

2008年中国科大

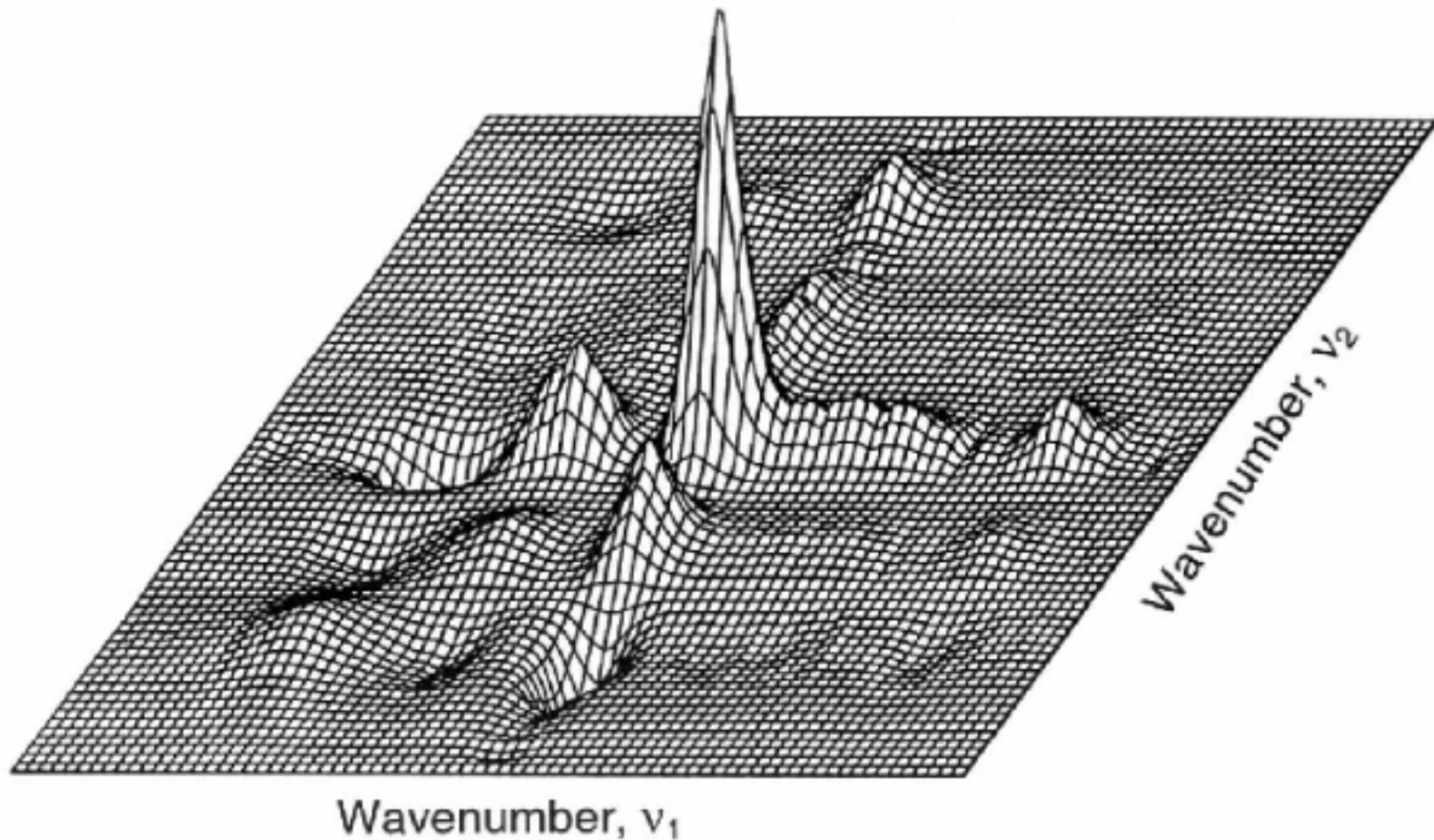
Two-Dimensional (2D) Correlation Spectroscopy

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2008-12-7

Two-Dimensional (2D) Spectroscopy





Generalized 2D Correlation Spectroscopy

- Generally applicable to a broad range of spectroscopic techniques
- Based on a set of spectral data from a system under some perturbation
- Either time-dependent or static spectra may be used
- Enhance spectral resolution by spreading peaks along the second dimension
- Selective development of 2D peaks provides better access to information not readily observable in conventional 1D spectra
- Sign of cross peaks to determine relative direction of intensity changes and sequential order of events
- Comparison of different spectral data via hetero-correlation

Generalized 2D Correlation Spectroscopy

Generalized Two-Dimensional Correlation Method Applicable to Infrared, Raman, and Other Types of Spectroscopy

I. NODA

The Procter and Gamble Company, Miami Valley Laboratories, P.O. Box 200877, Cincinnati, Ohio 45220-8777

A two-dimensional (2D) correlation method generally applicable to any type of spectroscopy, including IR and Raman spectroscopy, is introduced. In the proposed 2D correlation scheme, an external perturbation is applied to a system which has been measured to obtain spectroscopic data. With the application of a correlation analysis to spectra taken only during the perturbation, new types of spectra defined by two independent spectral variables are obtained. Such two-dimensional correlation spectra emphasize spectral features not readily observable in conventional one-dimensional spectra. While a single 2D correlation formulation has already been developed in the past for analysis of single sinusoidally varying IR signals, the newly proposed formulation is designed to handle signals fluctuating as an arbitrary function of time, or any other physical variable. This development makes the 2D correlation approach a universal spectroscopic tool, generally applicable to a very wide range of applications. The basic property of 2D correlation spectra obtained by the new method is described first, and several practical data sets are analyzed by the proposed scheme to demonstrate the utility of generalized 2D correlation spectra. Potential applications of this 2D correlation approach are then explored.

Indexing: Correlation spectra; Fourier transform; Infrared; Raman Spectroscopy; Perturbation; Time-resolved spectroscopy; Two-dimensional spectroscopy; 2D-IR.

INTRODUCTION

The basic concept of constructing two-dimensional (2D) IR spectra from perturbation-induced time-dependent fluctuations of IR signals was first introduced in 1980.¹ Unlike the time-domain double Fourier transform methods based on multiple pulse excitations used extensively in NMR,^{2,3} a simple cross-correlation analysis was applied to sinusoidally varying dynamic IR signals to construct a set of 2D IR correlation spectra.^{4,5} Such dynamic 2D IR spectra were found to be especially useful in emphasizing spectral features not readily observable in conventional one-dimensional spectra. 2D IR correlation spectroscopy has been especially successful in the studies of systems stimulated by a small-amplitude mechanical or electrical perturbation.⁶⁻¹¹ One of the major shortcomings of the previously developed approach, however, is that the time-dependent behavior (i.e., waveform) of dynamic spectral intensity variations must be a simple sinusoid to effectively employ the original data analysis scheme.¹²

In this paper, a more generally applicable, yet essentially simple, mathematical formulation is proposed to obtain two-dimensional correlation spectra from any transient or time-resolved spectra having an arbitrary waveform. The 2D spectra obtained by this method can present any useful information often observed in the original time-resolved spectra. This development opens up

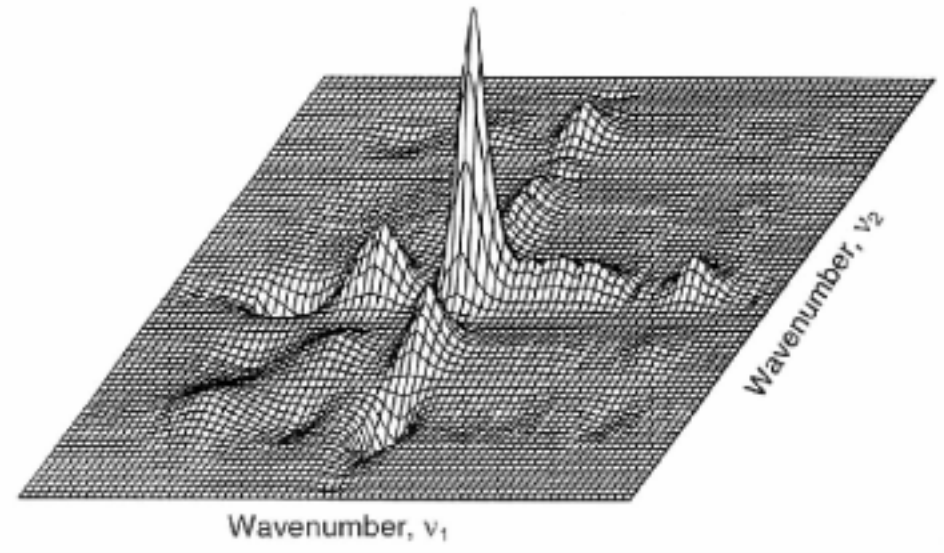
the possibility of introducing the powerful and versatile capability of 2D correlation analysis to much wider ranges of applications, including complex reaction kinetics,¹³ electrochemistry, and photochemistry.¹⁴ Further extension to other areas of spectroscopy, such as UV, Raman, and ultra-fast time-resolved spectroscopy, should also be quite straightforward.

BACKGROUND

The basic scheme for generating two-dimensional correlation spectra from perturbation-induced dynamic fluctuations of spectroscopic signals is similar to that already described.¹⁵ The general experimental approach used in 2D correlation spectroscopy is shown in Fig. 1. When an external perturbation (stimulus) is applied to a system, various chemical constituents of the system are selectively excited.¹⁶ The excitation and subsequent relaxation processes toward the equilibrium are monitored with electromagnetic probes. Typical spectral changes observed under dynamic perturbation are the variation of intensity, shift of spectral band positions, and change in the shape of peaks. The monitored fluctuation of spectral signals is then transformed into two-dimensional spectra by using a correlation method.

As pointed out previously,⁴ the conceptual scheme to include a dynamic spectrum described in Fig. 1 is a very general one. It does not specify the physical nature or mechanisms through which the applied perturbation affects the system. There are, of course, many different types of external perturbations which could be used to stimulate a system of interest. For example, various molecular-level excitations may be induced by electrical, thermal, magnetic, chemical, acoustic, or mechanical excitations. Each perturbation affects the system in a unique and selective way, governed by the specific interaction mechanisms relating the macroscopic stimuli and microscopic or molecular responses of individual system constituents. The type of physical information contained in a dynamic spectrum, therefore, is determined by the selection of perturbation method and electromagnetic probe.

The interpretation of specific physical information obtained by the 2D correlation analysis, however, is beyond the scope of this paper. In order to emphasize the general applicability of the proposed 2D correlation method to a wide variety of spectroscopic problems, discussion on the subject of a specific relationship between the applied physical stimulus and dynamic spectra representing the system response is intentionally omitted. Thus, the fluctuation of spectral signals is treated on purely phenomenological grounds as a simple set of multivariate time series data.^{17,18}



Perturbation-based 2D correlation spectroscopy

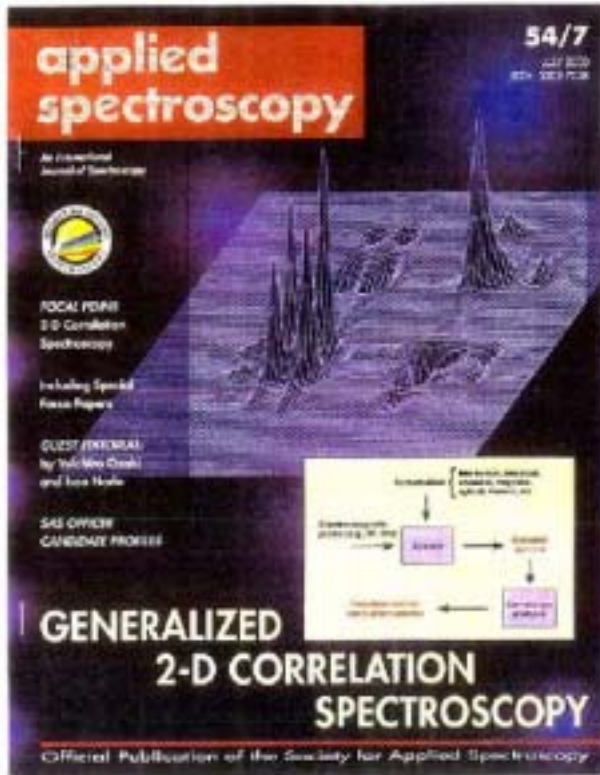
Received 26 March 1993

Volume 47, Number 5, 1993

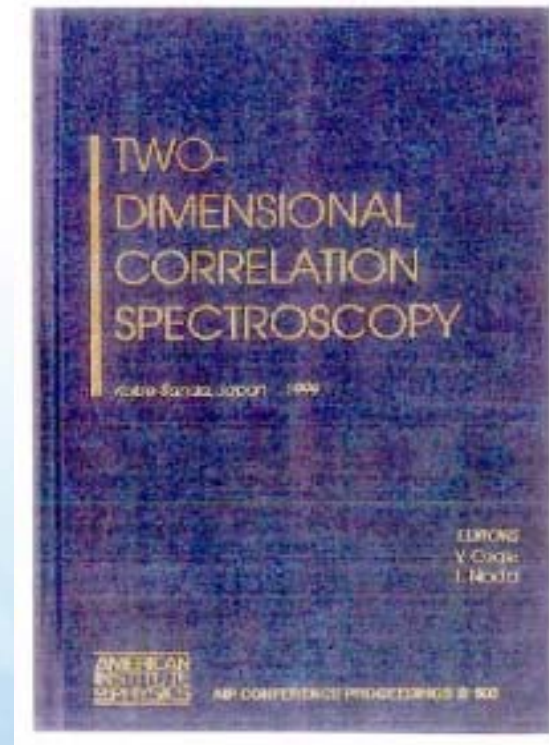
0021-8995/93/051329-08\$04.00/0

APPLIED SPECTROSCOPY 1329

Reference Literature



Applied Spectroscopy, vol. **54**, no. 7, July, 2000. (Special issue on generalized 2D correlation spectroscopy)



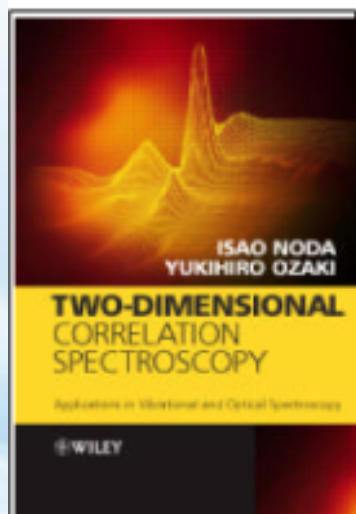
Y. Ozaki and I. Noda, Eds. *Two-Dimensional Correlation Spectroscopy*, AIP Conference proceedings **503**, AIP: Melville, 2000.

Book

Two-Dimensional Correlation Spectroscopy

Applications in Vibrational and Optical Spectroscopy

Isao Noda, Procter and Gamble Company, Cincinnati, Ohio, USA
and Yukihiro Ozaki, Kwansai Gakuin University, Japan



In the last decade or so, perturbation-based generalized two-dimensional (2D) correlation spectroscopy has become a powerful and versatile tool for the detailed analysis of various spectroscopic data. This seemingly straightforward idea of spreading the spectral information onto the second dimension, by applying the well-established classical correlation analysis methodology, has turned out to be very fertile ground for the development a new generation of modern spectral analysis techniques.

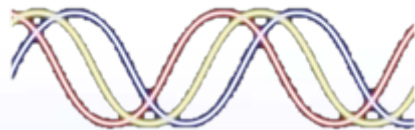
This book is a valuable tool for individuals using correlation spectroscopy and those who want to start using this technique. Written by two of the biggest names in the field – Isao Noda is the founder of this technique – this is the first book on 2D vibrational and optical spectroscopy available in one single source.

This book serves as an introductory text for newcomers to the field, as well as presents a survey of specific interest areas for the experienced practitioner.

Generalized Two-Dimensional Correlation Spectroscopy

Electromagnetic Probe

IR, NIR, laser



Chemical System



Dynamic Spectra



External Perturbation

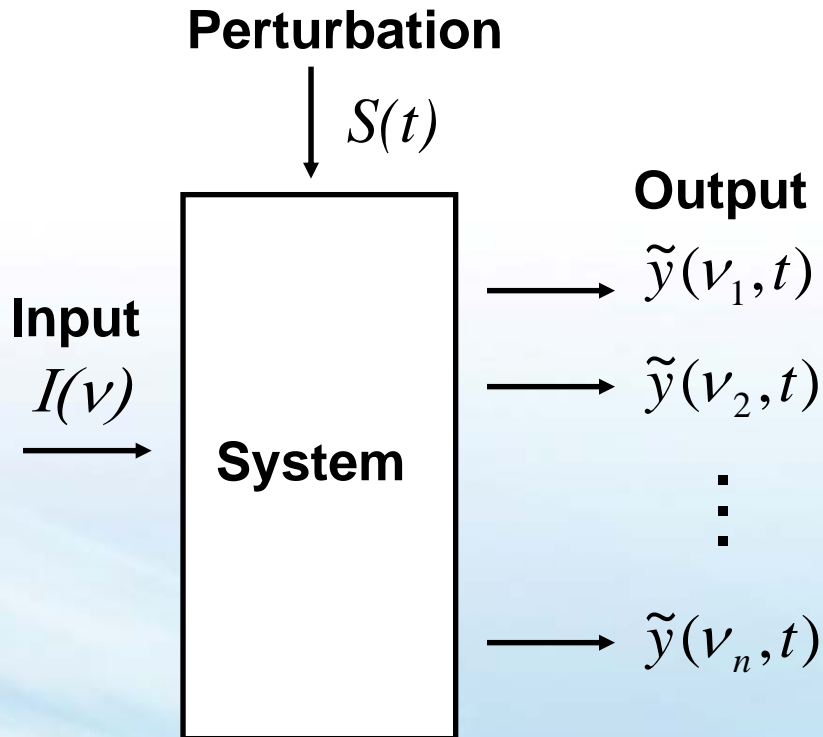
Temperature, pressure, time, concentration,
electromagnetic field



2D Correlation Spectra

Acquisition of 2D Correlation Spectra

2D Correlation Analysis



Comparison of two signals
measured at different ν along t

Cross-correlation function

$$X(\nu_1, \nu_2) = \langle \tilde{y}(\nu_1, t) \cdot \tilde{y}(\nu_2, t') \rangle$$

$$= \Phi(\nu_1, \nu_2) + i \Psi(\nu_1, \nu_2)$$

Synchronous spectrum

$$\Phi(\nu_1, \nu_2) = \text{Similarity of signal dependence on } t$$

Asynchronous spectrum

$$\Psi(\nu_1, \nu_2) = \text{Dissimilarity of signal dependence on } t$$

Generalized 2D Correlation Formalism

Dynamic spectrum

$$\tilde{y}(v, t) = \begin{cases} y(v, t) - \bar{y}(v) & \text{for } T_{\min} \leq t \leq T_{\max} \\ 0 & \text{otherwise} \end{cases}$$

$$\text{where } \bar{y}(v) = \frac{1}{T_{\max} - T_{\min}} \int_{T_{\min}}^{T_{\max}} y(v, t) dt.$$

Fourier transform

$$\tilde{Y}_1(\omega) = \int_{-\infty}^{\infty} \tilde{y}(v_1, t) e^{-i\omega t} dt$$

$$\tilde{Y}_2^*(\omega) = \int_{-\infty}^{\infty} \tilde{y}(v_2, t) e^{+i\omega t} dt$$

2D correlation spectra

$$\Phi(v_1, v_2) + i \Psi(v_1, v_2) = \frac{1}{\pi (T_{\max} - T_{\min})} \int_0^{\infty} \tilde{Y}_1(\omega) \cdot \tilde{Y}_2^*(\omega) d\omega$$

$\Phi(v_1, v_2)$ = **synchronous** spectrum

$\Psi(v_1, v_2)$ = **asynchronous** spectrum

Discrete spectral sampling

$$\tilde{y}_j(\nu) = \begin{cases} y_j(\nu) - \bar{y}(\nu) & \text{for } 1 \leq j \leq m \\ 0 & \text{otherwise} \end{cases} \quad \bar{y}(\nu) = \frac{1}{m} \sum_{j=1}^m y_j(\nu)$$

Discrete Hilbert transform

$$\tilde{z}_j(\nu_2) = \sum_{k=1}^m N_{jk} \cdot \tilde{y}_k(\nu_2) \quad \text{where} \quad N_{jk} = \begin{cases} 0 & \text{if } j = k \\ 1 / \pi(k - j) & \text{otherwise} \end{cases}$$

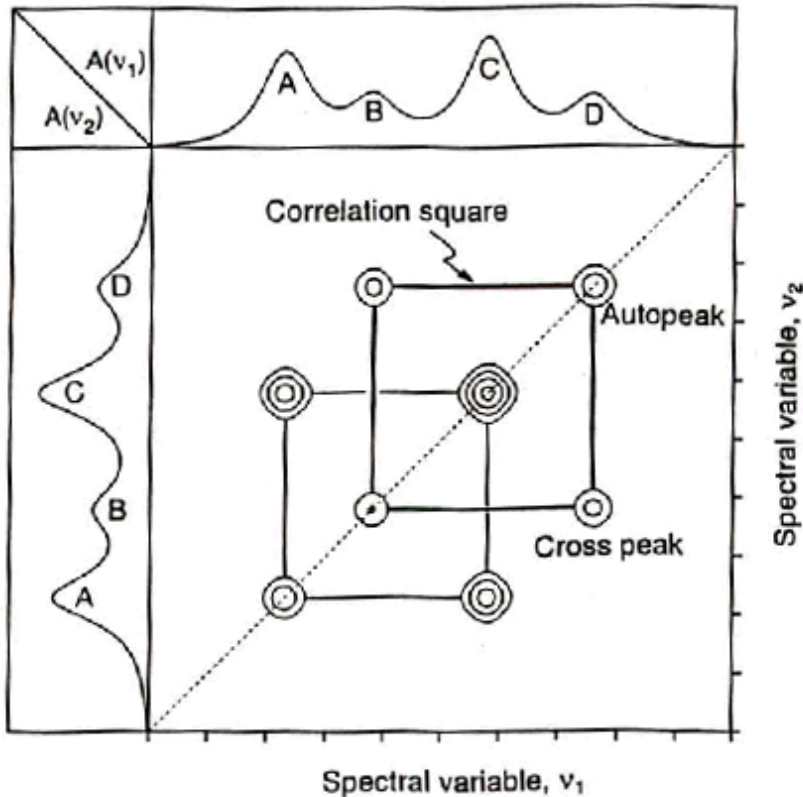
2D correlation spectra

$$\Phi(\nu_1, \nu_2) = \frac{1}{m-1} \sum_{j=1}^m \tilde{y}_j(\nu_1) \cdot \tilde{y}_j(\nu_2)$$

$$\Psi(\nu_1, \nu_2) = \frac{1}{m-1} \sum_{j=1}^m \tilde{y}_j(\nu_1) \cdot \tilde{z}_j(\nu_2)$$

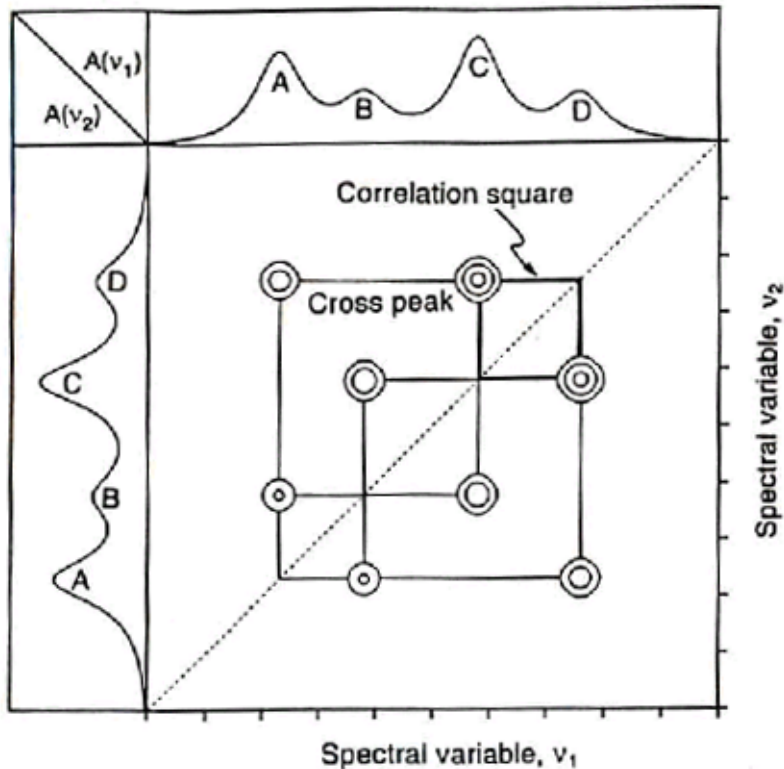
Rapid and straightforward computation
of 2D correlation spectra

Synchronous correlation spectrum: $\Phi(v_1, v_2)$



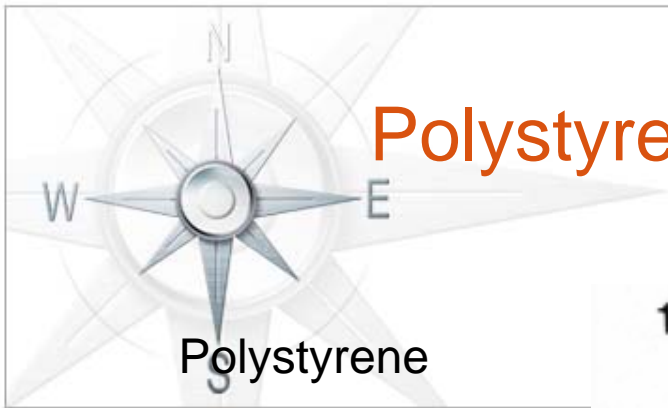
- **Autopeaks** at diagonal positions represent the **extent** of perturbation-induced dynamic fluctuations of spectral signals
- **Cross peaks** represent **simultaneous changes** of spectral signals at two different wavenumbers, suggesting a coupled or related origin of intensity variations
- If the **sign** of a cross peak is **positive**, the intensities at corresponding wavenumbers are increasing (or decreasing) together. If the sign is **negative**, one is increasing, while the other is decreasing.

