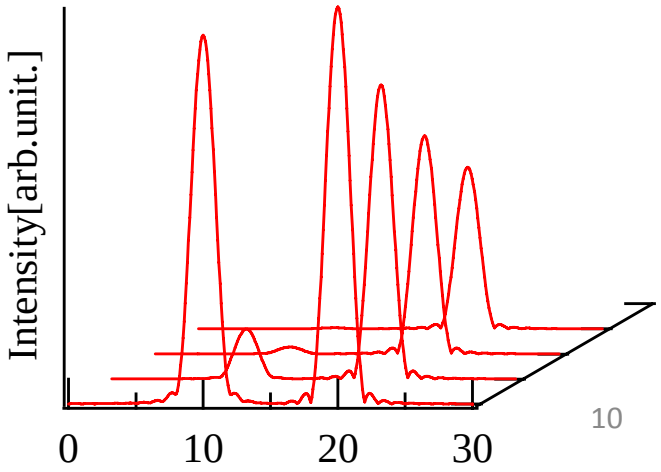


各時間でHanning窓をかける



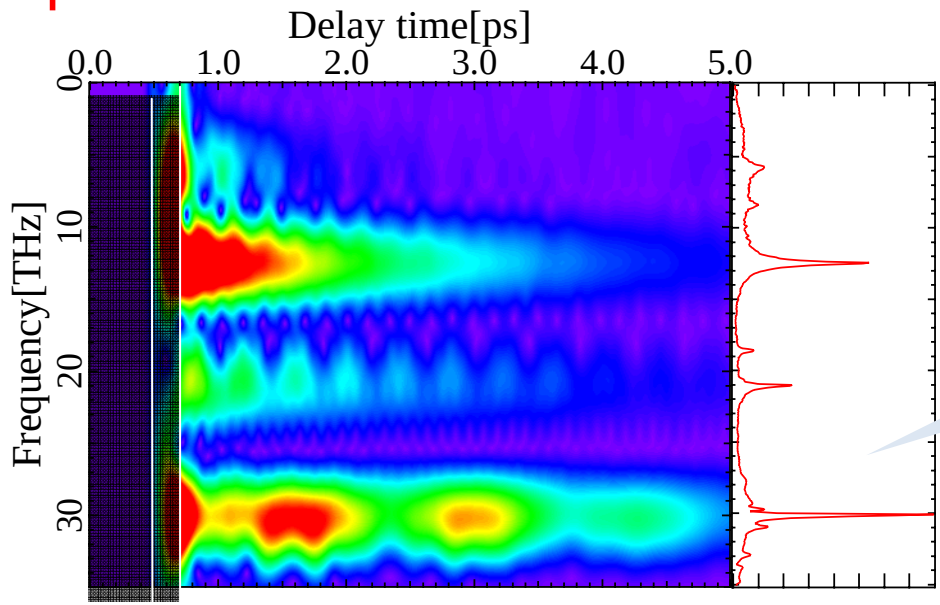
各時間窓でのFFT

各時間でのFFT強度



Time-resolved Spectral Intensity

Liquid



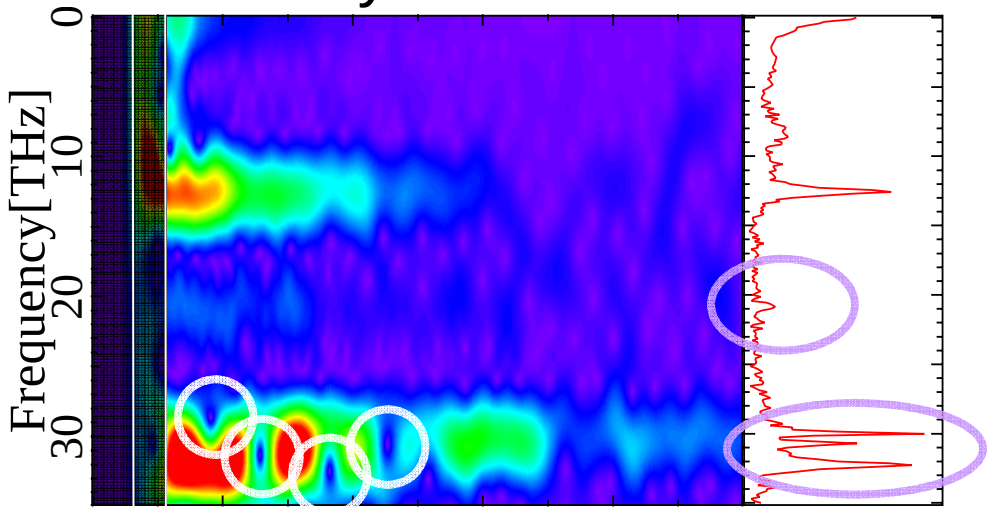
Time-resolved FFT

Window:Hanning function