Asynchronous correlation spectrum: $\Psi(\nu_1, \nu_2)$



- **Cross peaks** develop only if the intensity varies **out of phase** with each other for some Fourier frequency components of signal fluctuations
- The **sign** of a cross peak is **positive** if the intensity change at ν_1 occurs **before** ν_2 .
- The **sign** of a cross peak is **negative** if the intensity change at ν_1 occurs **after** ν_2 .
- The above sign rules are reversed if $\Phi(\nu_1, \nu_2) < 0$.

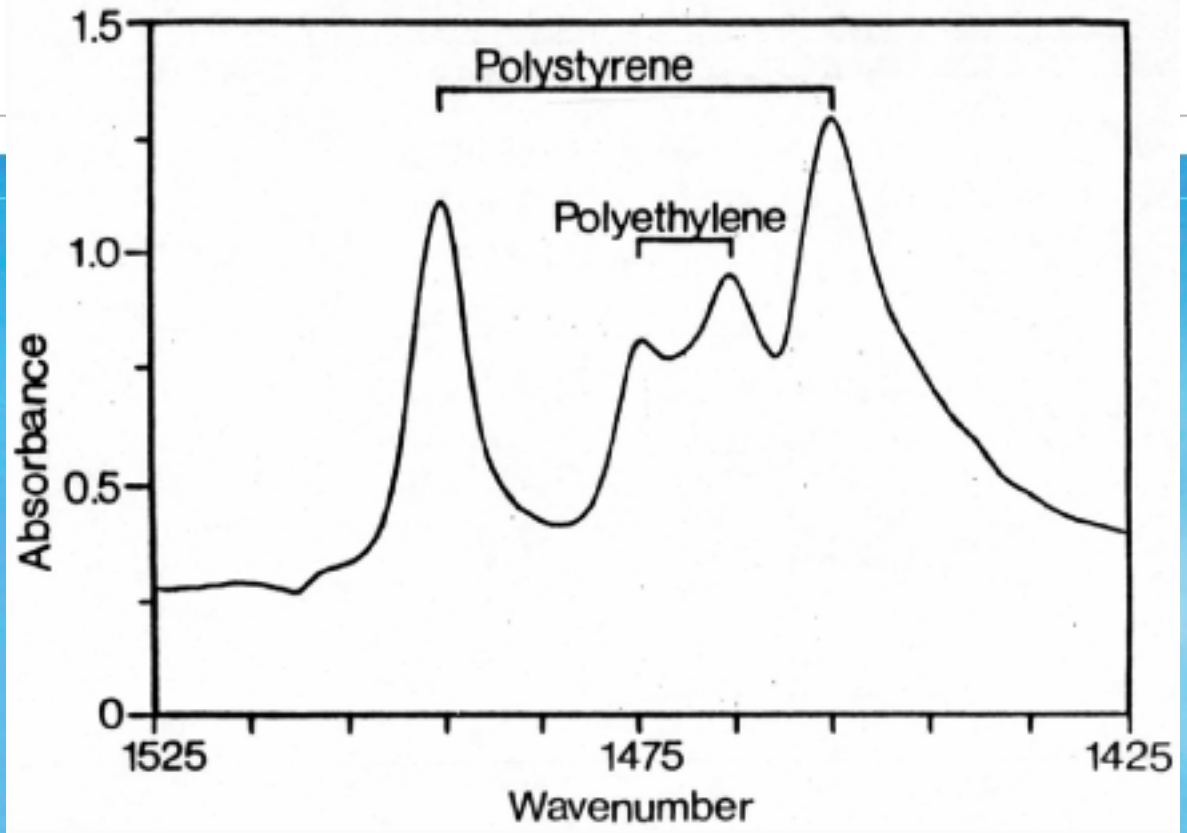
Polystyrene/Polyethylene Blend



Polystyrene

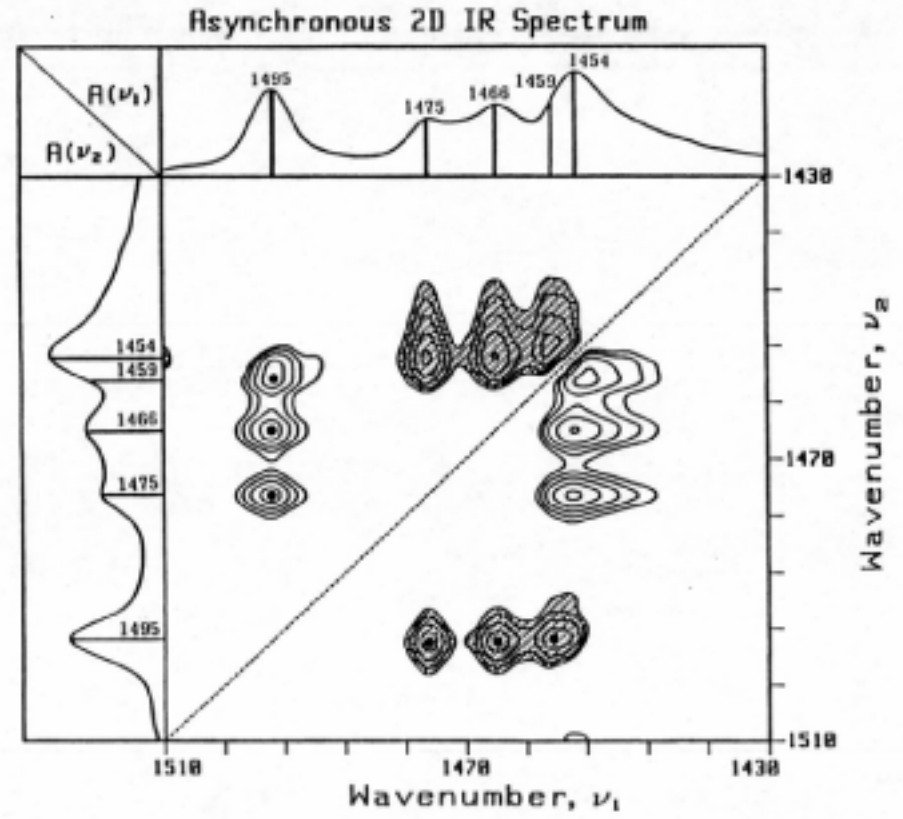
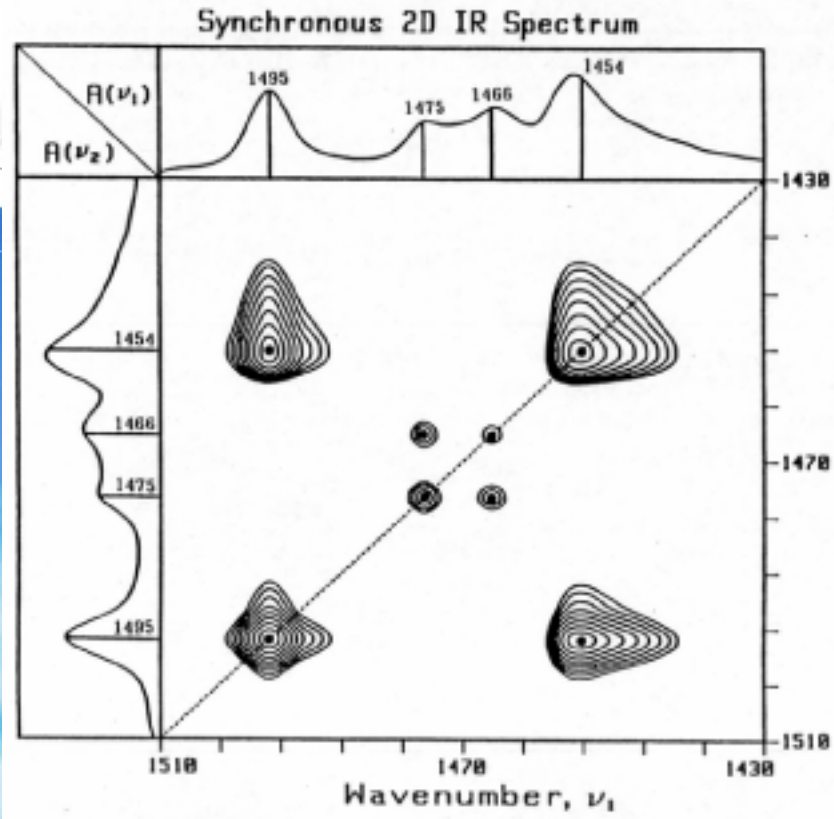


Polyethylene



- PS and PE are immiscible (phase separated)
- No molecular level interactions

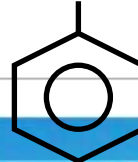
Polystyrene/Polyethylene Blend



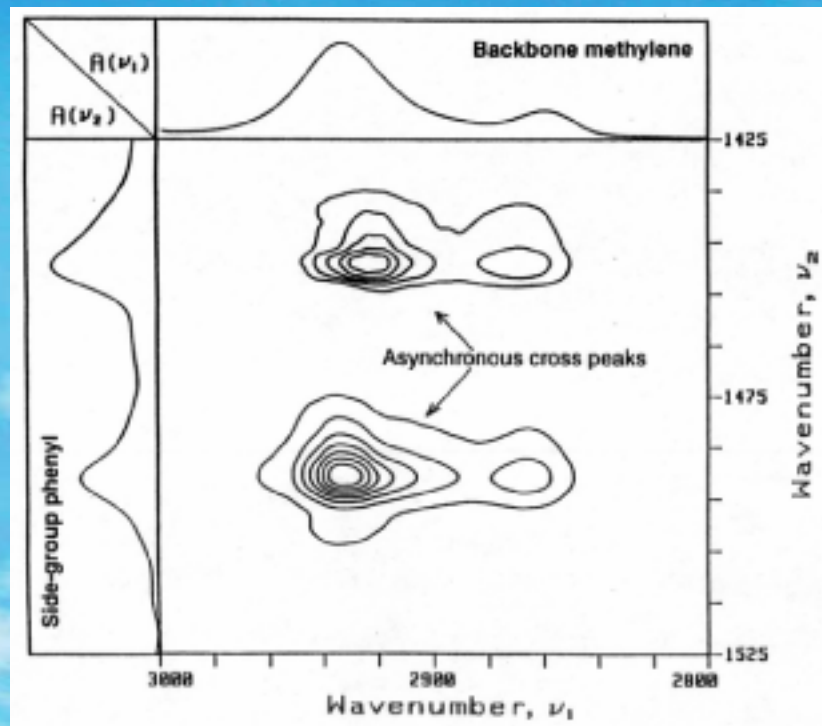
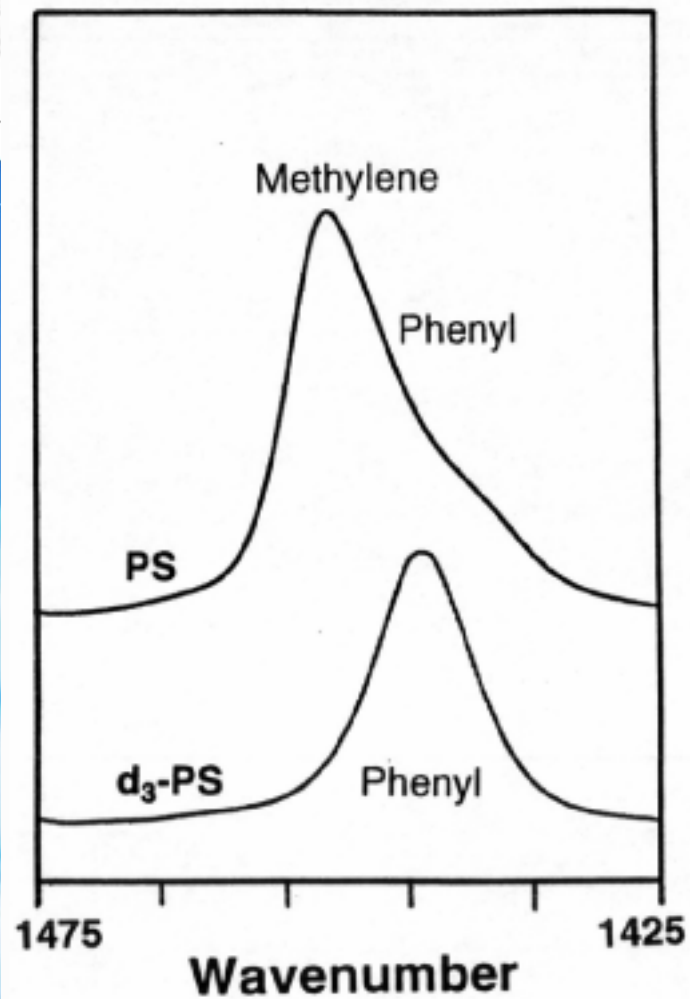
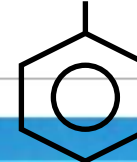
- Separate synchronous correlations for PS and PE bands
- Asynchronous correlation between PS and PPE bands
- Asynchronicity within PS bands (backbone vs. side group)

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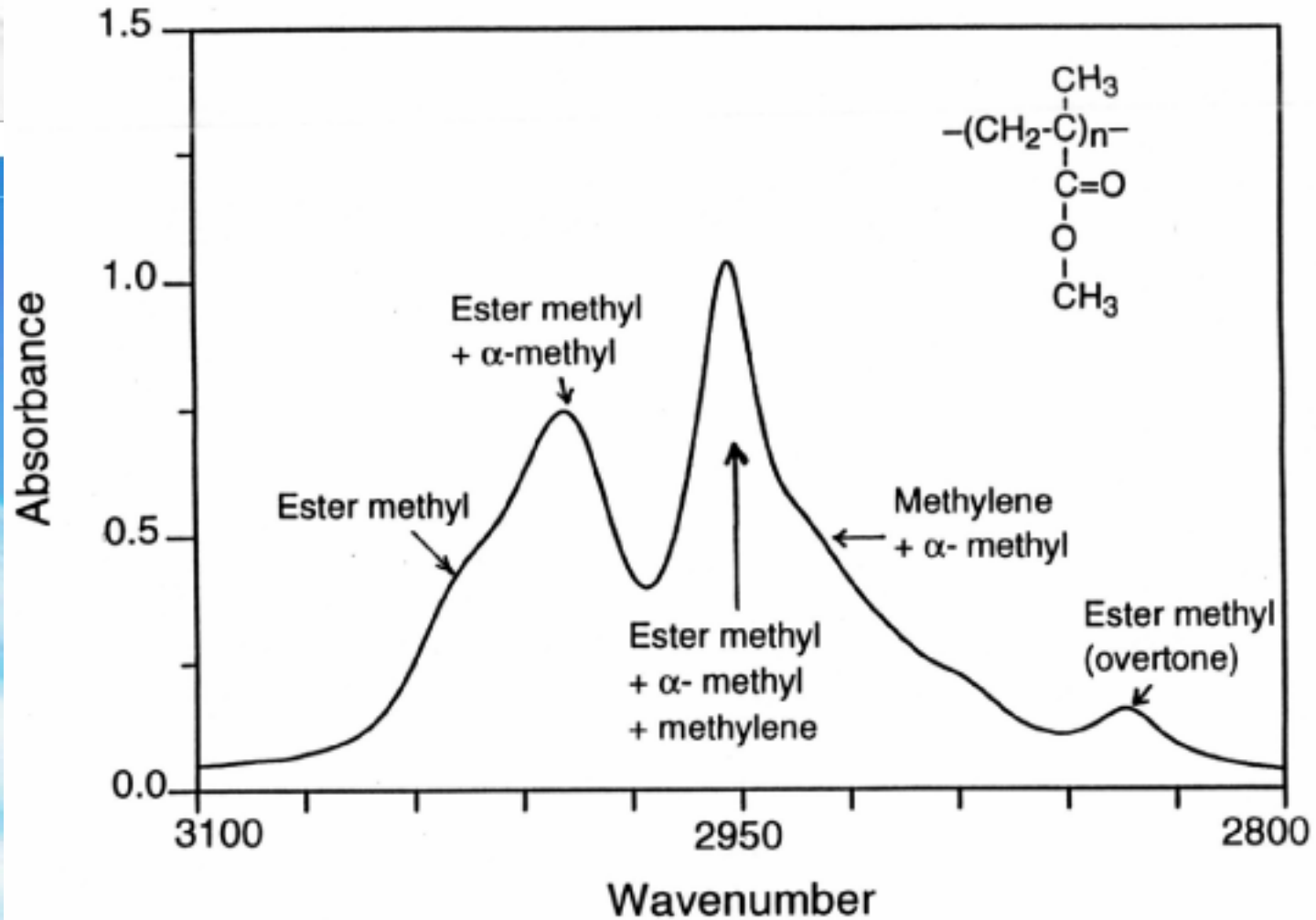
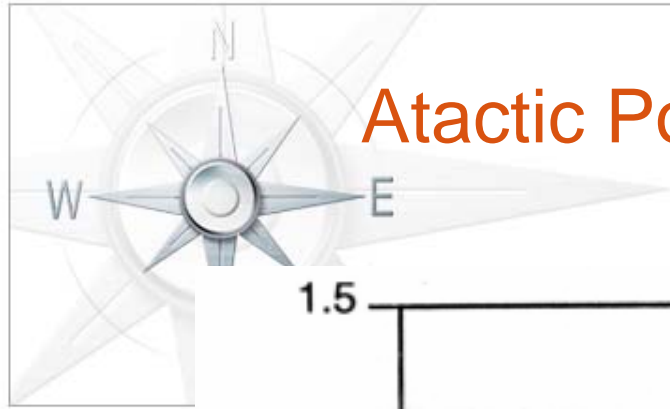
Selectively Deuterated Polystyrene



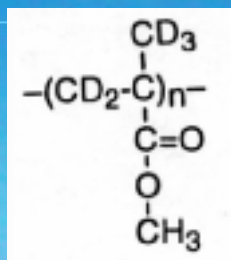
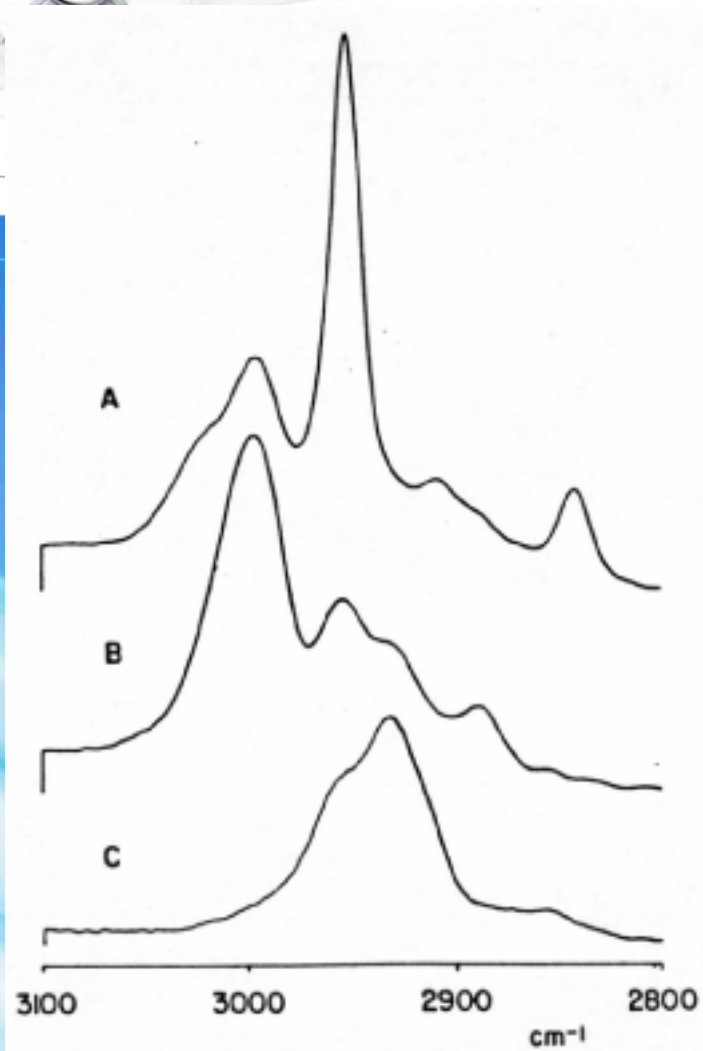
vs.