width 0.3ps

F.T. of whole signal

Time-course of intensity
of each component

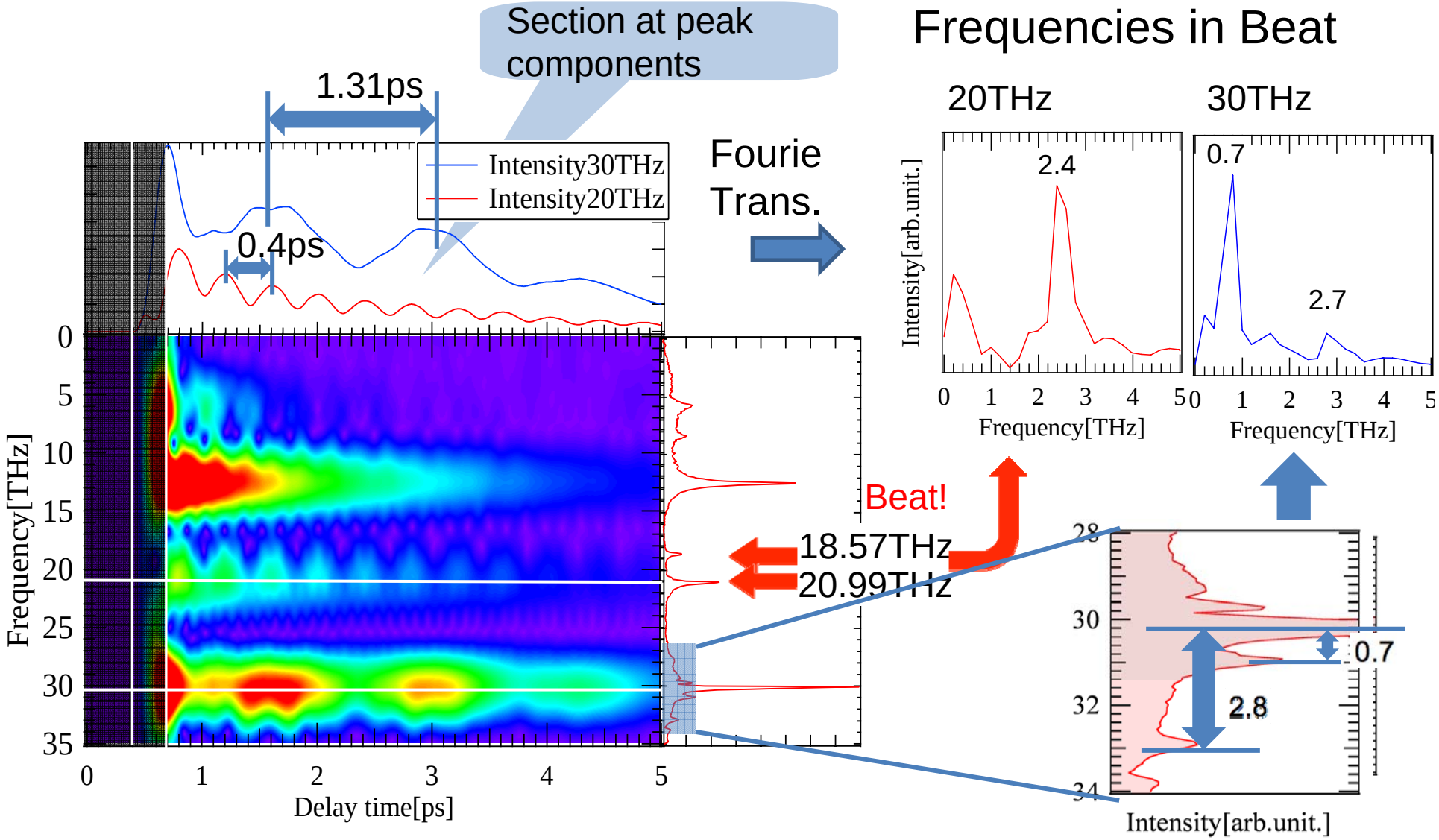
Adsorbed Layer



Liquid vibrations
fluctuate in-phase

Different Modulation

Time-course of Intensity in Liquid



Simple Beat: Sum of Close Modes -----> Independent Vibration

Time-course of Initial Phase in Liquid

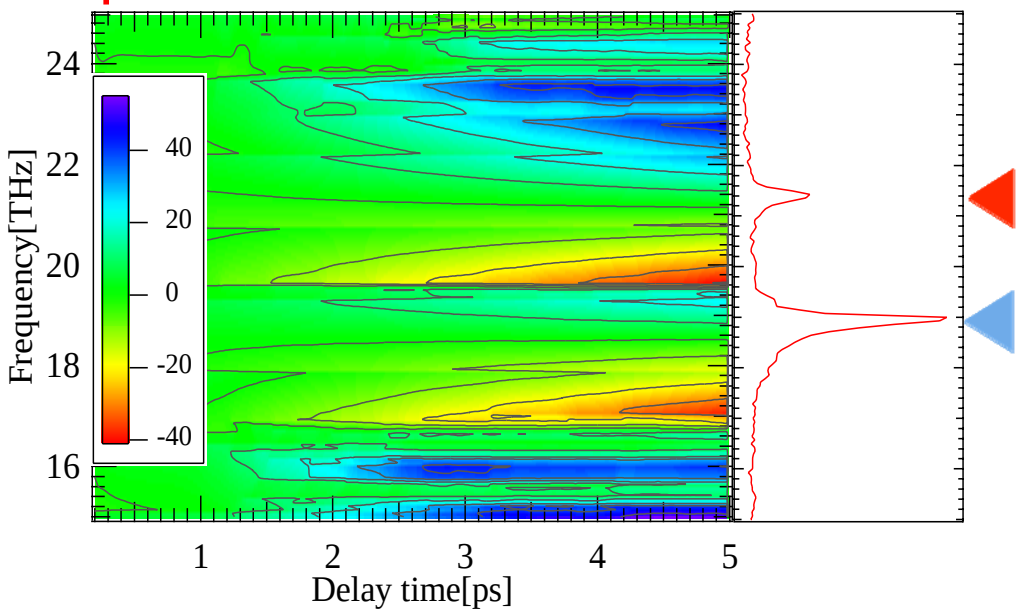
Initial Phase ϕ in a Sinusoidal Wave

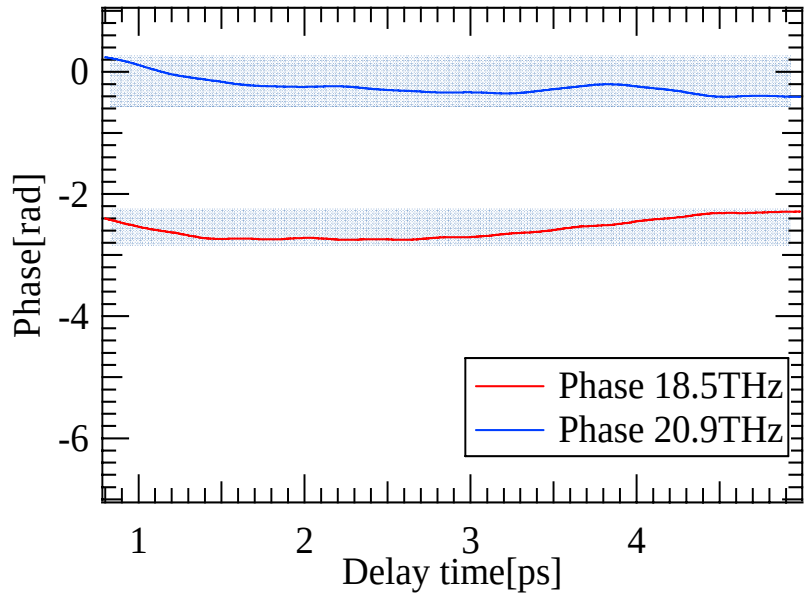
Fourier Component