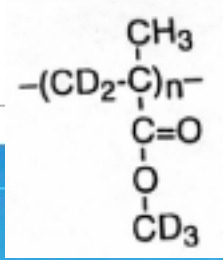
Atactic Poly(methyl methacrylate)



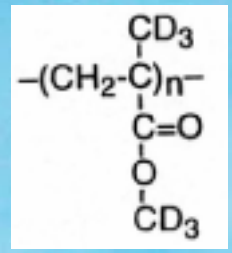
Pure Group Frequency Spectra of PMMA



A. Ester methyl



B. Alpha methyl



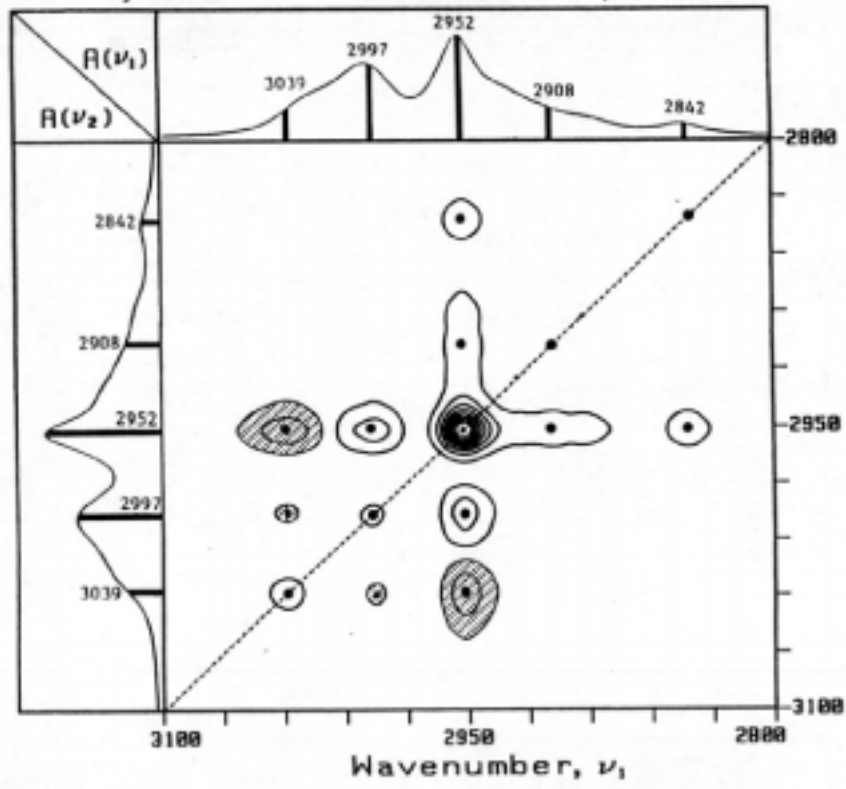
C. Methylene

S.K. Dirlikov and J.L. Koenig
Appl. Spectrosc. 33, 555 (1979).

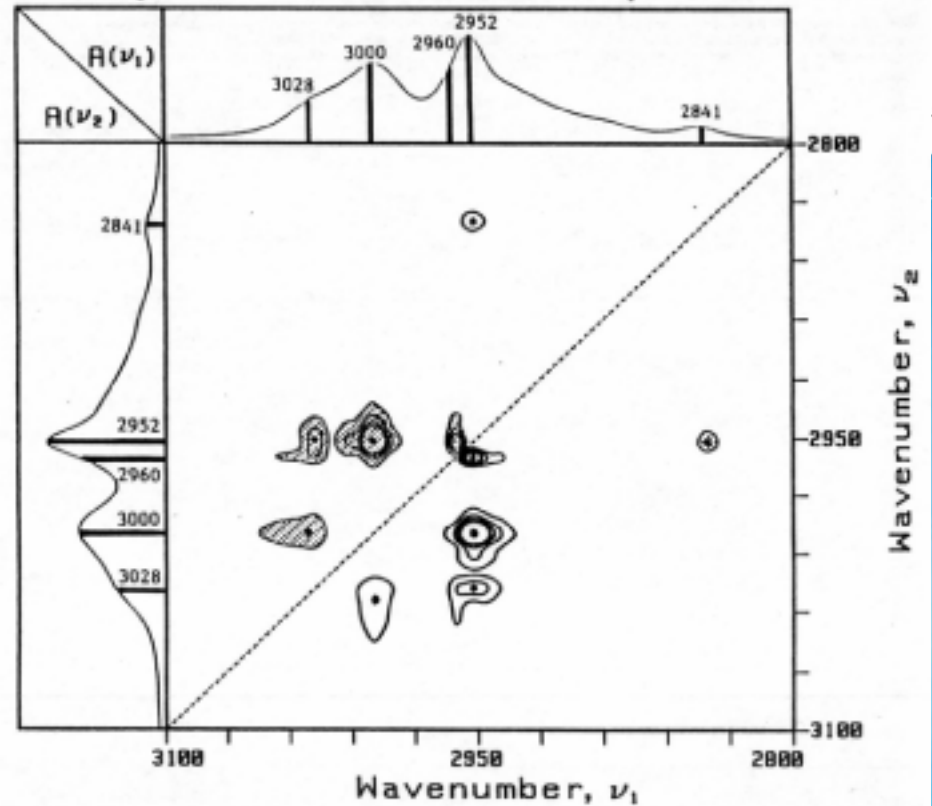
Atactic PMMA



Synchronous 2D IR Dichroism Spectrum



Asynchronous 2D IR Dichroism Spectrum



- Ester methyl peaks are in the synchronous spectrum almost exclusively
- Alpha methyl and methylene found in the asynchronous spectrum

Human Hair Keratin



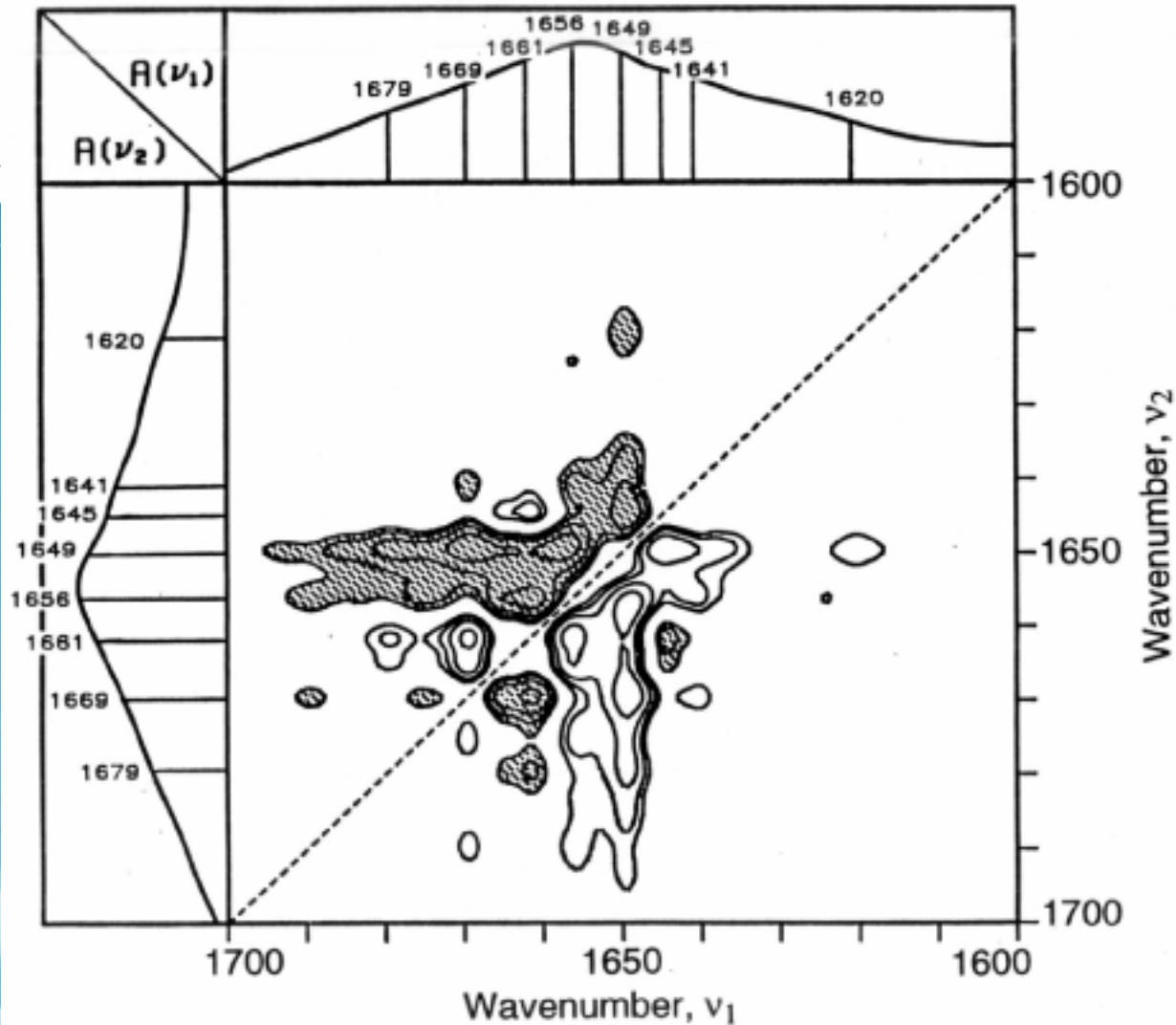
Assignments (cm⁻¹)

α-helix S
1661, 1649

β-like extended chains and turns
1679, 1669, 1645
1641, 1620

Disordered structures
1656

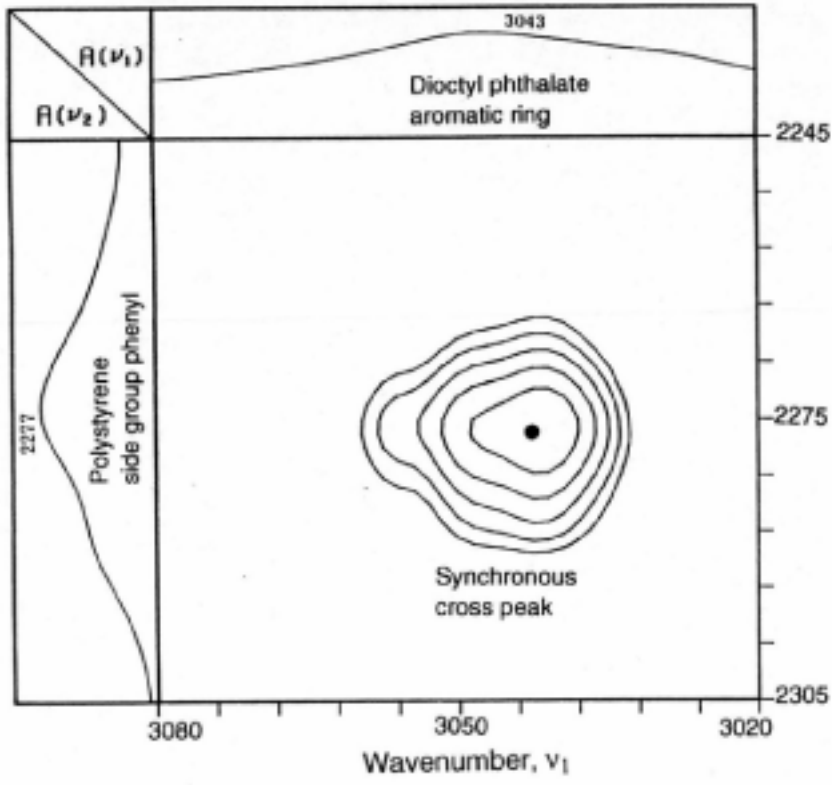
Asynchronous 2D IR Dichroism Spectrum



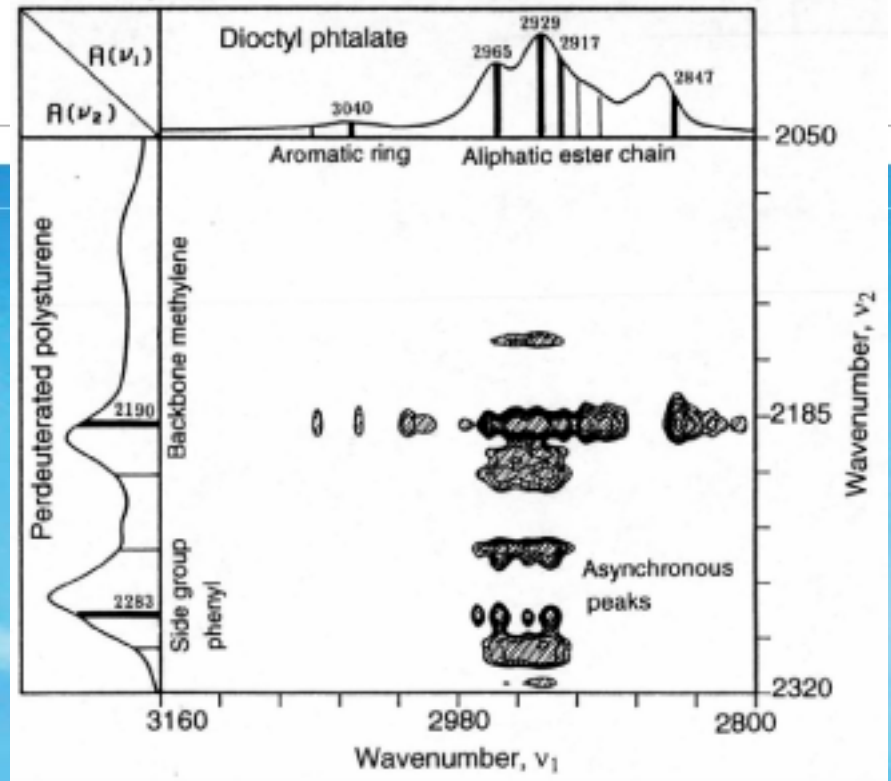
Plasticized Polystyrene



Synchronous 2D IR Dichroism Spectrum



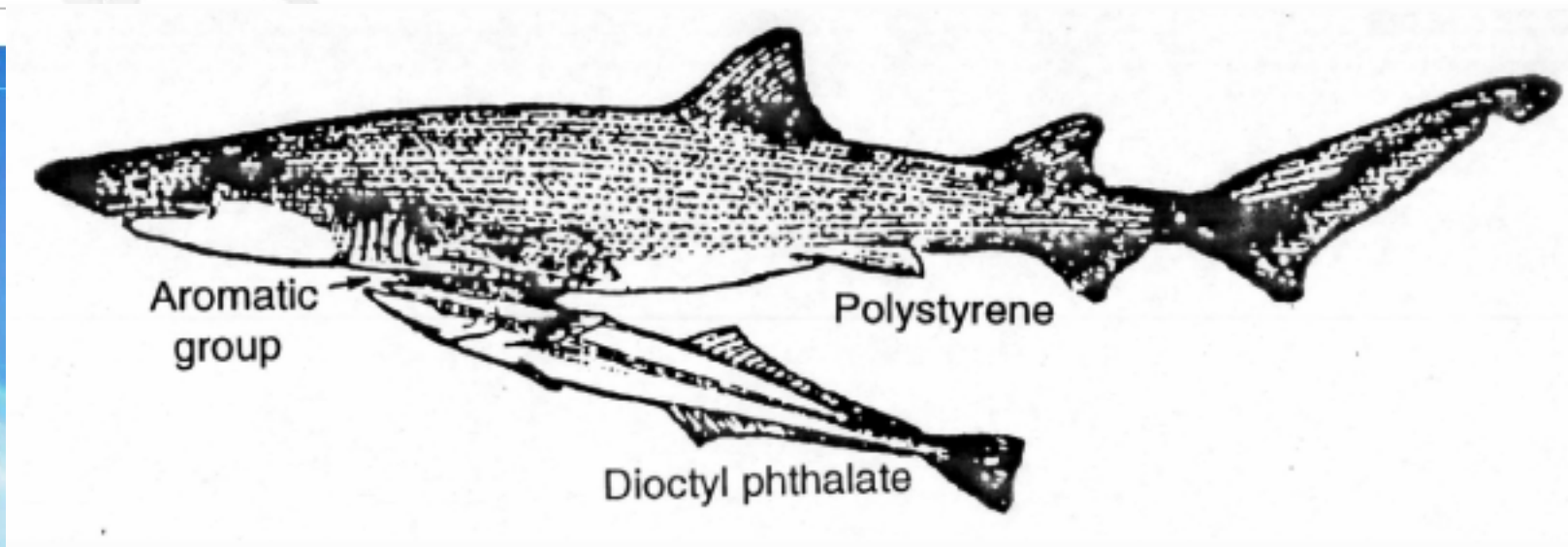
Asynchronous 2D IR Dichroism Spectrum



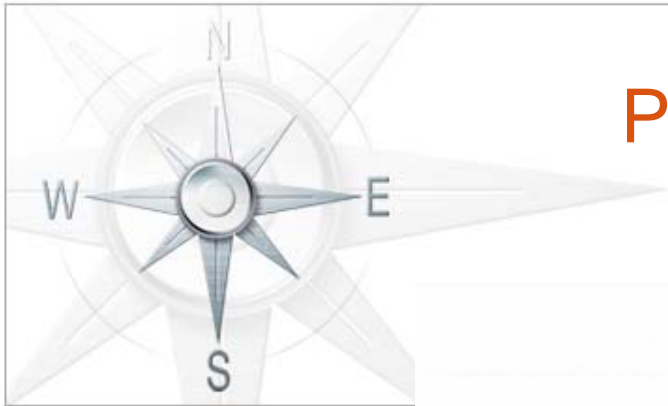
- Motions of aromatic groups of PS and DOP are synchronized
- DOP aliphatic chains move asynchronously (independently) with respect to PS phenyl rings



Remora Model of Plasticization

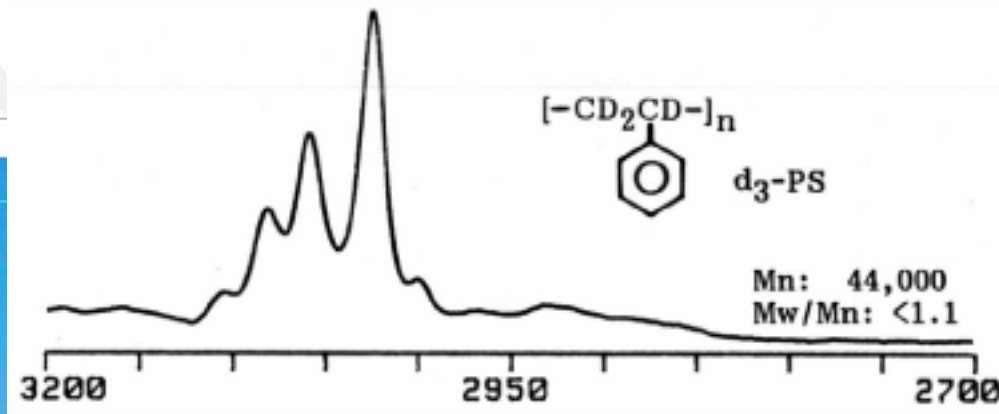


rem'o-ra, *n.* [L., hinderance.] 1. Any of several fishes (genera *Echeneis*, *Remora*, family Echeneidae), with a suctional disk on the head by which they cling to other fishes or to ships. 2. A clog; drags; hinderence.

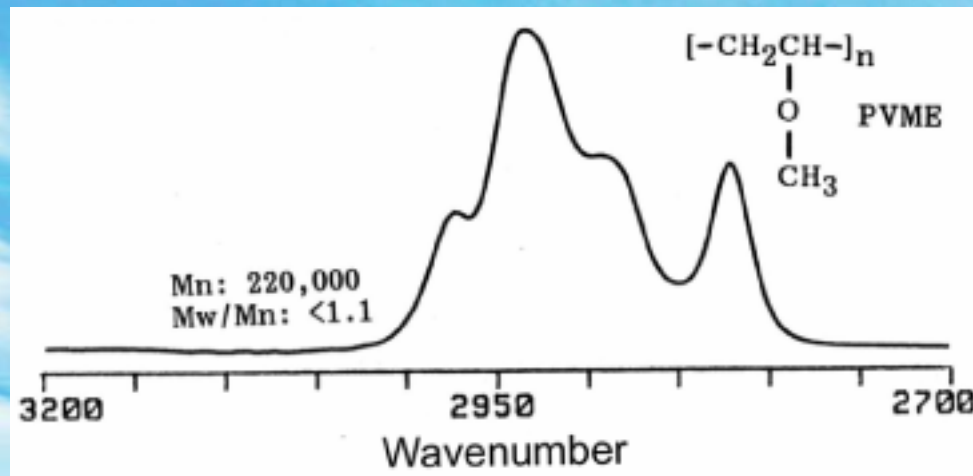


PS/PVME Blends

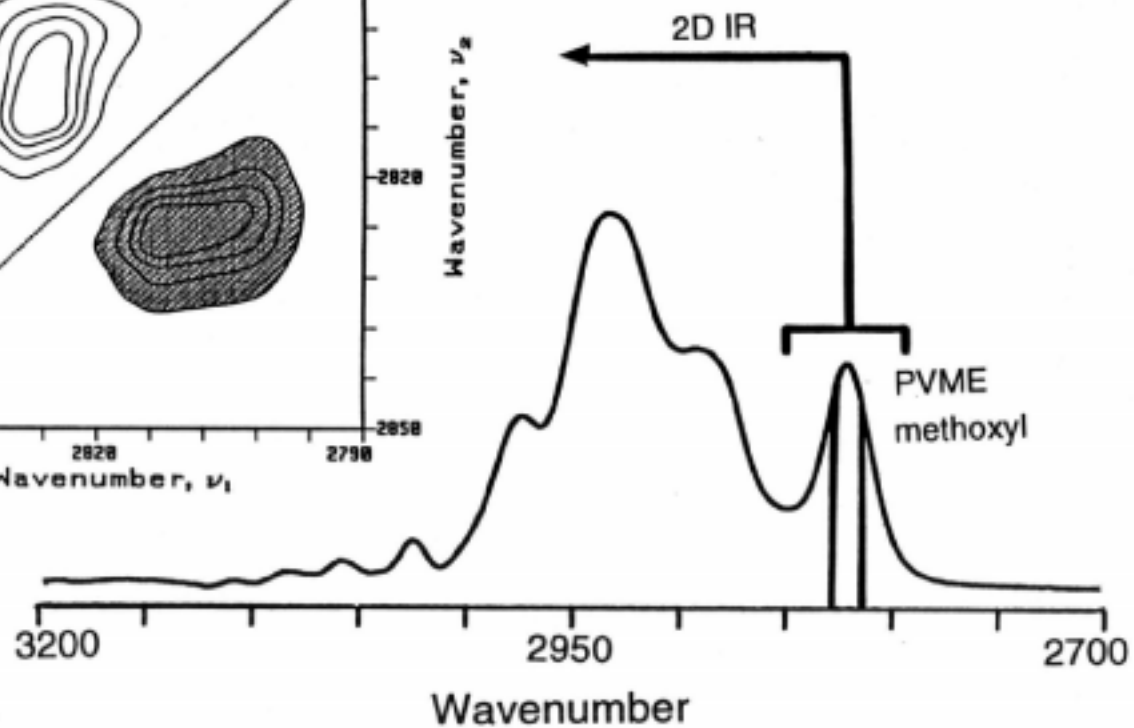
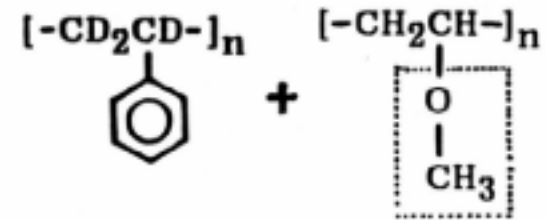
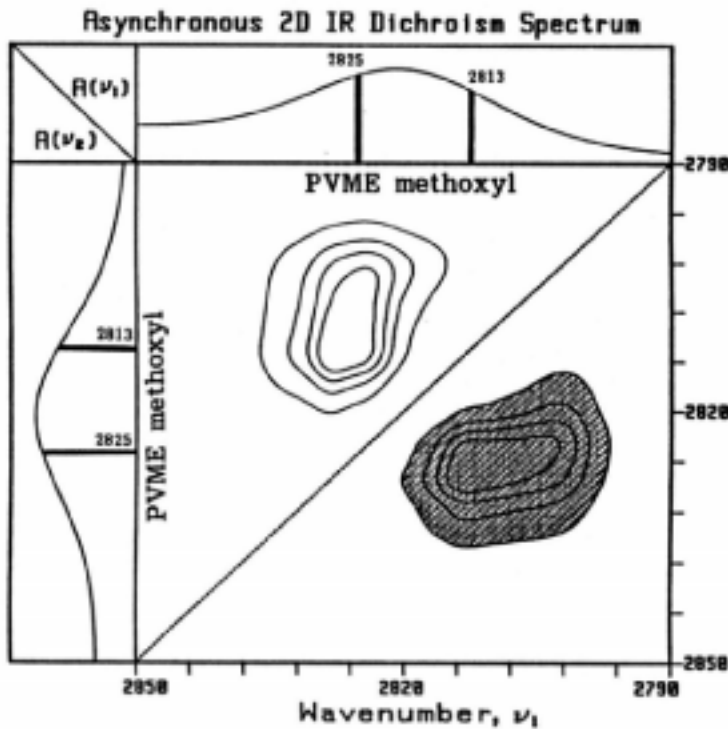
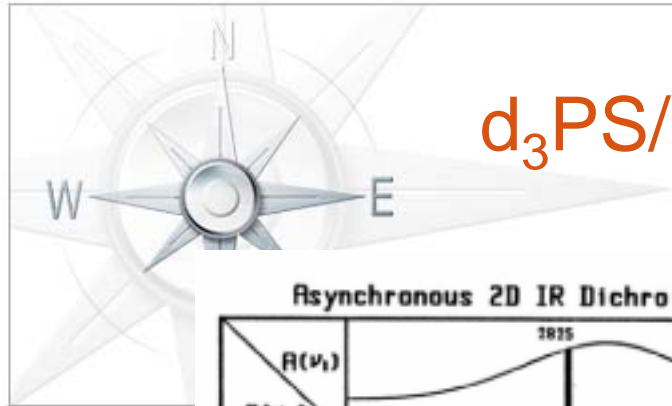
Polystyrene (chain-deuterated)