$$E = A\sin(\omega t + \phi)$$

Liquid

Hanning window: 0.8ps



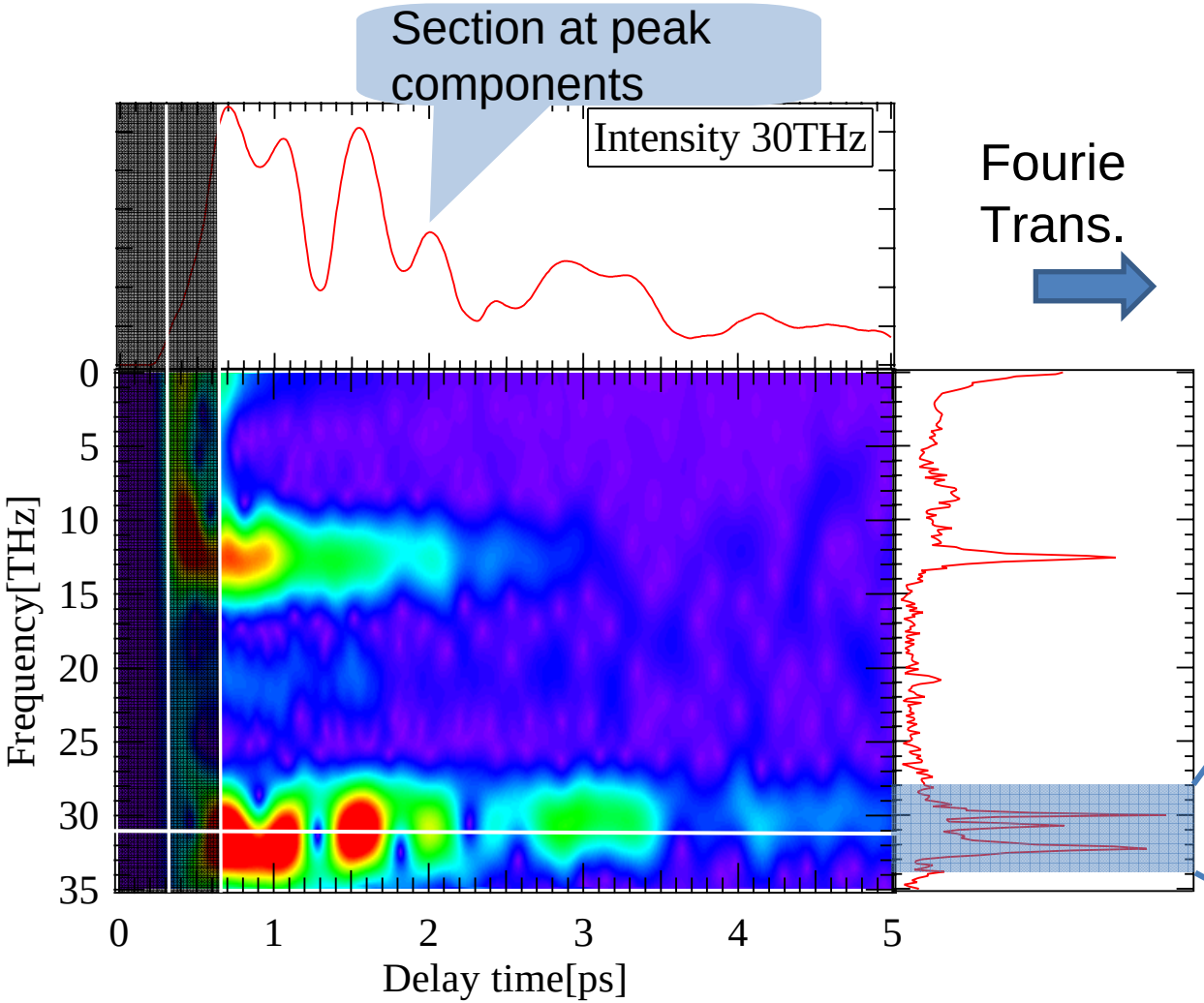


The two componts have constant ϕ.

Two modes vibrate independently.

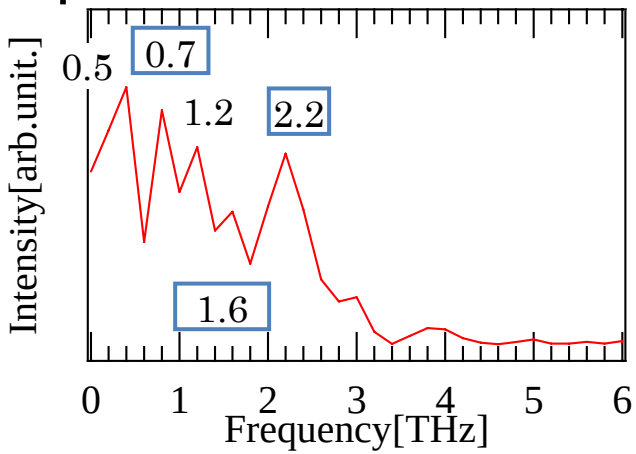
Time-course of Initial Phase in Adsorbed Layer