Poly(vinyl methyl ether)

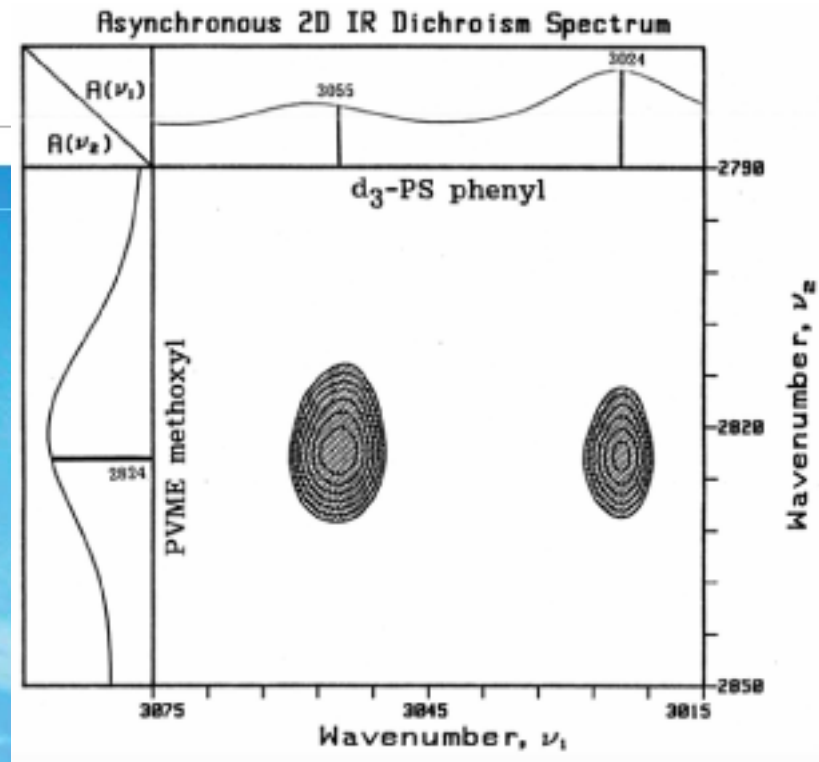
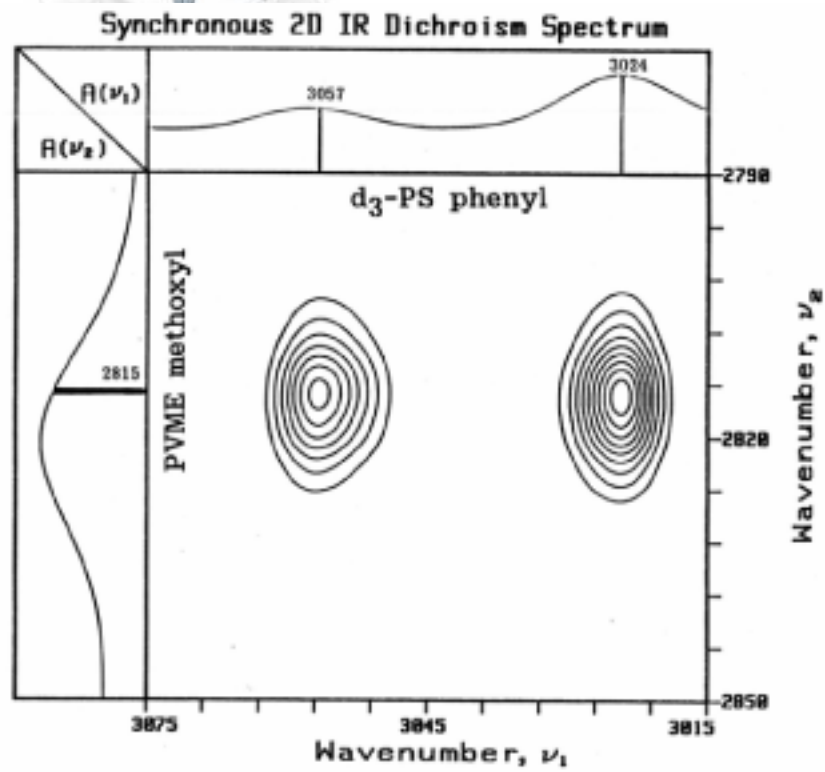


d_3 PS/PVME (25:75) Blend





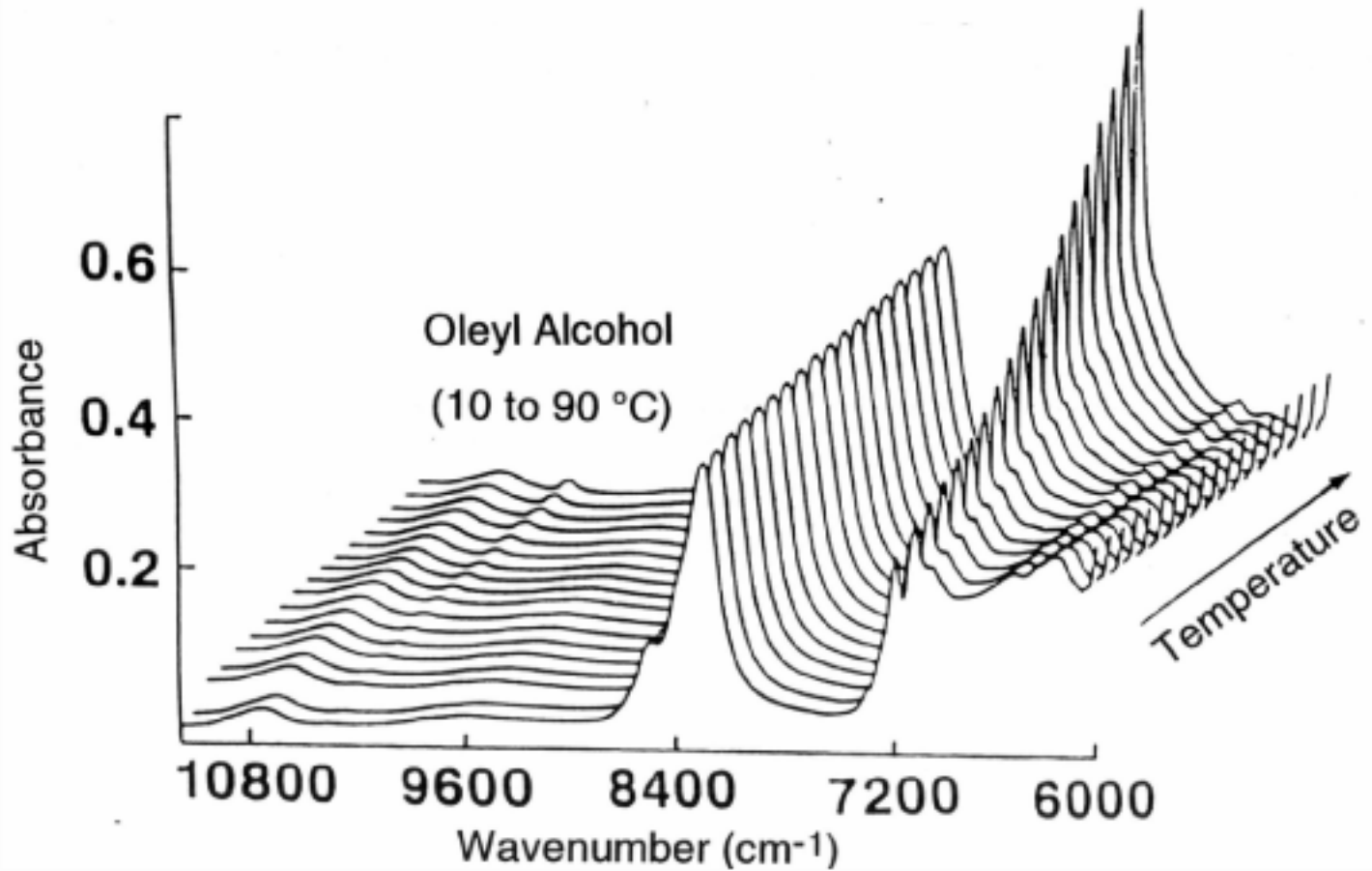
d_3 PS/PVME (25:75) Blend



- Band split of PVME methoxyl groups into 2815 cm^{-1} and 2824 cm^{-1}
- Motion of PVME 2815 cm^{-1} is synchronized with PS phenyl



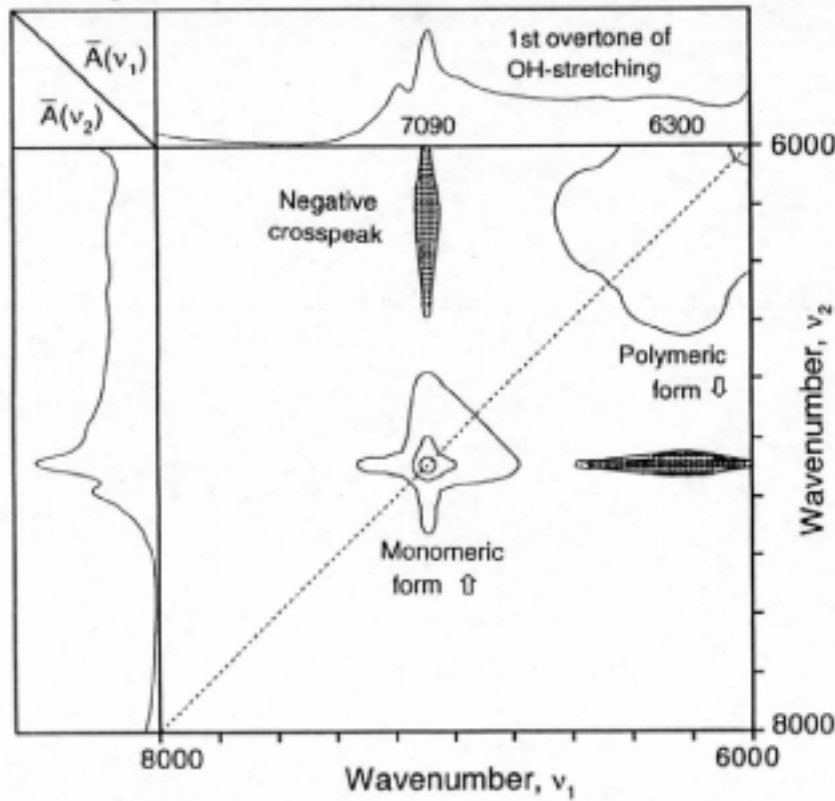
FT NIR Spectra of Oleyl Alcohol



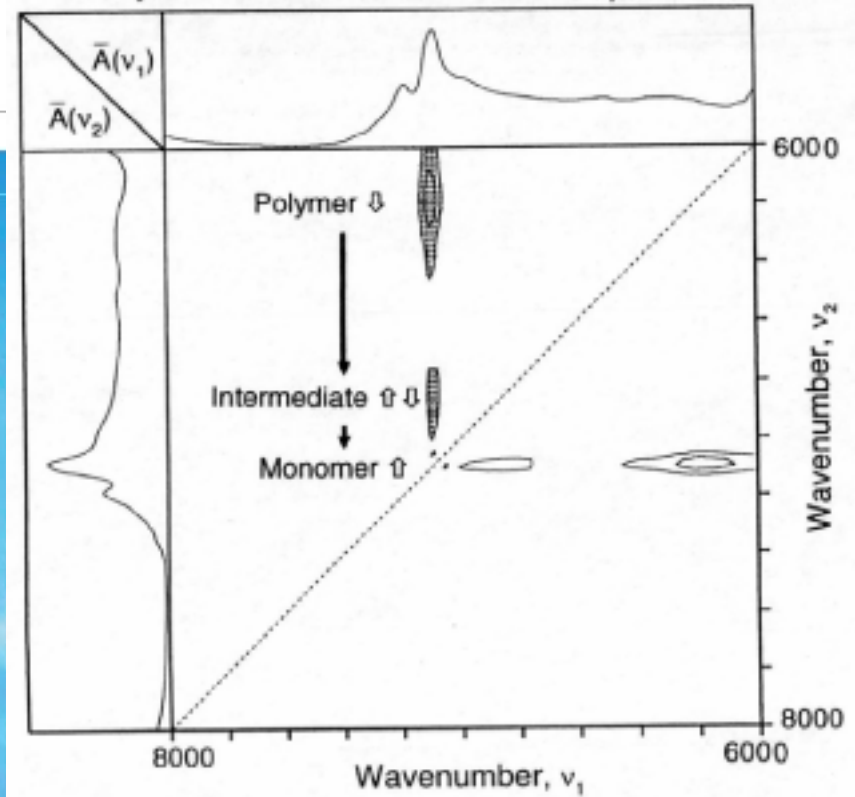
Thermal 2D NIR of Oleyl Alcohol



Synchronous 2D NIR Correlation Spectrum

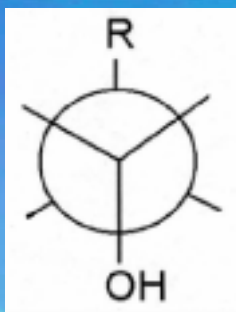


Asynchronous 2D NIR Correlation Spectrum

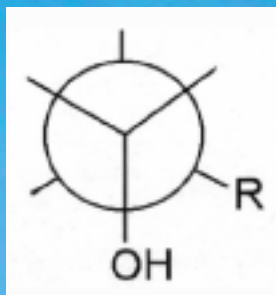


- Associated “polymers” decrease, as monomers increase
- Not a direct conversion (asynchronous peaks)
- Intermediate states (e.g., dimers) exist

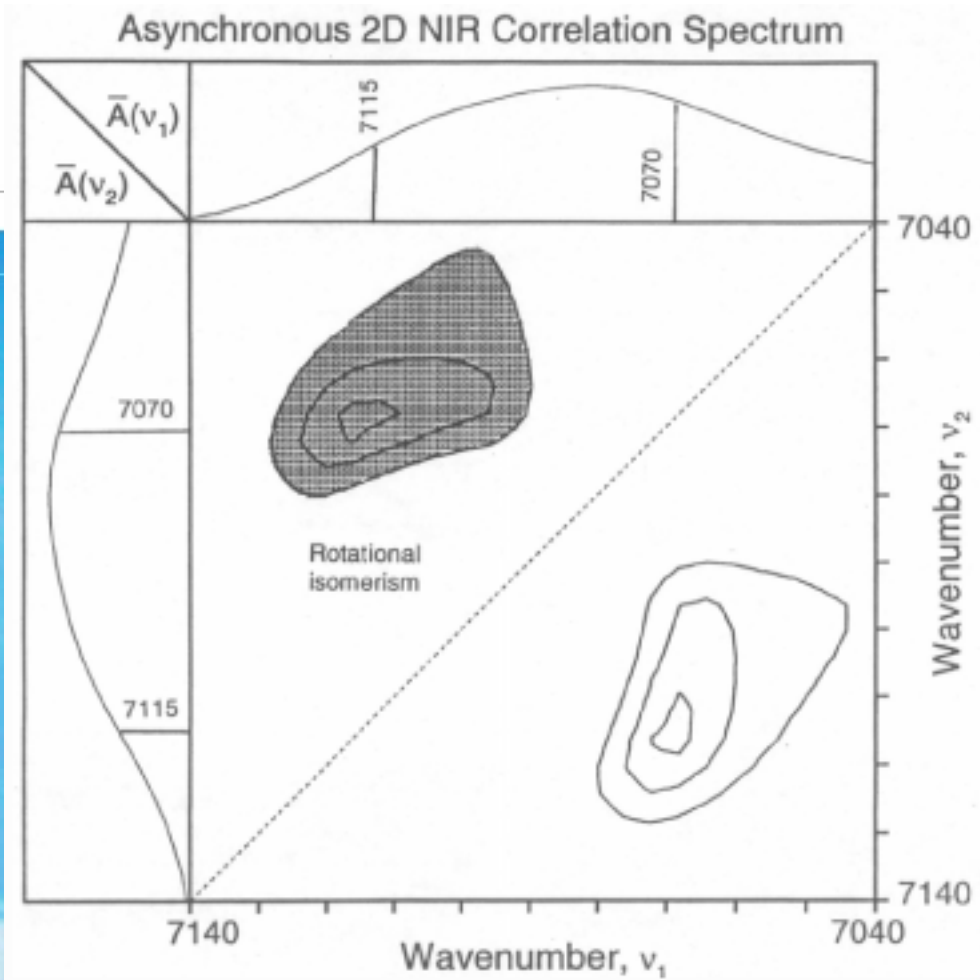
Thermal 2D NIR of Oleyl Alcohol



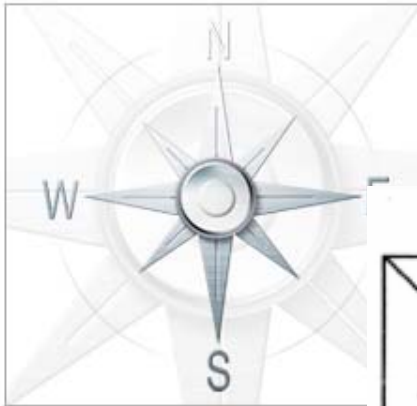
Trans



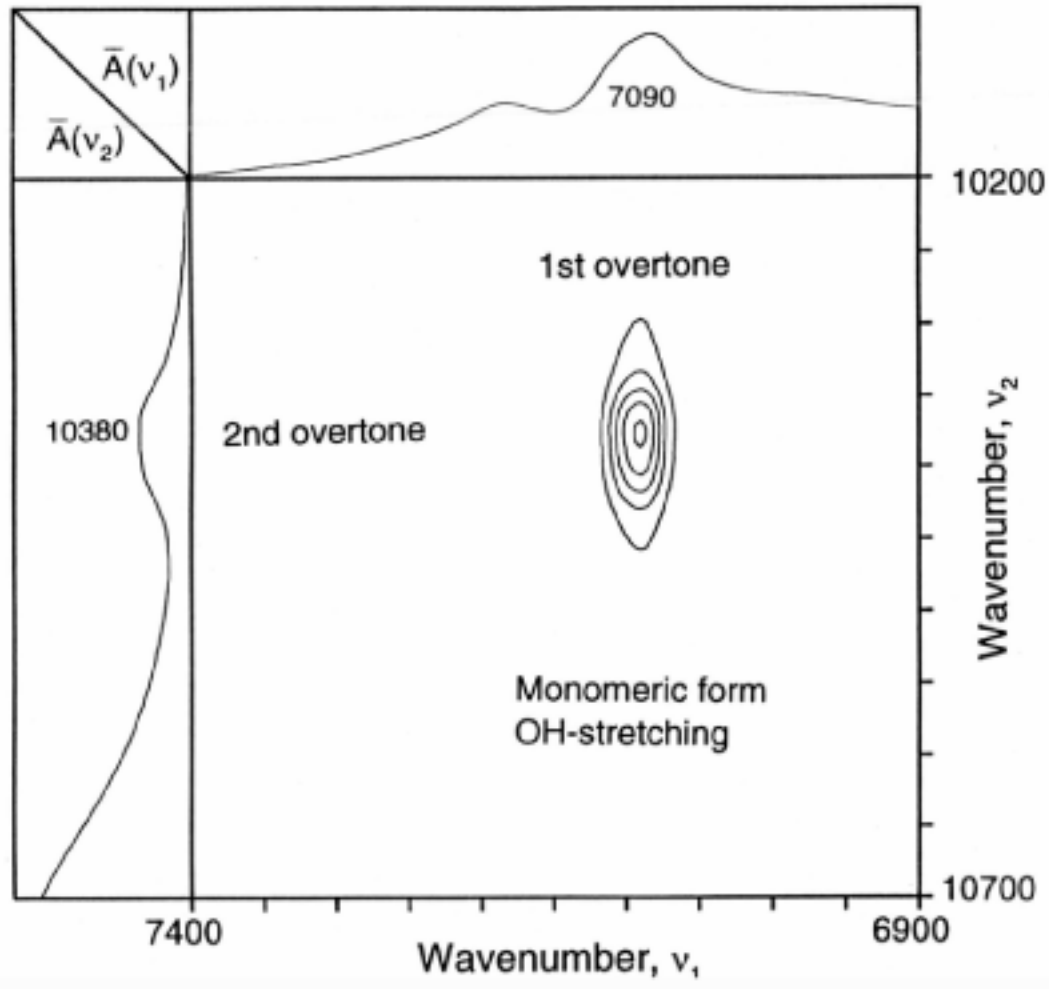
Gauche



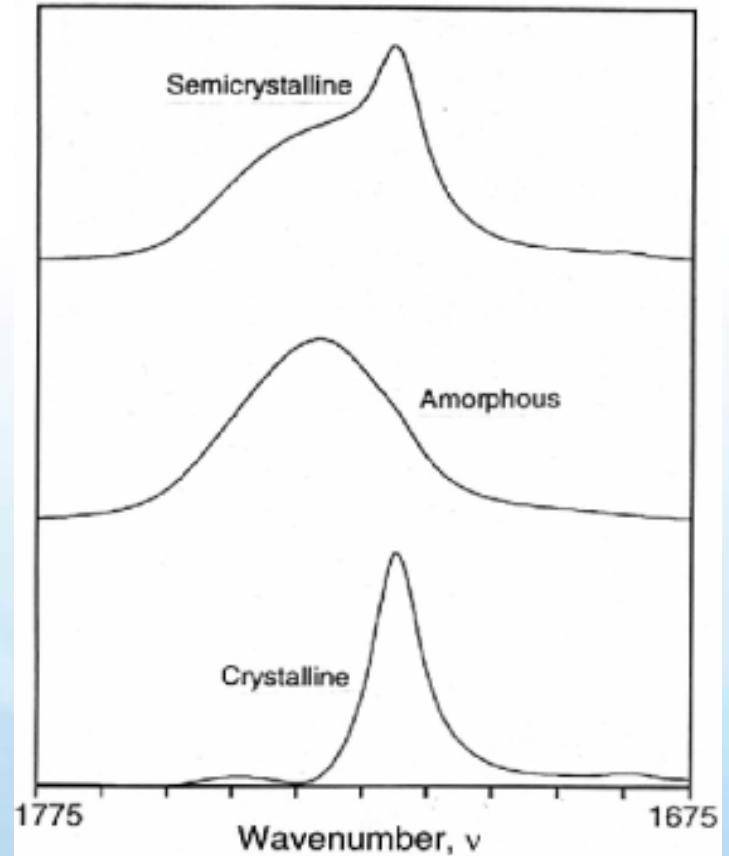
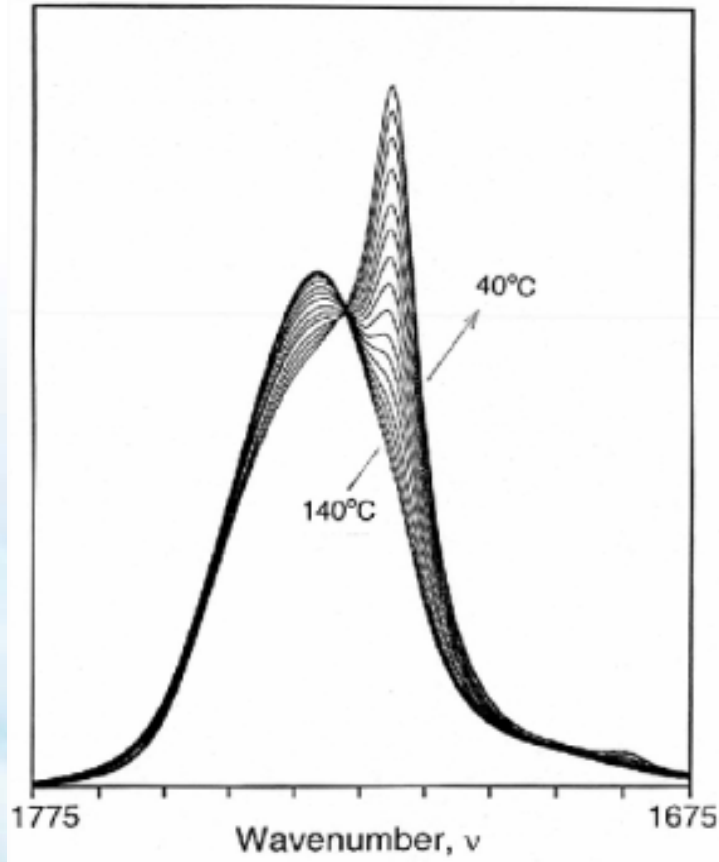
Thermal 2D NIR of Oleyl Alcohol



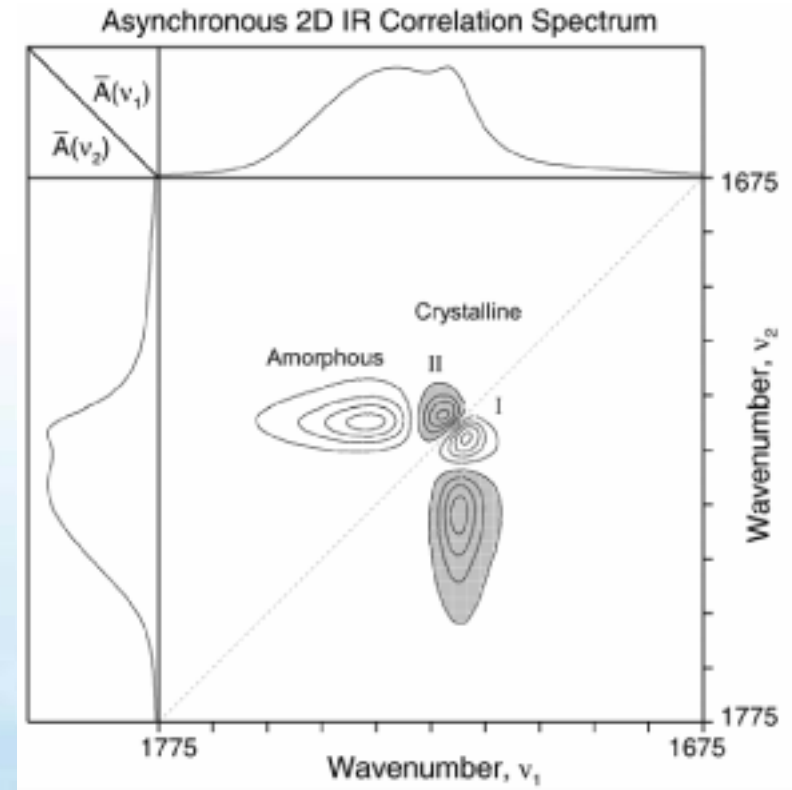
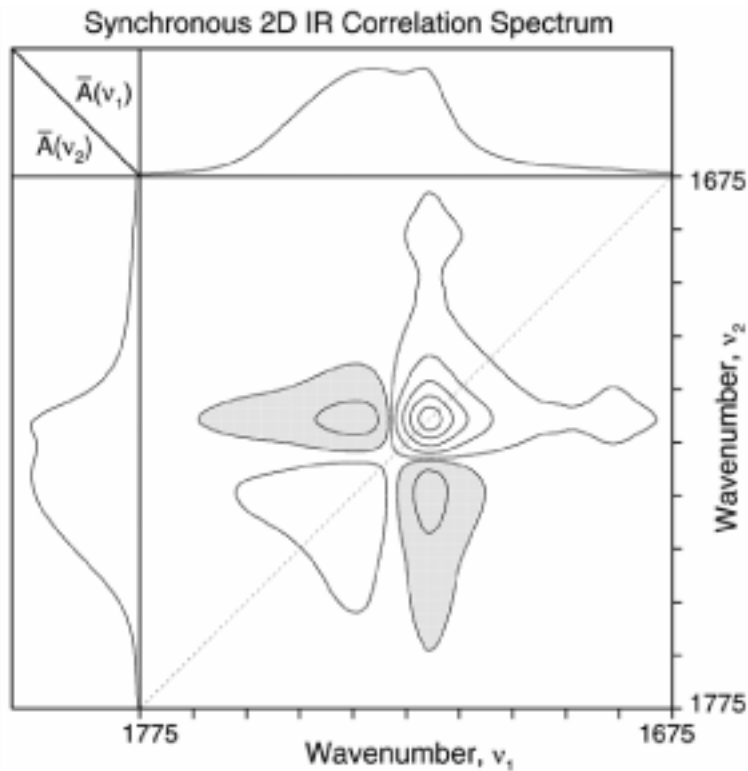
Synchronous 2D NIR Correlation Spectrum



Crystallization of *Nodax*TM (PHBHx)



Crystallization of Nodax™ (PHBHx)



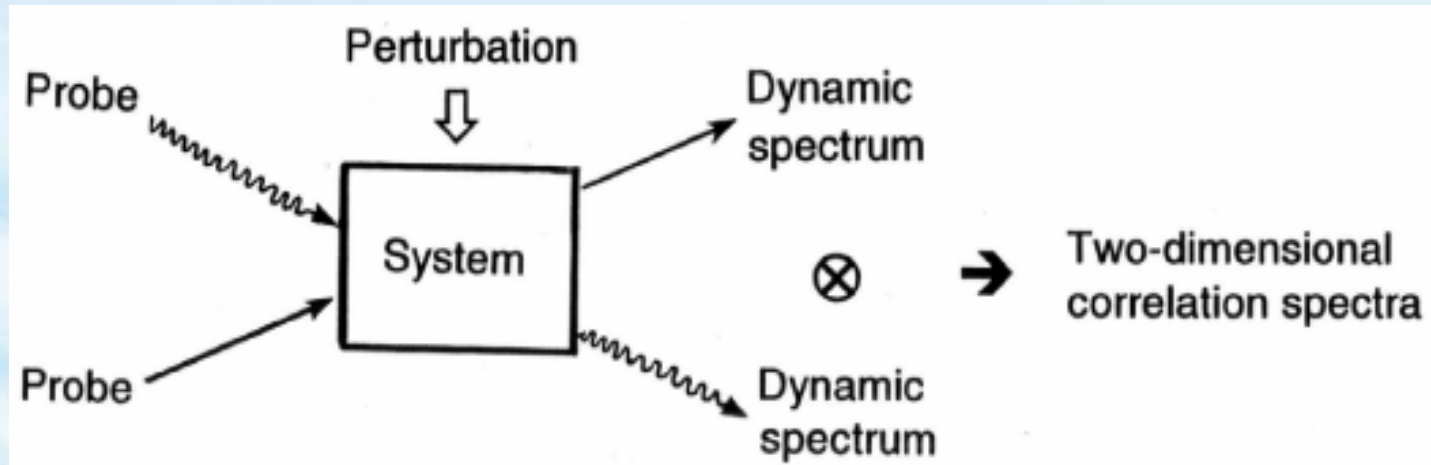
- Highly ordered crystals (I) grow **first** when *Nodax*TM is cooled from the melt
- Less ordered (II) crystals grow **later**, while the amorphous component keeps decreasing as the temperature is further lowered

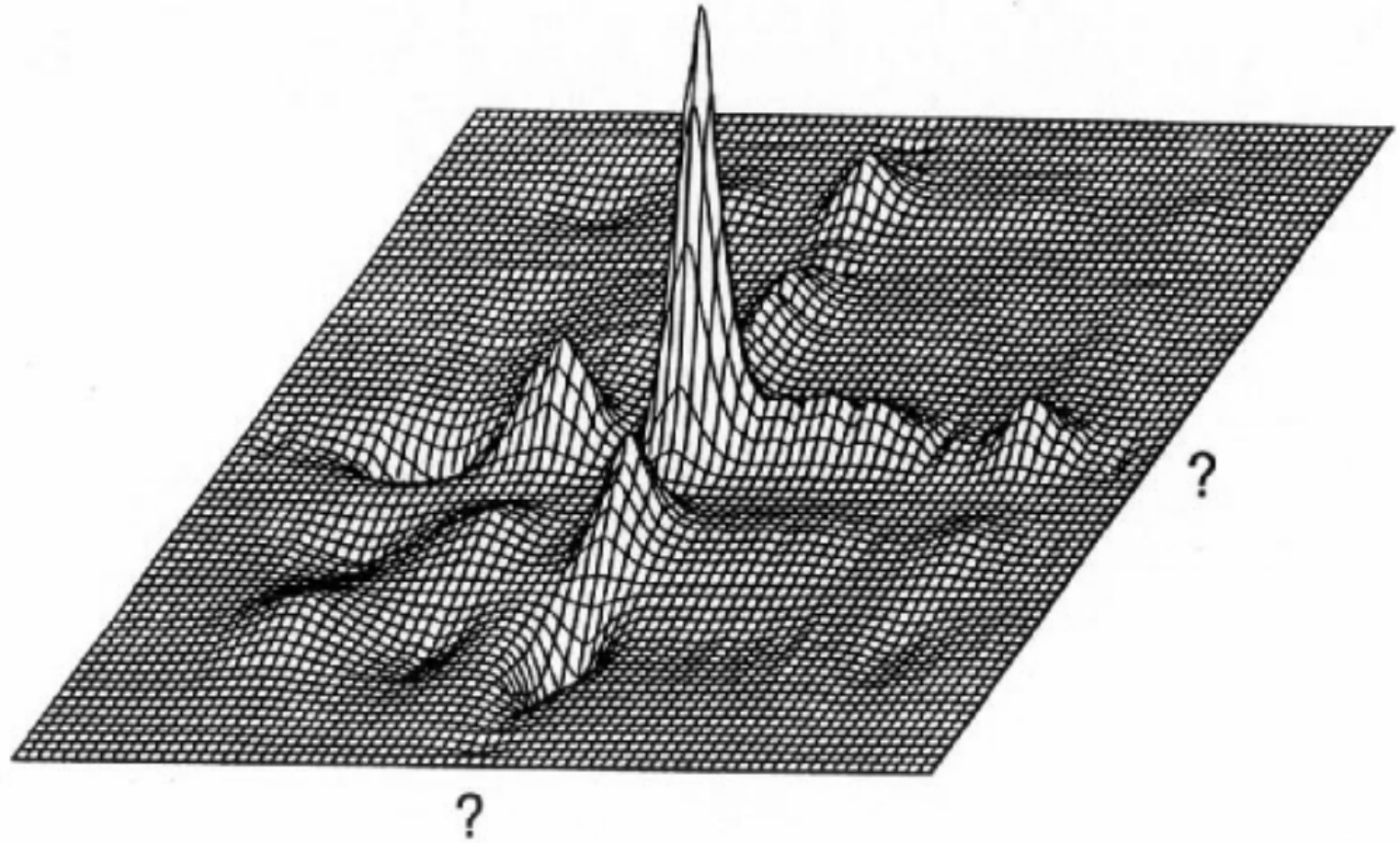
Two-Dimensional Correlation Spectroscopy

<IR, IR>
 <Raman, Raman>
 (SAXS, SAXS)
 <UV, UV>
 <NIR, NIR>
etc.

or

<IR, Raman>
 <SAXS, IR>
 <ESR, Acoustic>
 <Microwave, SANS>
 <UV, NMR>
etc.





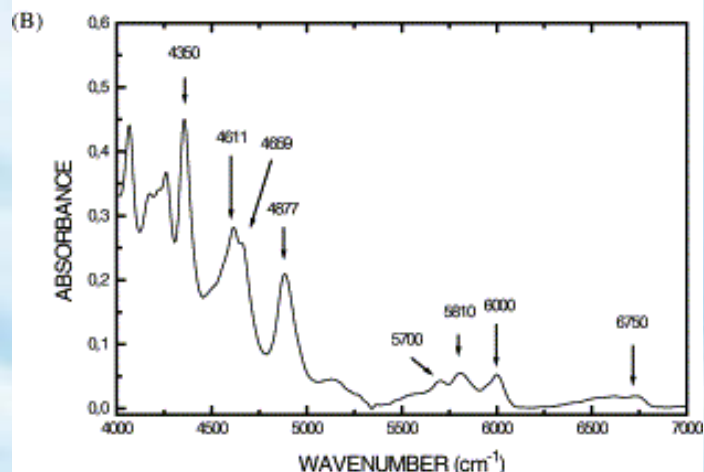
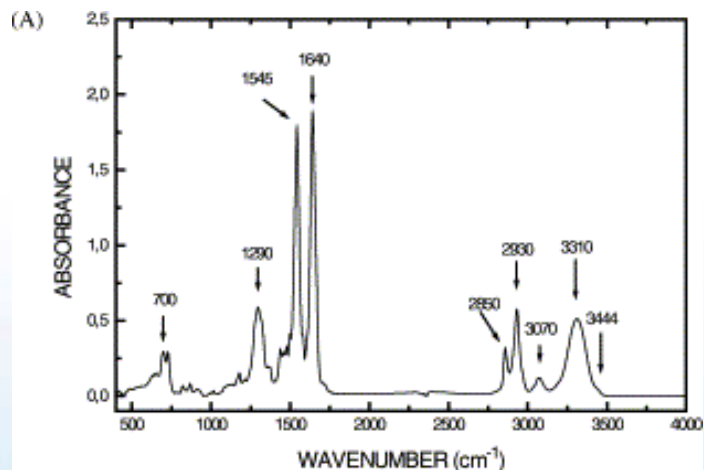


无定形聚酰胺的二维近红外相关光谱研究

摘要

利用二维近红外相关光谱研究了25–200 °C的无定形聚酰胺。检测到**5种不同的CH结构**，其中两种对温度相应较灵敏，检测到**自由的和氢键结合的NH**，其中**自由的NH**又分为两种。

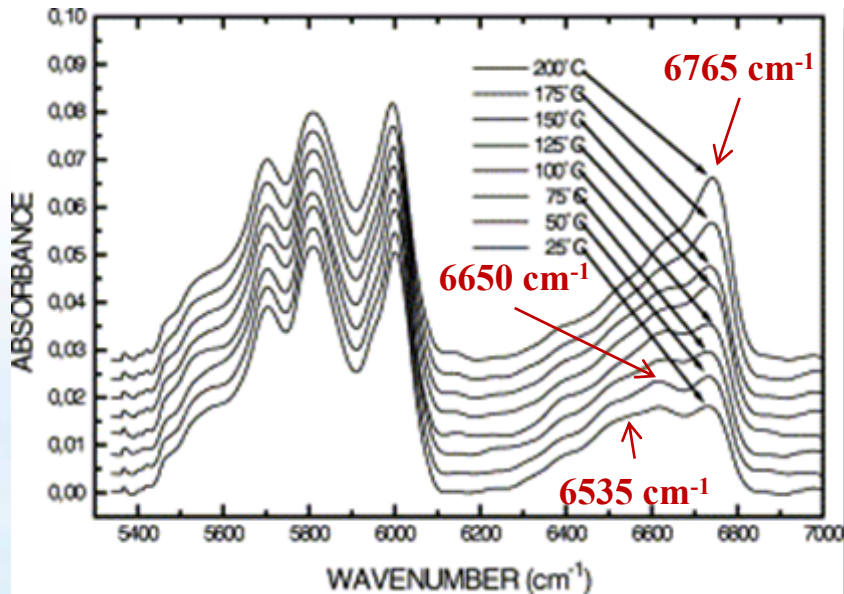
中红外近红外吸收峰归属表



Wavenumber (cm ⁻¹)	Intensity	Tentative assignment
3444	w	$\nu(\text{NH})_f$
3310	s	$\nu(\text{NH})_b$
3080	w	$\nu_{ar}(\text{CH})/2^*$ Amide II
2930	s	$\nu_{as}(\text{CH}_2)$
2850	s	$\nu_{as}(\text{CH}_2)$
1640	s	Amide I
1545	s	Amide II
1290	m	Amide III
700	m	Amide V
6765	w	$2^* \nu(\text{NH})_f$
6520	m	$2^* \nu(\text{NH})_b$
6010	m	$2^* \nu_{ar}(\text{CH})$
5980	m	$2^* \nu_{ar}(\text{CH})$
5900	m	$2^* \nu_{ar}(\text{CH})$
5810	m	$2^* \nu_{as}(\text{CH}_2)$
5690	m	$2^* \nu_s(\text{CH}_2)$
4877	m	$\nu(\text{NH})_b + \text{Amide II}$
4659	m	3^*Amide II
4611	m	$\nu(\text{NH})_b + \text{Amide III}$
4350	s	$\nu_s(\text{CH}_2) + \nu_{as}(\text{CH}_2)$

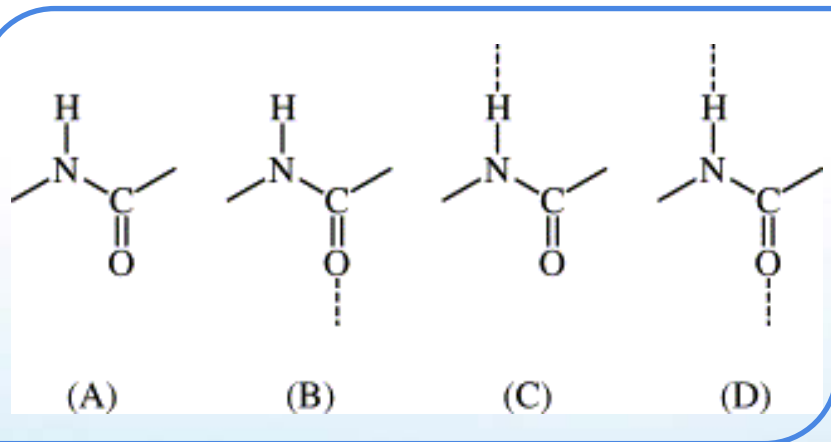
近红外变温实验结果

聚酰胺中不同氢键结构



Temperature-dependent FTNIR spectra obtained from 25 to 200 °C of the investigated amorphous polyamide in the spectral range 5400–7000 cm^{-1} .

Bruker IFS 88, 256scan, 4 cm^{-1} , 5°C step



特征峰随温度上升的变化规律

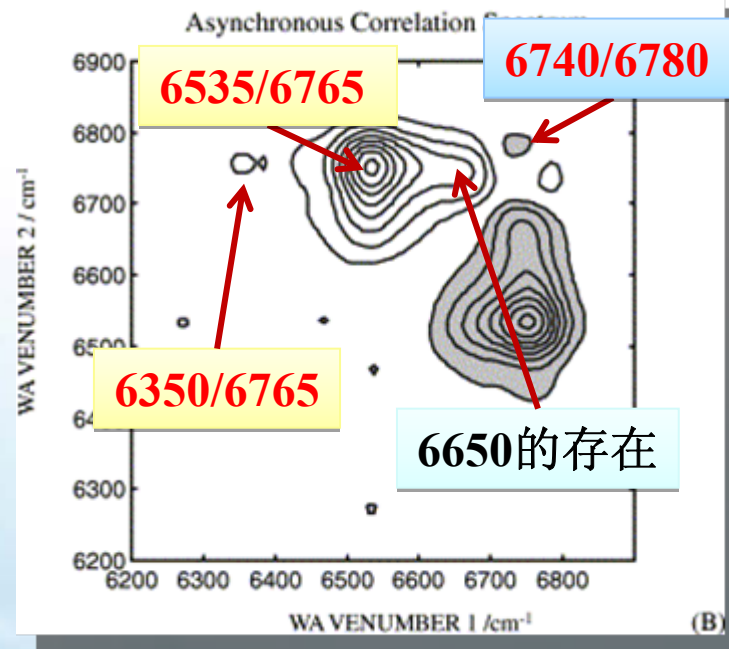
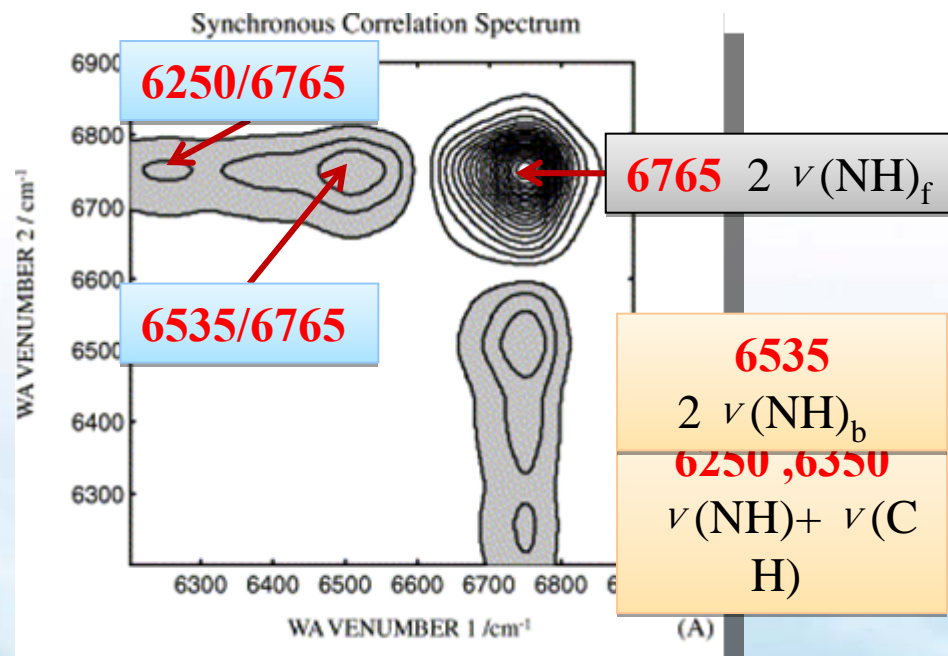
波数(cm^{-1})	峰位置	峰强度
6765	不变	快速增加
6650	不变	小幅增加
6535	蓝移	减弱

二维相关谱图 (6200–6900 cm^{-1})