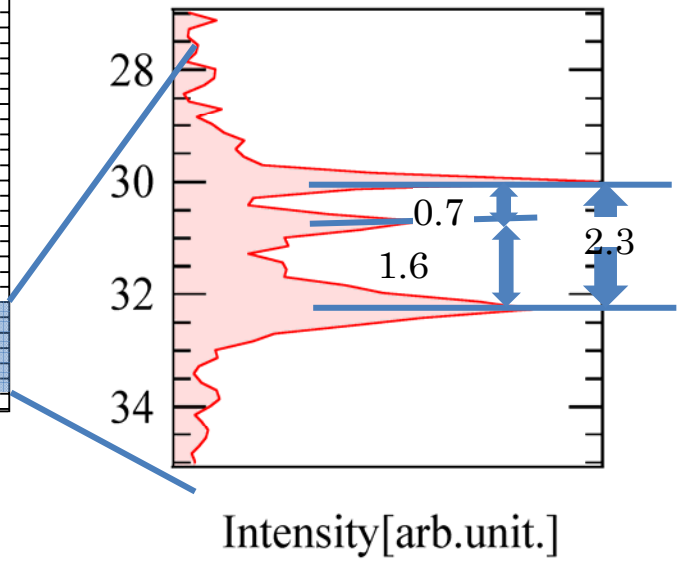
Intensity of Adsorbed Layer



Fourie Trans.

Frequencies in Beat

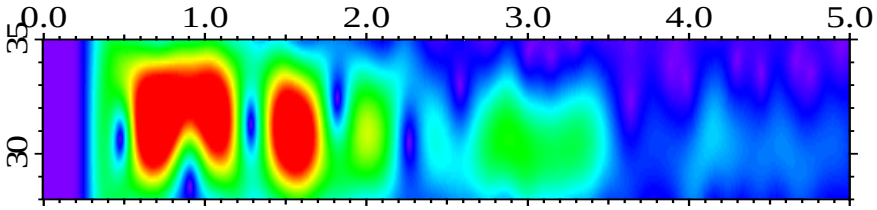


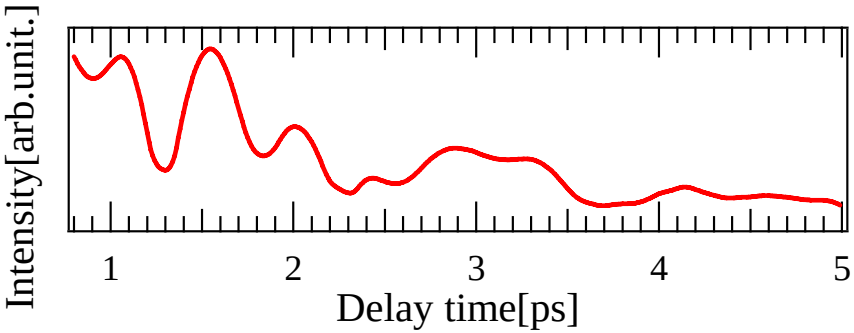


Interference is not simple summation of three componensts

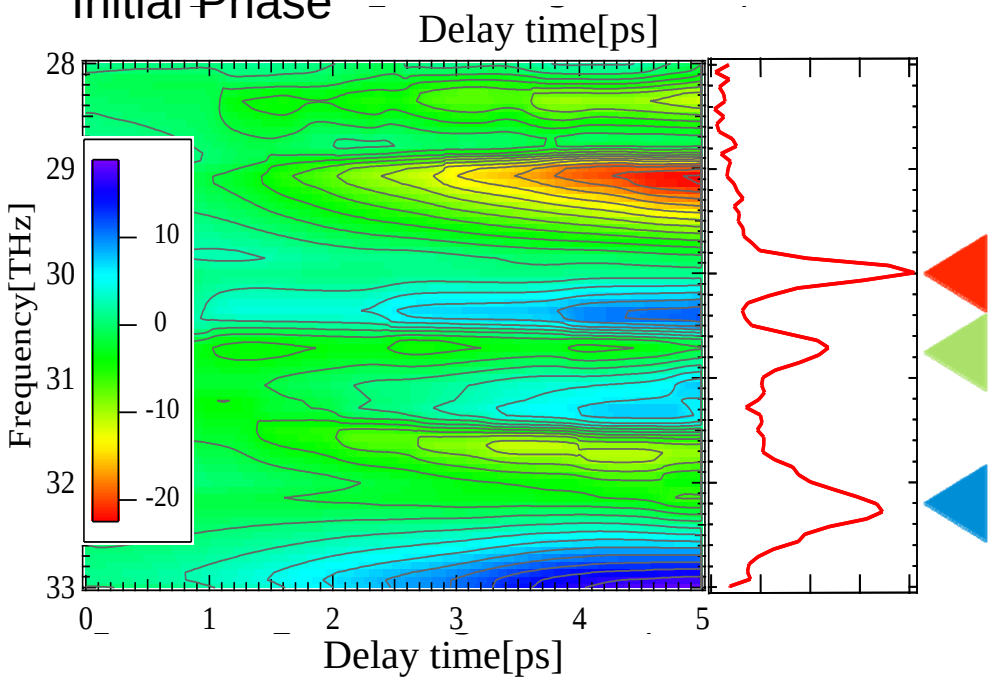
Time-course of Initial Phase in Adsorbed Layer