正峰

负峰

自相关



同步谱图负交叉峰说明吸收峰变化的方向相反，正峰则表示相同

6765 可能来源于6740与6780两个峰

结论

6535 变化先于6765

6780 变化先于6740

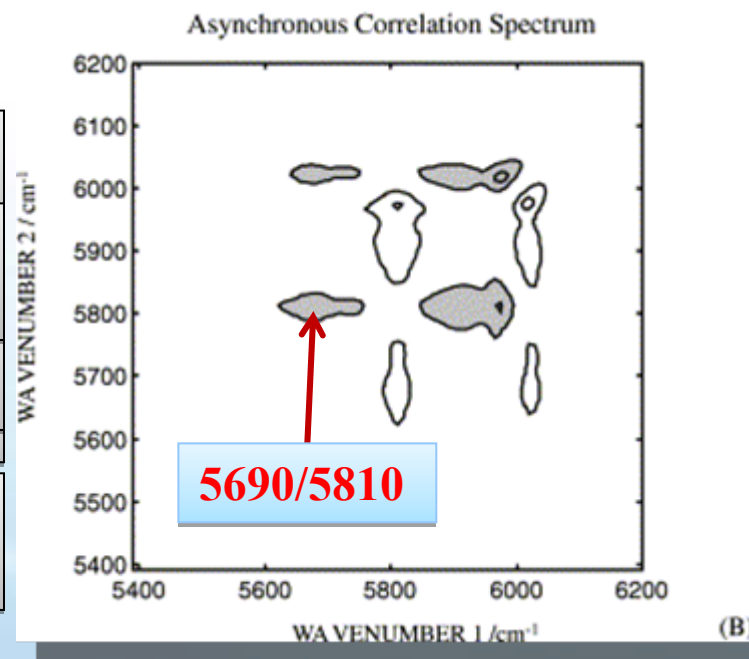
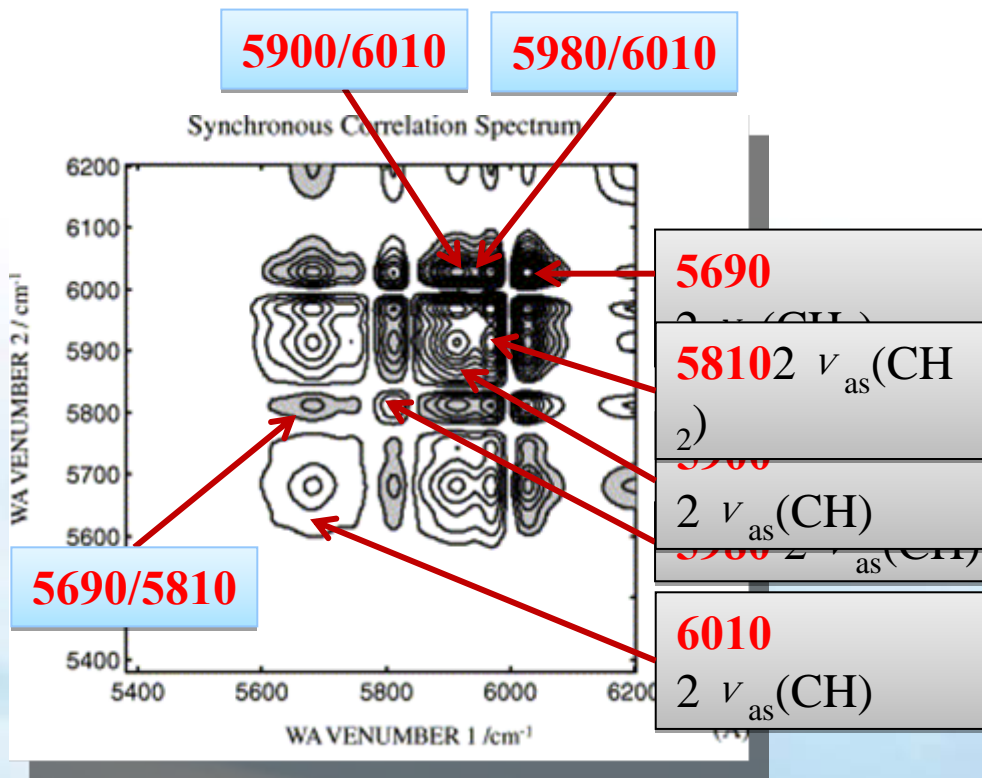
6350 变化先于6765

二维相关谱图 (5400–6200 cm^{-1})

正峰

负峰

自相关



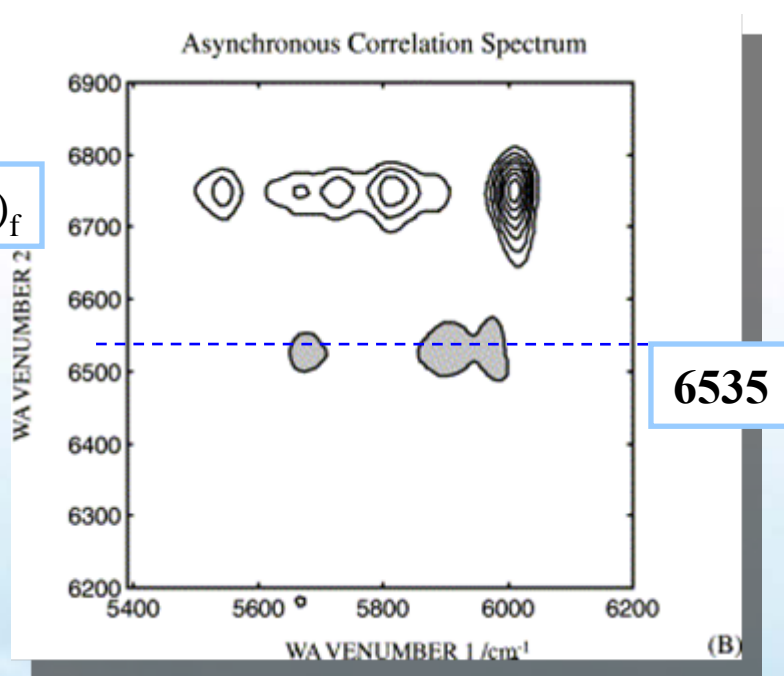
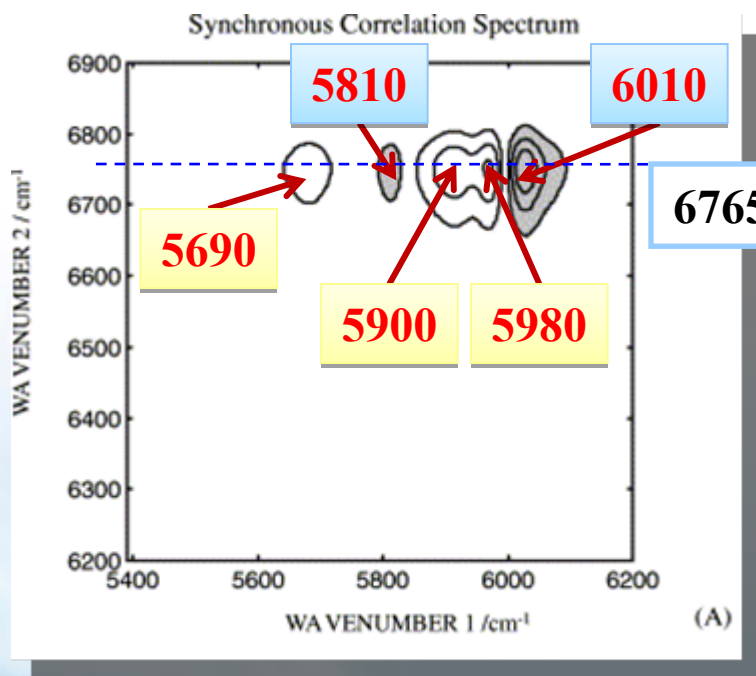
同步谱图存在五个自相关峰

结论

5810 变化先于5690

6010 变化先于5900, 5980

二维相关谱图(5400–6200 vs 6200–6900 cm^{-1})



CH与NH振动区域的关联

结论

5690, 5990, 5980变化先于6765

6535变化先于5690, 5990, 5980

5810与6010对温度变化敏感



聚丙烯膜中水扩散的二维ATR-FTIR光谱研究

摘要

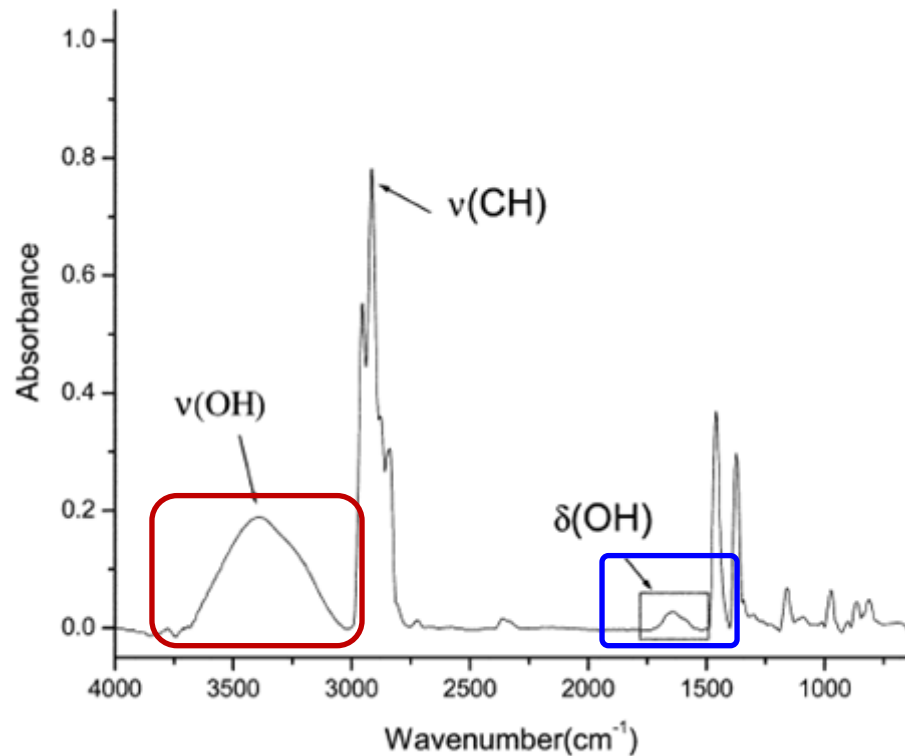
利用二维ATR-FTIR光谱研究水在聚丙烯膜中的扩散动力学。通过研究1800-1500 cm^{-1} 区域，分析得到三种不同结构水分子：强氢键结合水(1676)，中强氢键结合水(1645)及自由水(1592)

课题研究背景

水的伸缩振动区域 (3000-4000 cm^{-1}) 重叠峰较多，分析困难

水的弯曲振动区域 (1500-1700 cm^{-1}) 重叠峰较少，强度偏低

通过二维相关分析手段提高谱图分辨率分析水的弯曲振动区域



ATR-FTIR spectrum of sorbed water in S-PP in the range 4000-650 cm^{-1} .

变温实验条件及数据

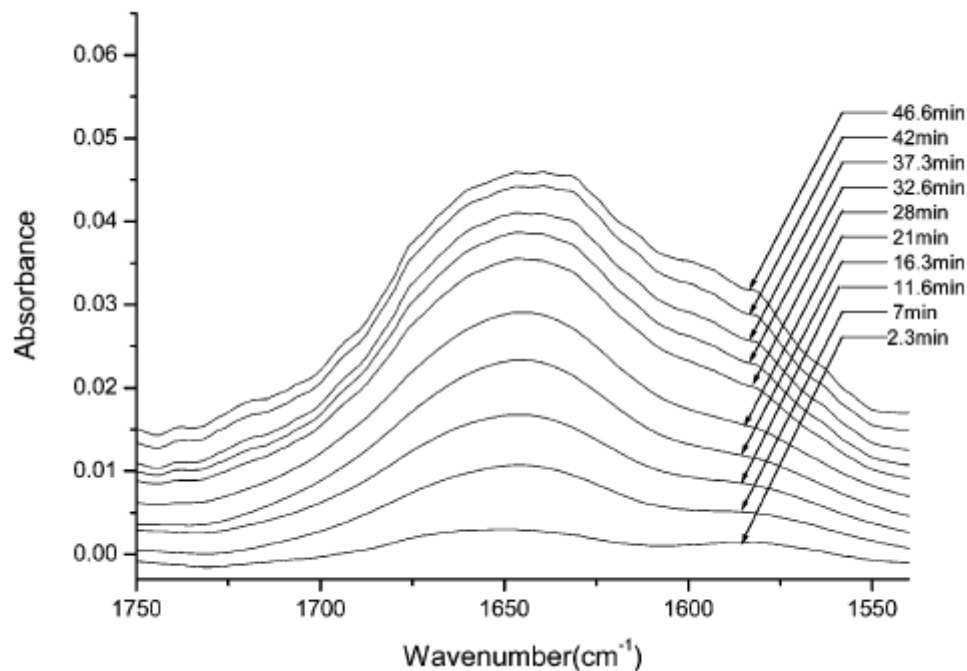
制样方法

将聚丙烯溶于二甲苯后浇膜，在室温下于真空烘箱中存放24 h

仪器及实验

Nexus470及ATR压板附件，16scan， 4cm^{-1}

将吸水滤纸附于膜表面，每2.5min采集数据

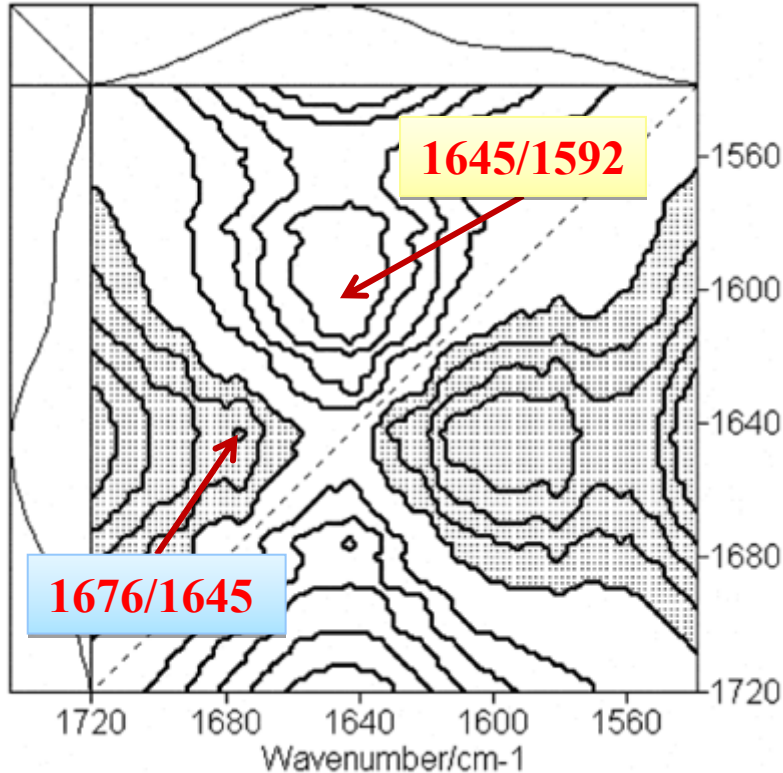


ATR-FTIR spectra of O-H bending band in the range $1750\text{-}1540\text{ cm}^{-1}$.

二维相关谱图 (1500–1800 cm^{-1})

正峰

负峰



不同结构水

峰位置

Type I water

1676

强氢键结合水

Type II water

1645

中强氢键结合水

Type III water

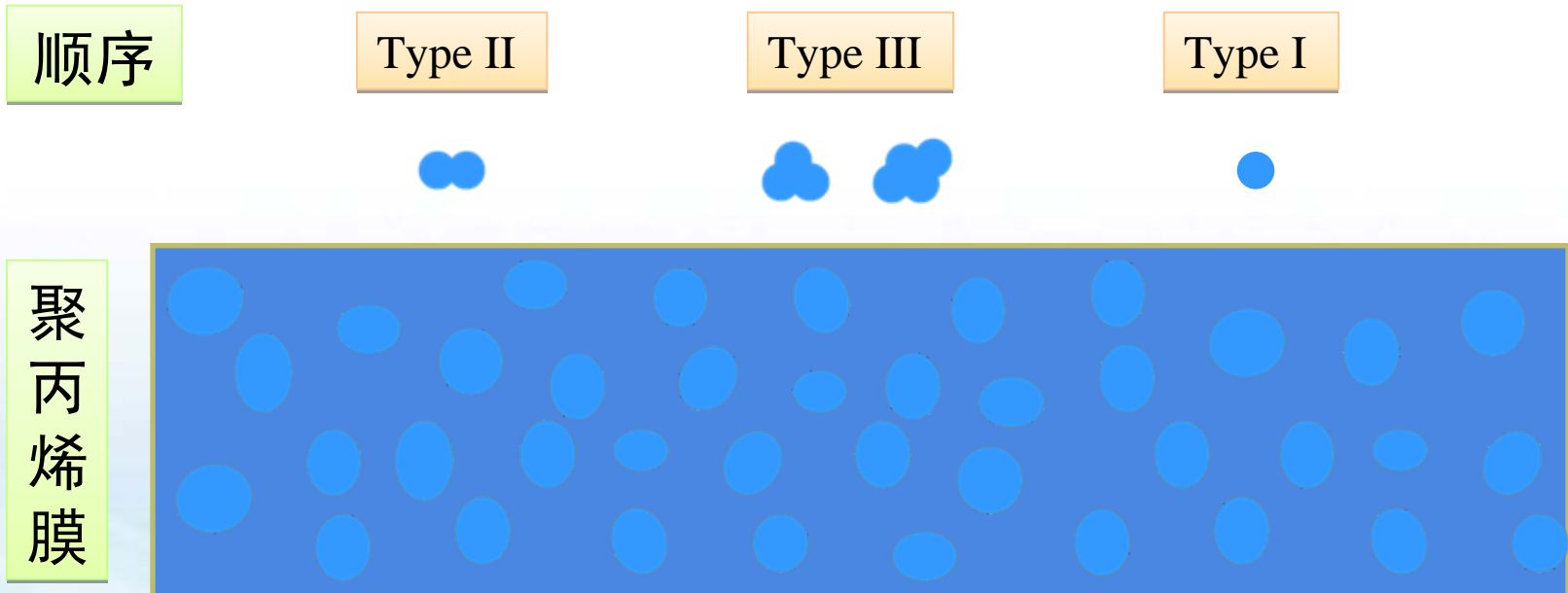
1592

极弱氢键结合水 (自由水)

Asynchronous 2D correlation spectra of water bending band in the range 1720-1540 cm^{-1} .

先后顺序: 1645 → 1676 → 1592

相关机理解释



一般纯水中以Type II型水分子居多， Type III型水分子体积较大，因此移动速度比Type II型水分子慢， PP膜中孔道被水填满后， Type I型水分子结构出现



尼龙6中脱水过程的二维近红外相关光谱研究

摘要

利用二维近红外相关光谱研究了不同温度下（50和80 °C）时尼龙6的脱水行为。实验表面在不同温度下，尼龙6存在不同脱水机理。



实验条件及仪器设备

样品制备及处理条件

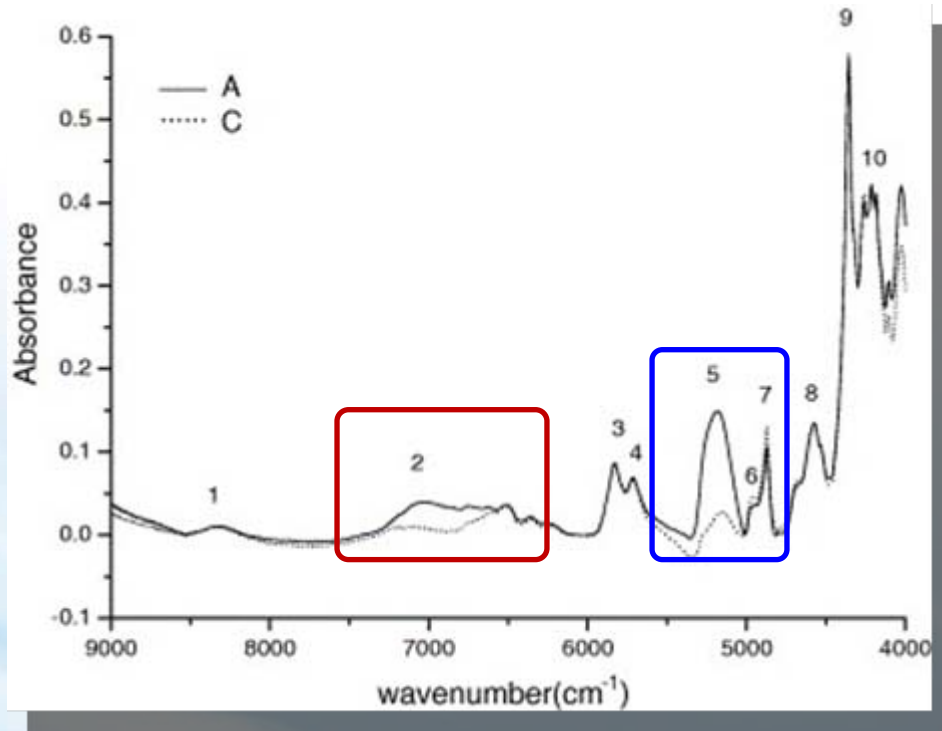
Sample	Preparation	Treatment
A	Immersed in a water bath over 12 h	Heated at 80 °C for about 1.5 h
B	Immersed in a water bath over 16 h	Heated at 50 °C for about 2 h
C	Kept in a desiccator	Heated at 80 °C for about 1.5 h
D	Kept in a desiccator	Heated at 50 °C for about 2.5 h

仪器及实验条件

Nexus 470 FT-IR/NIR, 液氮冷却MCT检测器, 分辨率 4cm^{-1}

分别在50和80 °C恒温扫描100min, 扫描范围 $3000\text{-}11000\text{cm}^{-1}$

尼龙6近红外光谱归属

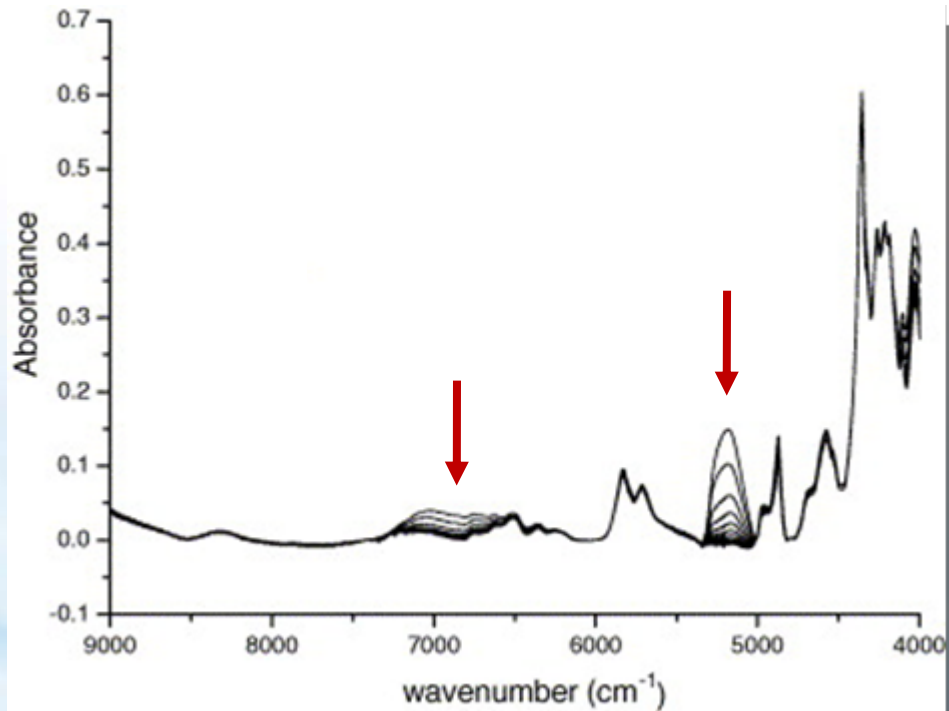


Near-infrared spectra recorded from the original films of sample A (—) and sample C (...) at room temperature.

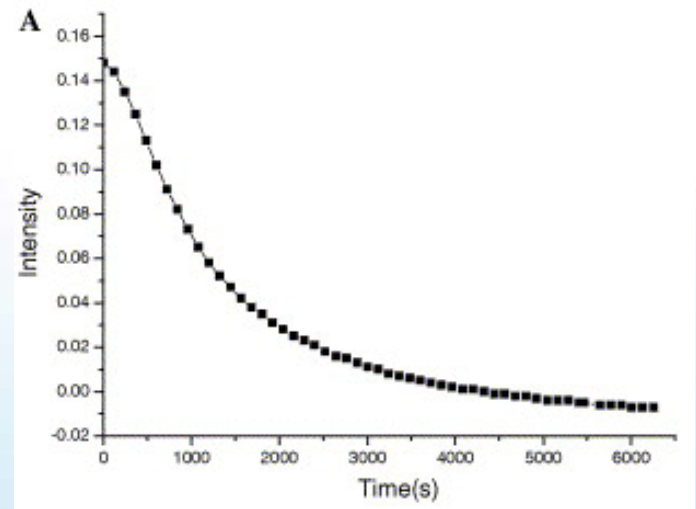
尼龙6近红外光谱归属表

1	8310	$3^*v(\text{CH}_2)$
	7220	$2^*v_{as}(\text{CH}_2) + \delta(\text{CH}_2)$
2	7020	$v_1(\text{OH}) + v_3(\text{OH})$
	6750	$v_1(\text{OH}) + v_3(\text{OH})$ and $2^*v(\text{NH})_f$
	6500	$2^*v(\text{NH})_b$
3	5860	$2^*v_{as}(\text{CH}_2)$
4	5740	$2^*v_s(\text{CH}_2)$
5	5280	$v_2(\text{OH}) + v_3(\text{OH}) (s_0)$
	5230	$v_2(\text{OH}) + v_3(\text{OH}) (s_1)$
	5140	$v_2(\text{OH}) + v_3(\text{OH}) (s_2)$
6	4990	$v(\text{NH})_b + \text{amide I}$
7	4880	$v(\text{NH})_b + \text{amide II}$
	4718	Amide I + 2^*amide II
8	4628	$v(\text{NH})_b + \text{amide III}$
9	4374	$v_s(\text{CH}_2) + \delta(\text{CH}_2)$
10	4283	$v_s(\text{CH}_2) + \delta(\text{CH}_2)$
	4230	$v_s(\text{CH}_2) + \gamma_w(\text{CH}_2)$
	4193	$v_s(\text{CH}_2) + \gamma(\text{CH}_2)$

80°C时尼龙膜脱水谱图



Near-infrared spectra of sample A in the range 9000 – 4000 cm^{-1} recorded every 10 min during isothermal treatment at 80 ° C.



5200 cm^{-1} 峰强随时间变化图

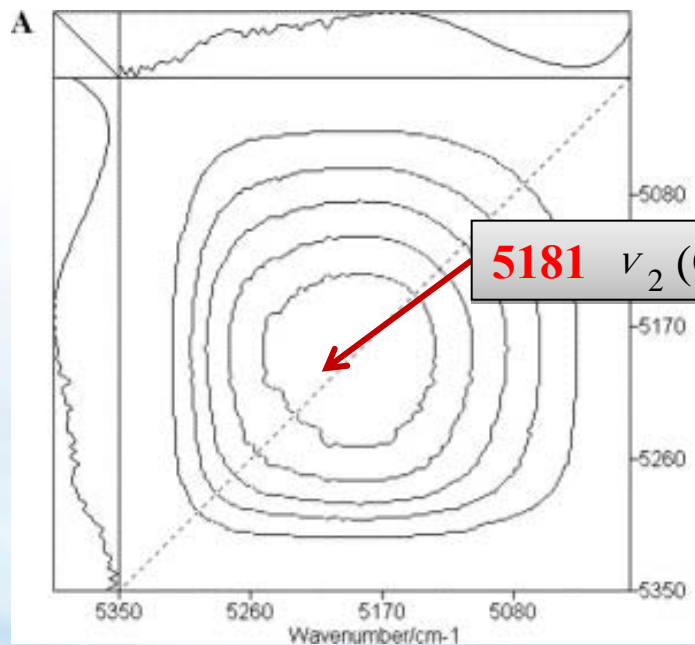
脱水过程呈现非线性变化

样品A二维相关谱图 (5000–5350 cm^{-1})

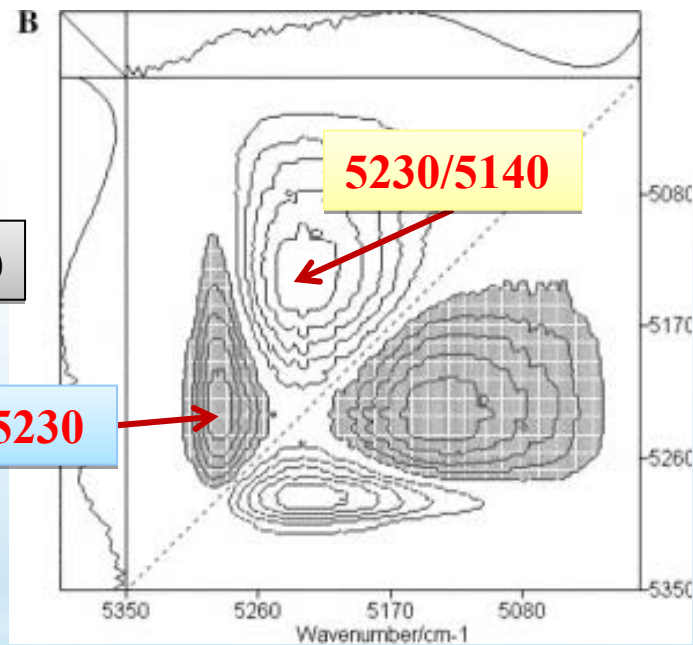
正峰

负峰

自相关



80 °C



5181 cm^{-1}
峰可能有
三个来源

5280: 自由水分子(s_0)

5230: 一端氢键水分子(s_1)

5140: 两端氢键水分子(s_2)

结
论

5230 变化先于5280

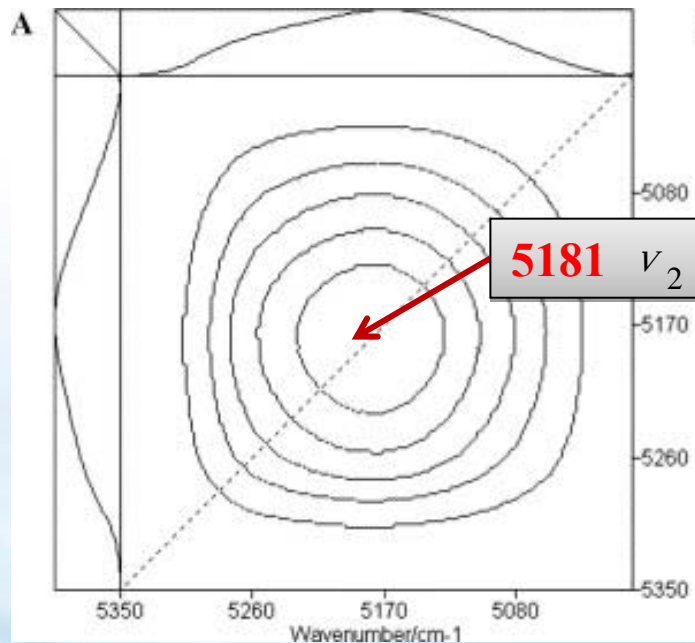
5230 变化先于5140

样品B二维相关谱图 (5000–5350 cm^{-1})

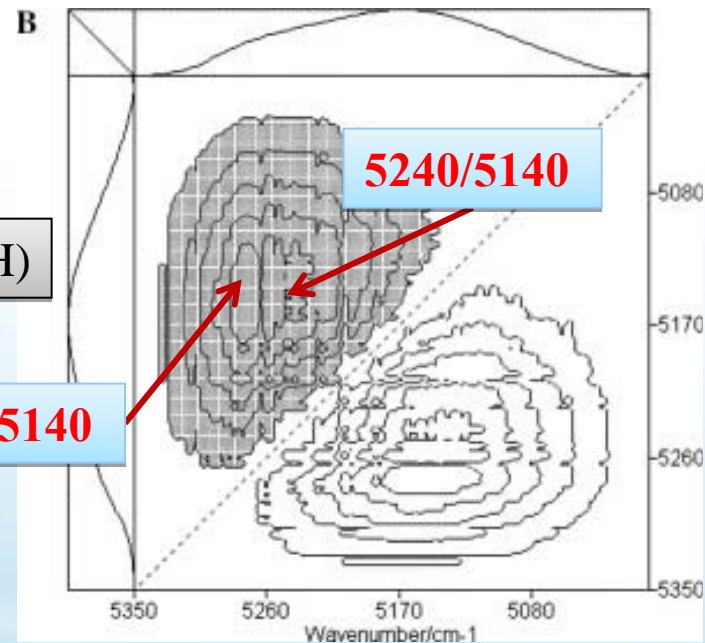
正峰

负峰

自相关



50°C



两端氢键
水分子(s_2)

变化
先于

自由水分子(s_0)

一端氢键水分子(s_1)

结
论

5140 变化先于5280

5140 变化先于5240

实验结果机理解释

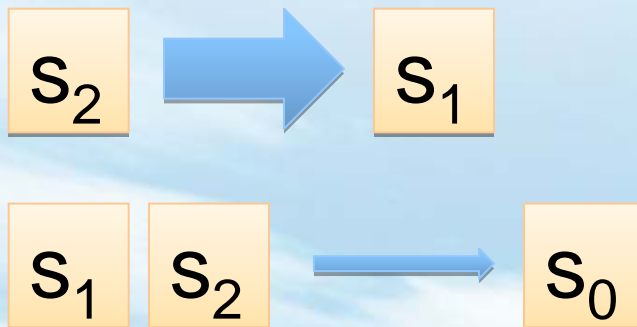
5280: 自由水分子(s_0)

5230: 一端氢键水分子(s_1)

5140: 两端氢键水分子(s_2)

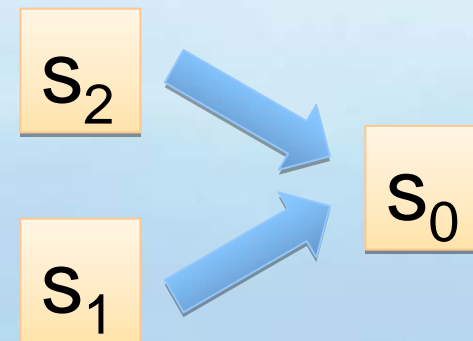
50°C

温度较低，能量较小



80°C

温度较高，能量较大



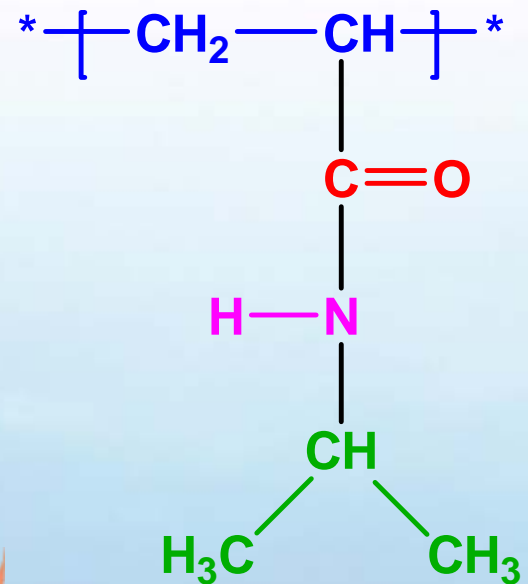


*FTIR and 2D-IR Spectroscopic Study
on Poly N-isopropylacrylamide (**PNIPAM**)*

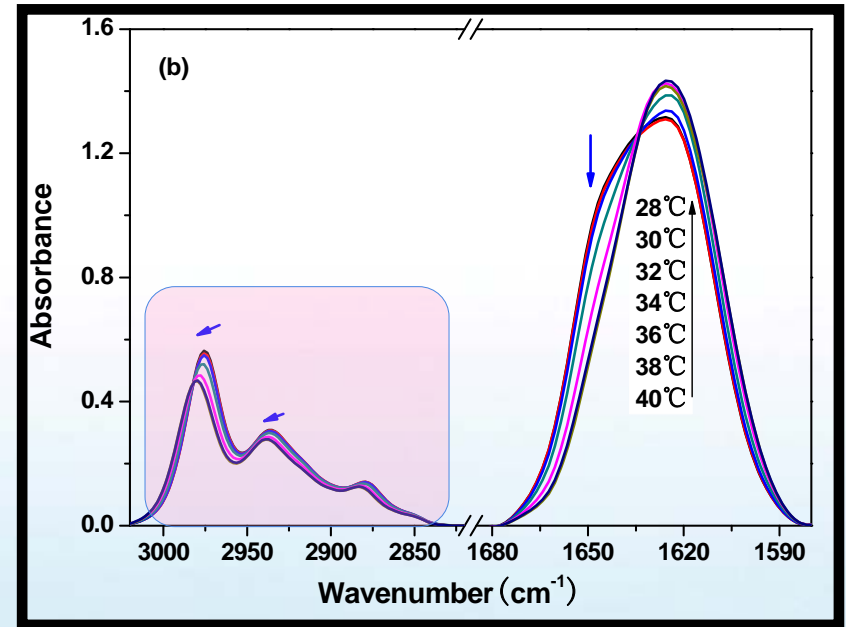
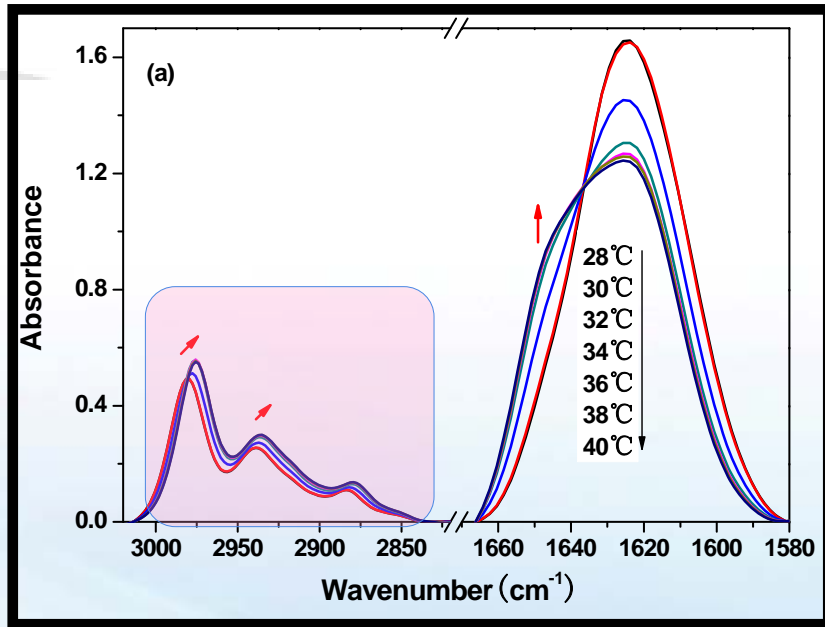


❏ Poly N-isopropylacrylamide (PNIPAM)

Chemical Structure

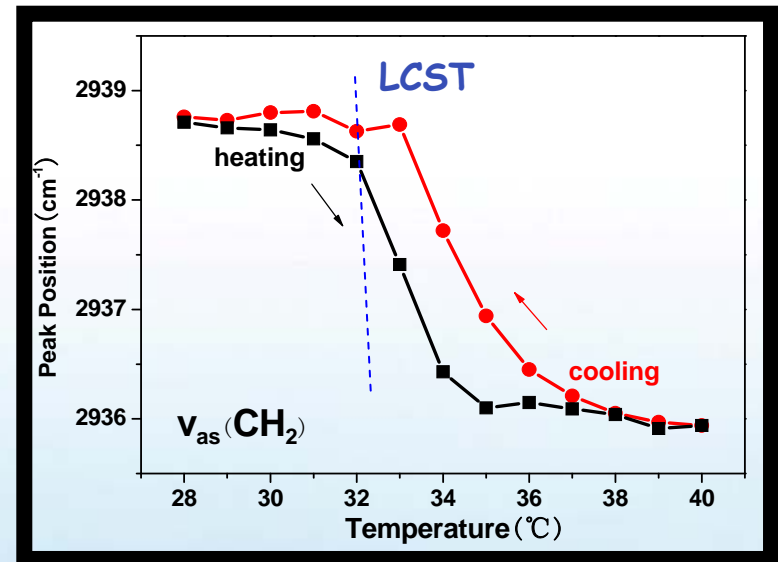
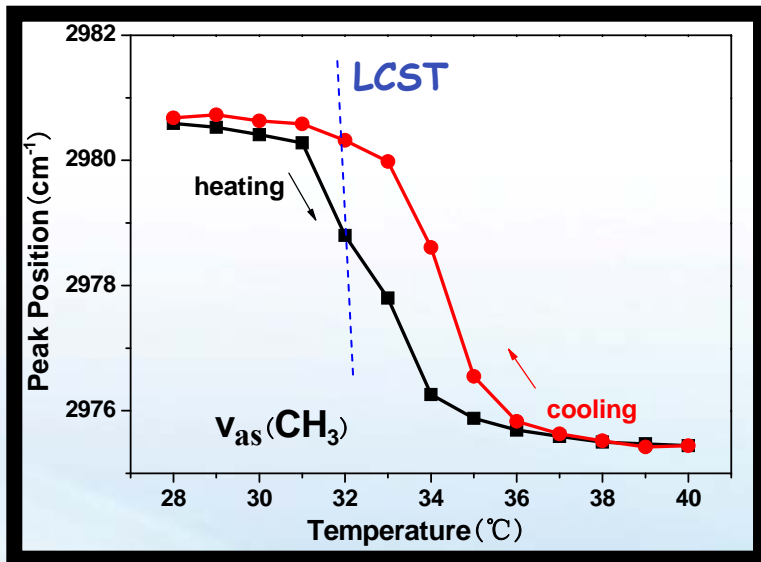


LCST ~ 32°C



FTIR spectra of PNIPAM 20wt% D₂O solution (28 ≐ 40 °C)