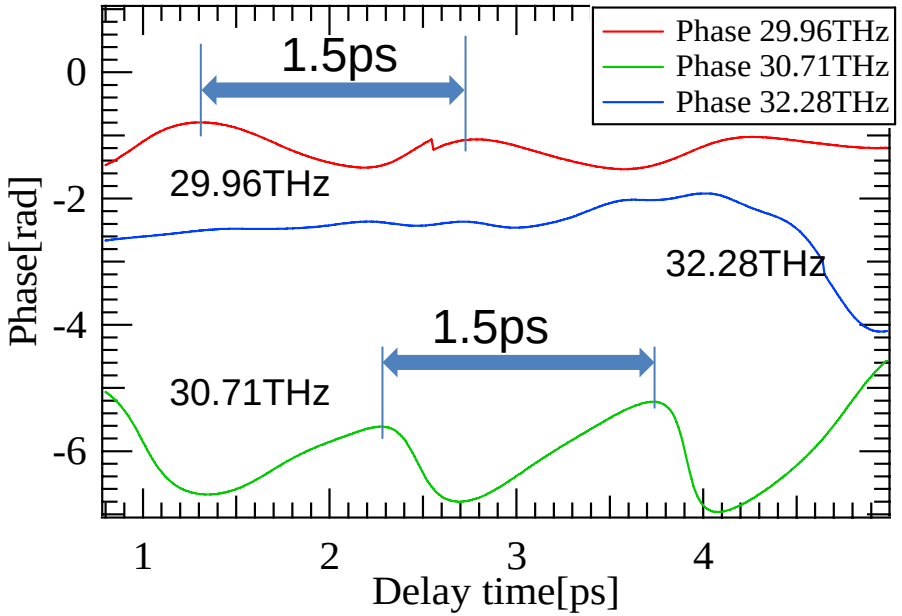
Intensity of peaks in Adsorbed Layer





Initial Phase



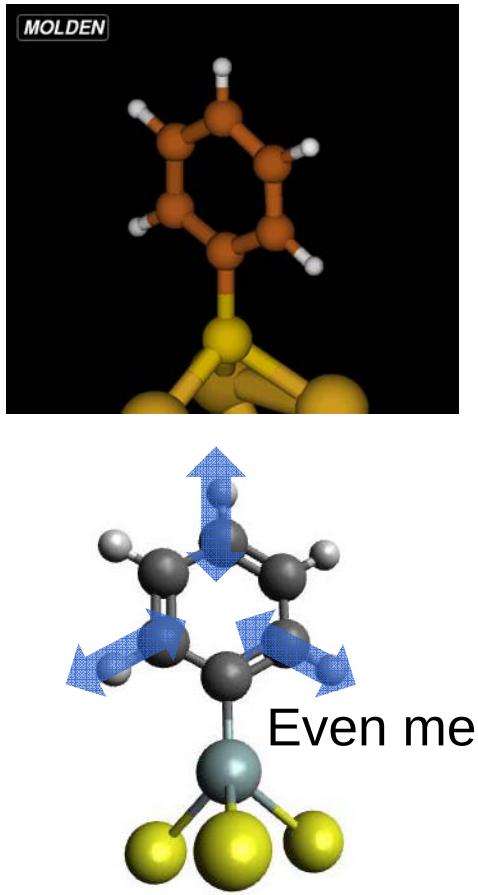


Two modes has phase shift along time.

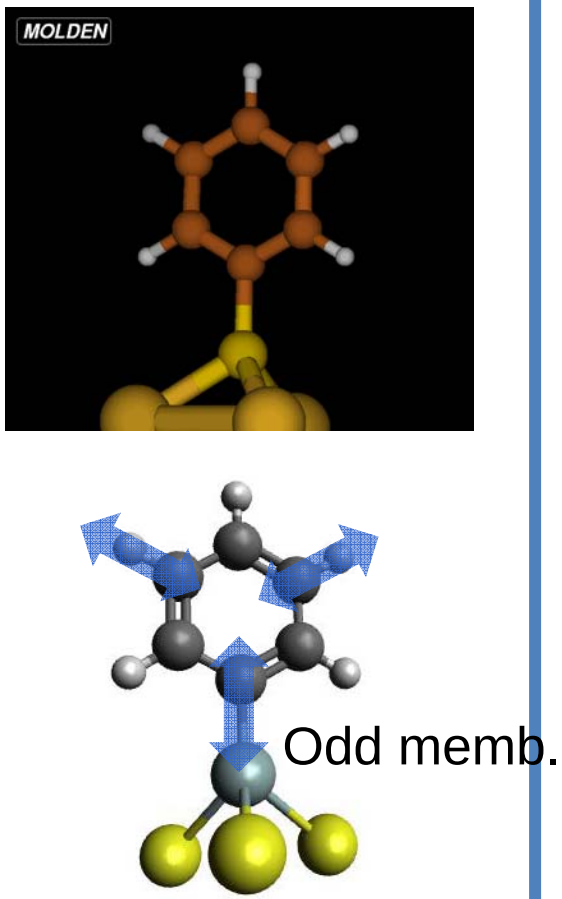
Interaction of the two out of the close three modes.

Surface vibronic modes in Adsorbed Layer

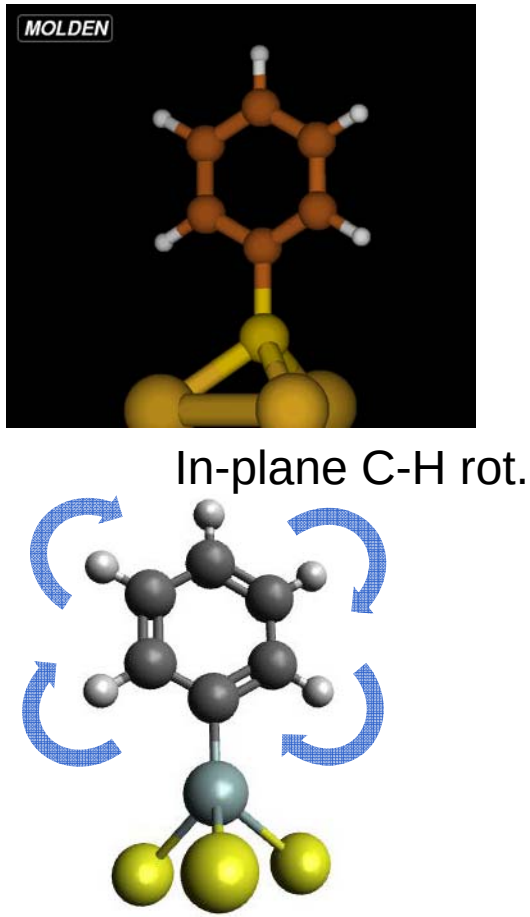
1011cm^{-1}(30.33THz)



1033cm^{-1}(30.99THz)



1087cm^{-1}(32.61THz)



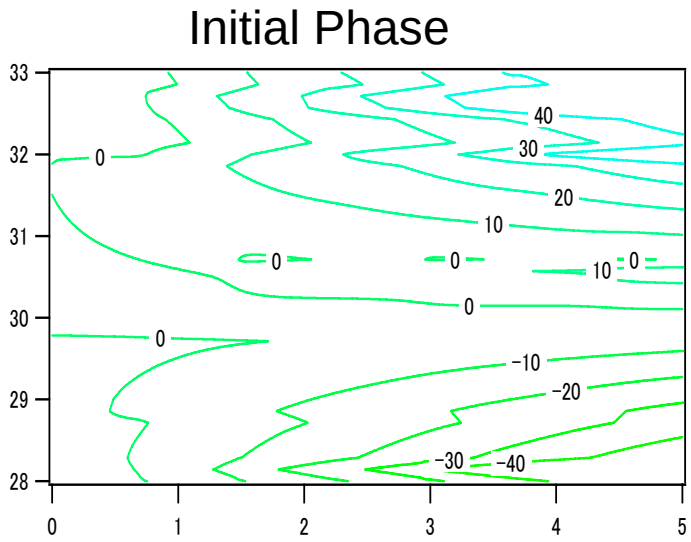
Two Interactiong Modes: Expanding of Odd/Even Carbons Due to Electronic? Or Configurationally?

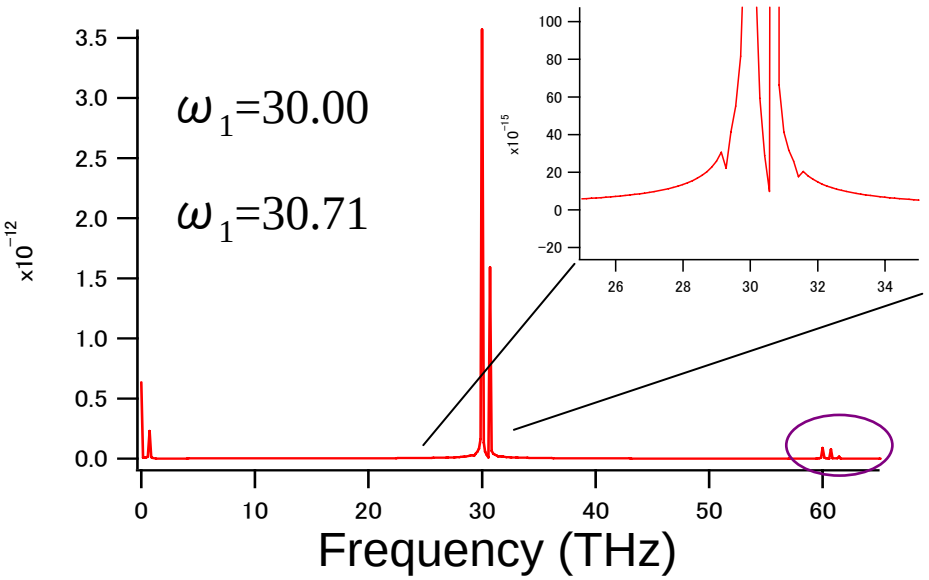
Numerical Analysis

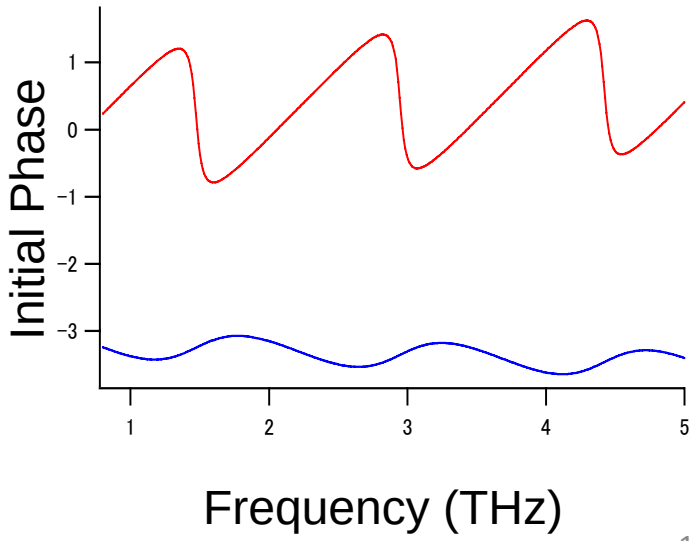
$$\frac{d^2x_1}{dt^2} = -\omega_1^{\,2}x_1 + \frac{C}{m}(x_2 - x_1)^2$$

$$\frac{d^2x_2}{dt^2} = -\omega_2^{\,2}x_2 - \frac{C}{m}(x_2 - x_1)^2$$

80.4% 19.6%







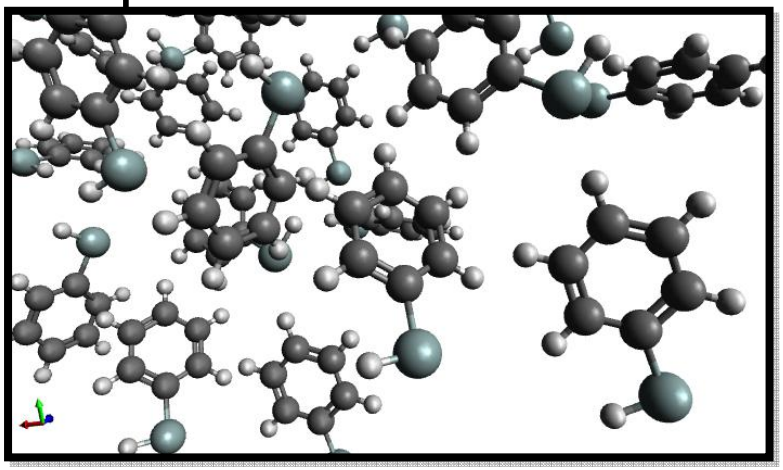
Summary

ベンゼンチオール 超高速計測

-時間分解計測
=フーリエ成分 → 振動
対称・非対称で強度比相違

- 単分子吸着層
= 反射配置：表面敏感計測
= 重ね合わせ → ビート
= 吸着層では位相変調
→偶数・奇数変形で結合
→ 非線形結合で説明

Liquid



Adsorbed Layer