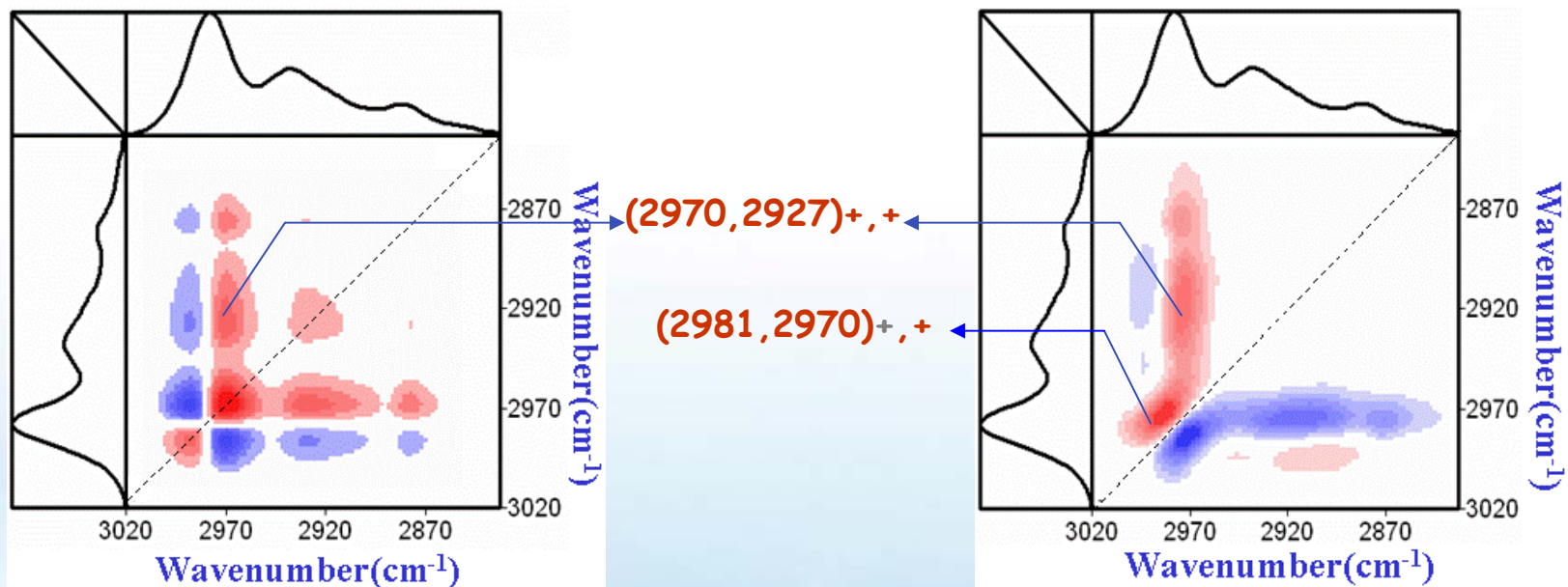
Quantitative Analysis



1

Reversible dehydration/hydration process of C-H group

Investigation of CH Bands - 2DIR



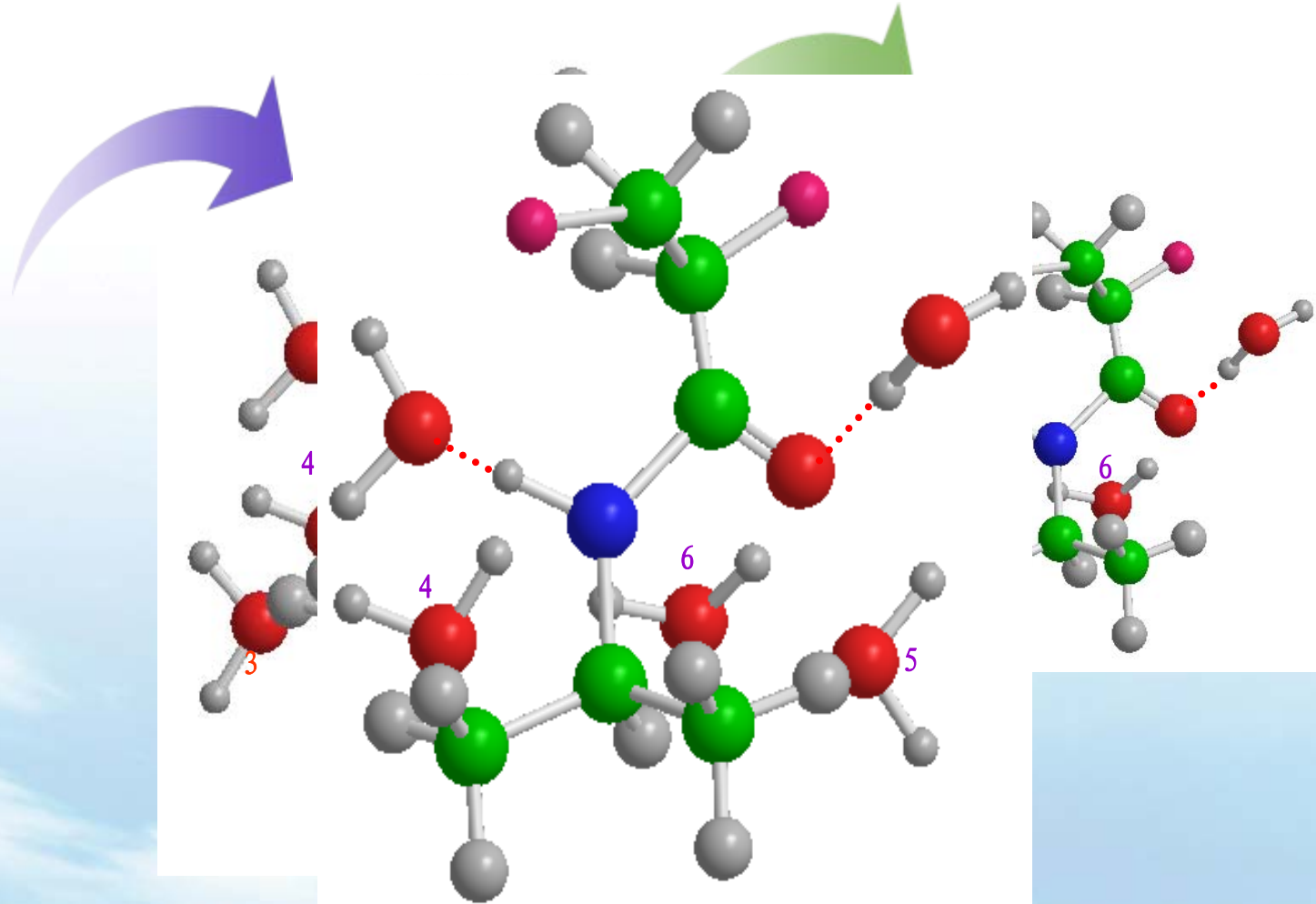
2

Two-step dehydration/hydration process of CH_3

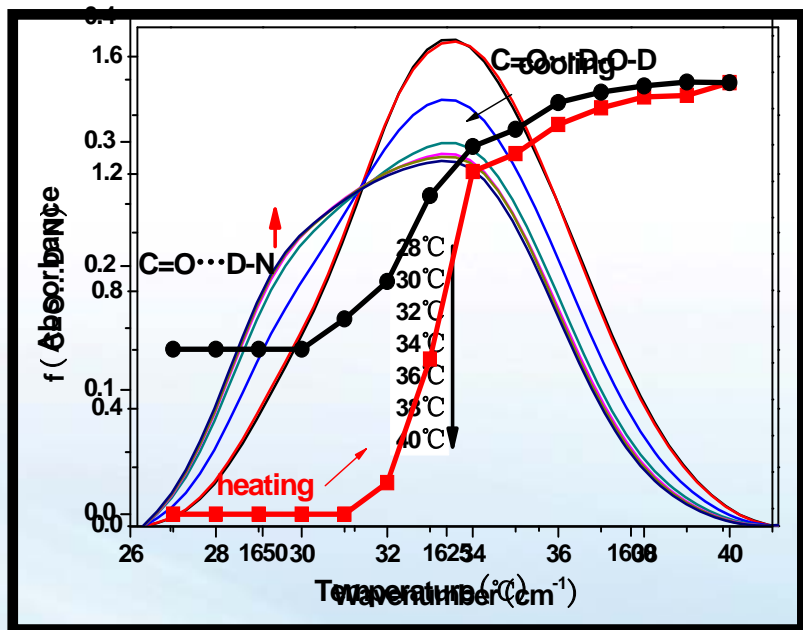
3

Dehydration of side-chain
> main-chain aggregation

Two-step dehydration mechanism of CH_3



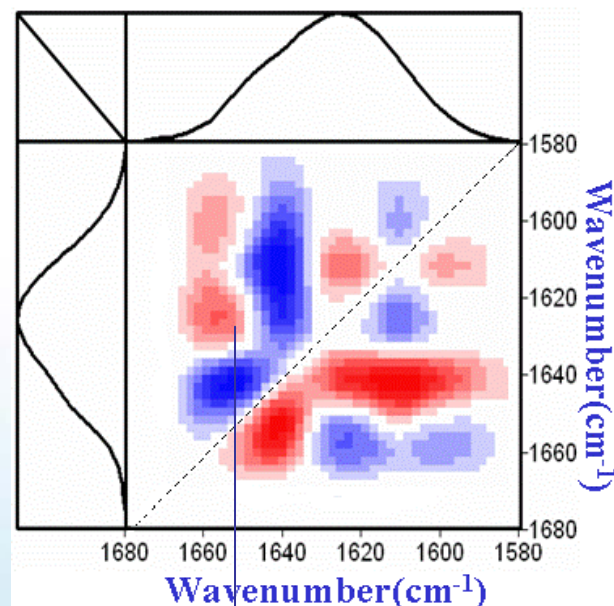
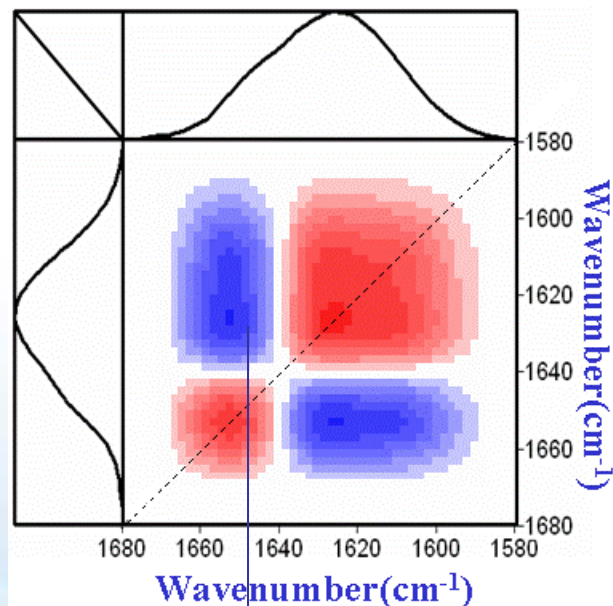
Investigation of Amide I band-FTIR



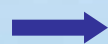
Wavenumber(cm^{-1})	Assignment
1649	$\nu(\text{C}=\text{O}\cdots\text{D}-\text{N})$
1624	$\nu(\text{C}=\text{O}\cdots\text{D}-\text{O}-\text{D})$

$$f(\text{C}=\text{O}\cdots\text{D}-\text{N}) = \frac{A_{1649}}{[A_{1649} + A_{1625} * (\epsilon_{1649} / \epsilon_{1625})]}$$

Investigation of Amide I band -2DIR



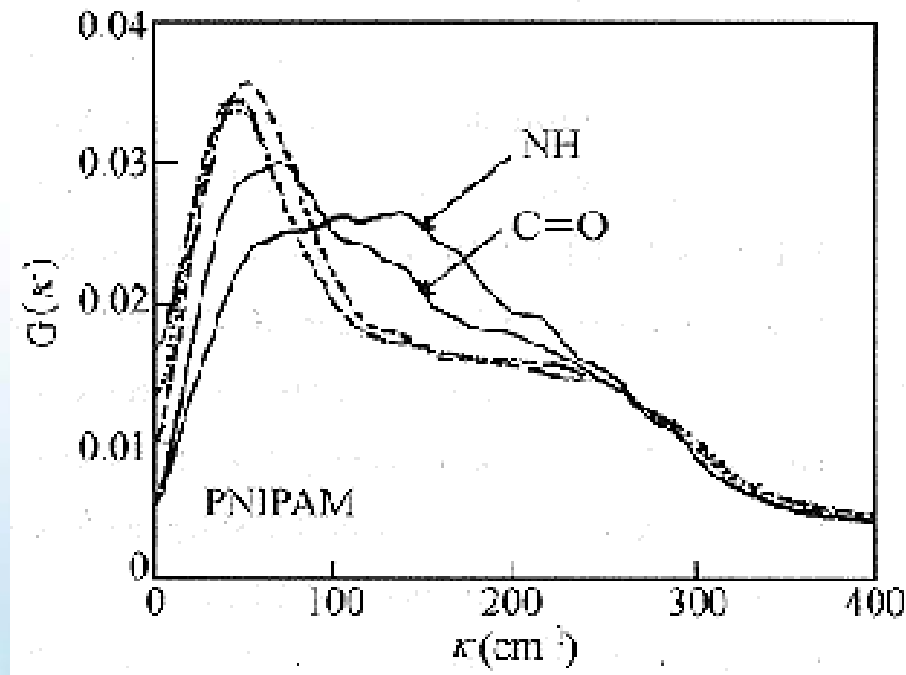
(1649, 1624)-, +



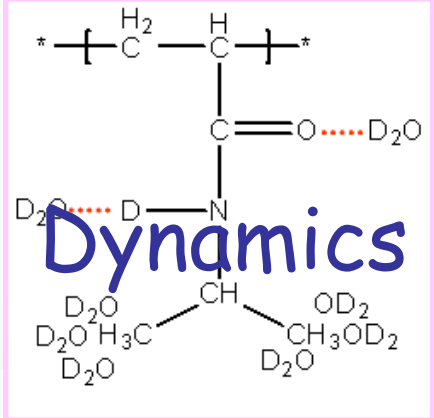
1624 > 1649

C=O...D-O-D > C=O...D-N

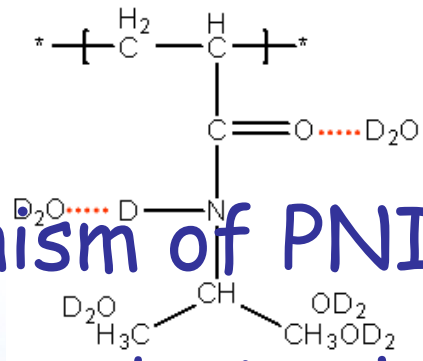
Dehydration and Hydration of N-D : Spectral Density Method



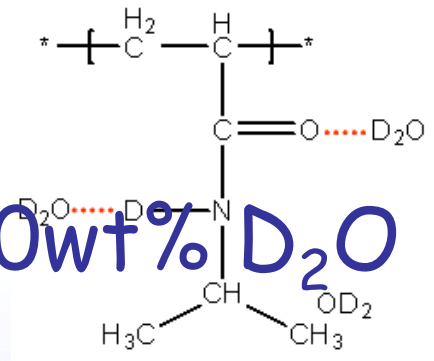
The formation and destruction of $\text{N-H}\cdots\text{O-H} > \text{C=O}\cdots\text{H-O-H}$



Dehydration
of CH₃(I)



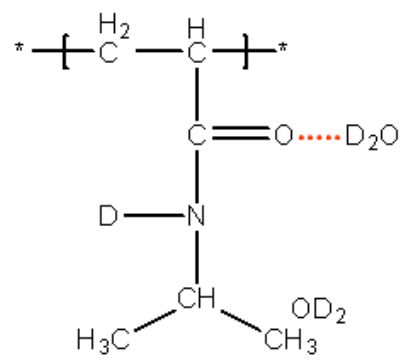
Dehydration
of CH₃(II)



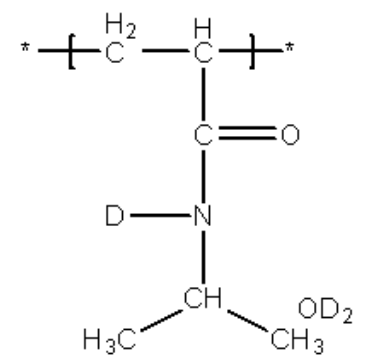
Dynamics mechanism of PNIPAM 20wt% D₂O solution during heating

Diffusion and
aggregation of
the main chains

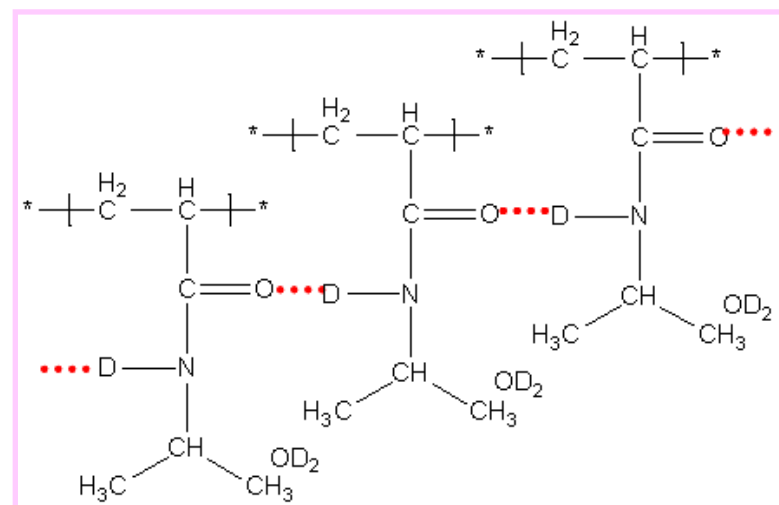
Breakage of
N-D...O-D



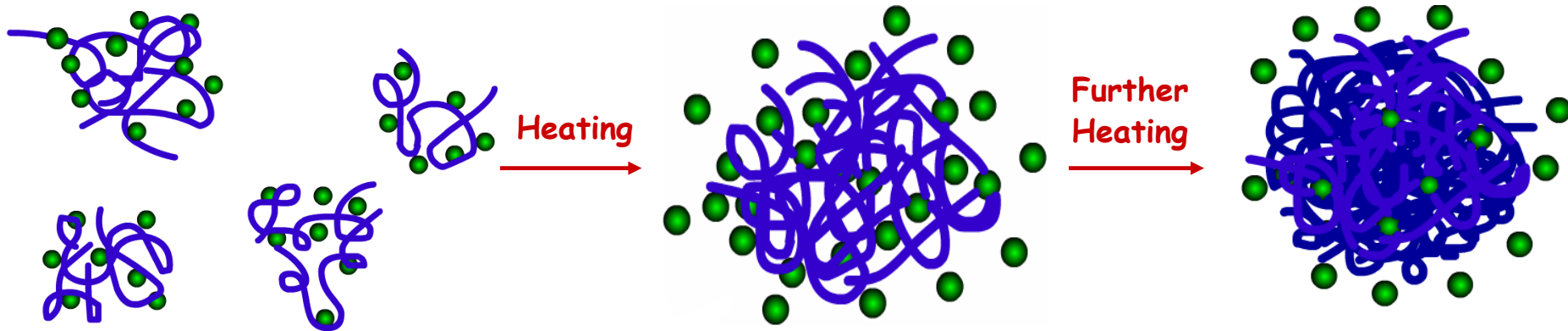
Breakage of
C=O...D-O



Formation of
C=O...D-N



Dynamics of chains in PNIPAM aqueous solution during heating

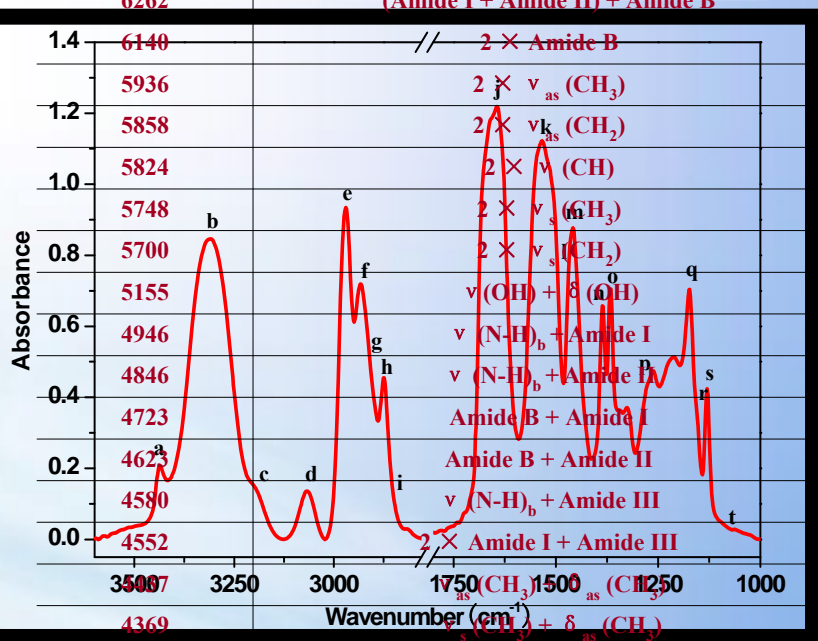


20wt%

Assignments of overtone and combination bands in the NIR spectrum of PNIPAM

6874	$2 \times \nu (\text{N-H})_f$
6600	$2 \times \nu (\text{N-H})_b$
6370	Amide B + $\nu (\text{N-H})_b$
6262	(Amide I + Amide II) + Amide B

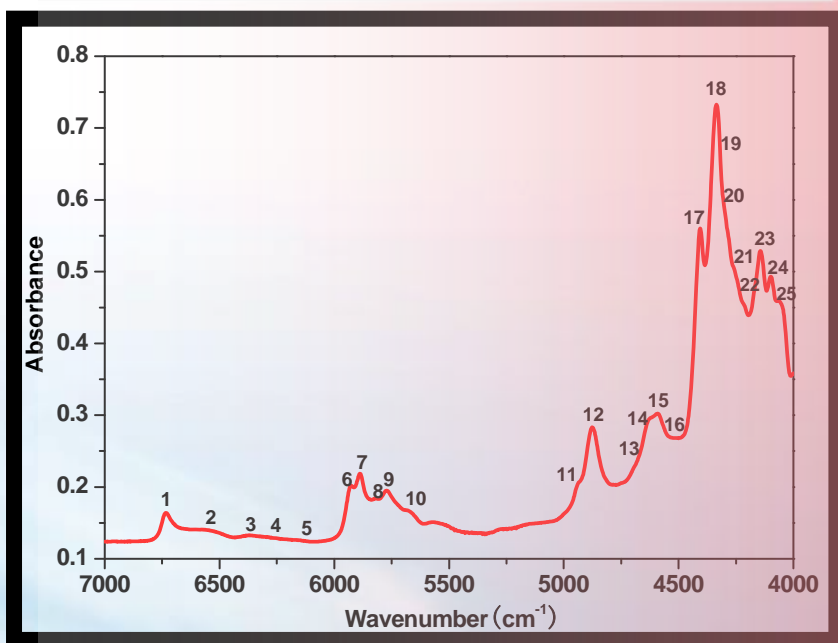
	Wavenumber (cm ⁻¹)	Assignment
a	3437	$\nu (\text{N-H})_f$
b	3300	$\nu (\text{N-H})_b$
c	3190	Amide I + Amide II
d	3070	Amide B
e	2968	$\nu_{as} (\text{CH}_3)$
f	2929	$\nu_{as} (\text{CH}_2)$
g	2912	$\nu (\text{CH})$
h	2874	$\nu_s (\text{CH}_3)$
i	2850	$\nu_s (\text{CH}_2)$
j	1646	Amide I
k	1546	Amide II
l	1469	$\delta_{as} (\text{CH}_3)$
m	1458	$\delta_{as} (\text{CH}_2)$
n	1387	$\delta_s (\text{CH}_3)$
o	1368	$\delta_s (\text{CH}_2)$
p	1280	Amide III
	1260	
q	1173	CH ₃ skeletal
r	1155	CH ₂ skeletal
s	1132	CH ₃ rocking
t	1096	CH ₂ rocking



MIR Spectrum of PNIPAM film (RT)

4369	$\nu_s (\text{CH}_3) + \delta_{as} (\text{CH}_3)$
4352	$\nu_{as} (\text{CH}_3) + \delta_s (\text{CH}_3)$
4308	$\nu_s (\text{CH}_2) + \delta_{as} (\text{CH}_2)$
4260	$\nu_s (\text{CH}_3) + \delta_s (\text{CH}_3)$
4218	$\nu_s (\text{CH}_2) + \delta_s (\text{CH}_2)$
4141	$\nu_{as} (\text{CH}_3) + \text{CH}_3$ skeletal
4098	$\nu_{as} (\text{CH}_3) + \text{CH}_3$ rocking
4064	$\nu_{as} (\text{CH}_3) + \text{CH}_2$ rocking

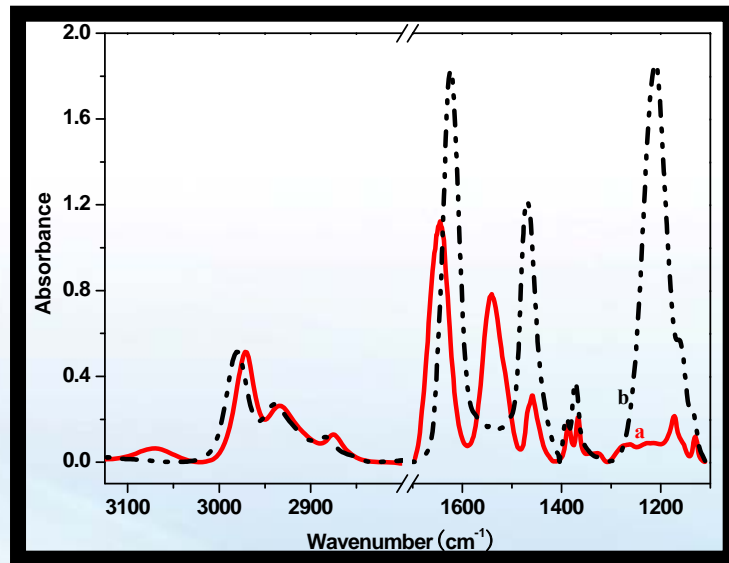
Assignments of overtone and combination bands in the NIR spectrum of PNIPAM



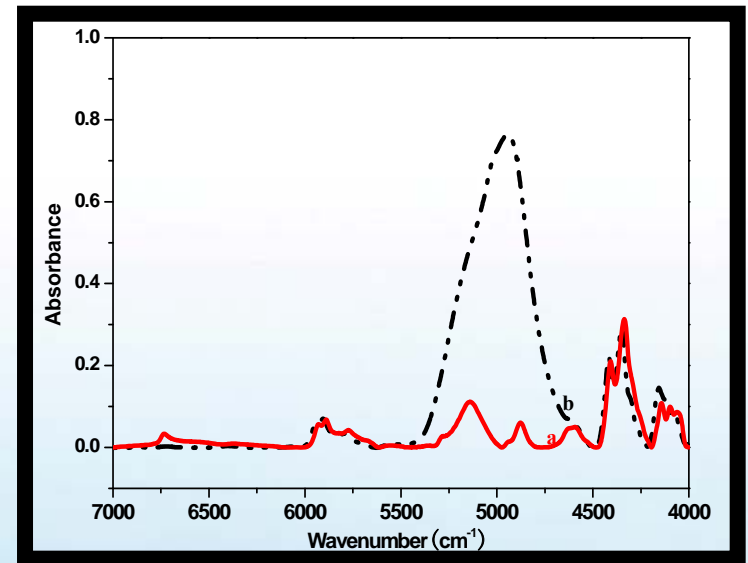
NIR Spectrum of PNIPAM film (RT)

	Wavenumber (cm ⁻¹)	Assignment
1	6736	$2 \times \nu (\text{N-H})_f$
2	6550	$2 \times \nu (\text{N-H})_b$
3	6368	Amide B + $\nu (\text{N-H})_b$
4	6258	(Amide I + Amide II) + Amide B
5	6140	$2 \times$ Amide B
6	5933	$2 \times \nu_{as} (\text{CH}_3)$
7	5889	$2 \times \nu_{as} (\text{CH}_2)$
8	5823	$2 \times \nu (\text{CH})$
9	5773	$2 \times \nu_s (\text{CH}_3)$
10	5675	$2 \times \nu_s (\text{CH}_2)$
11	5135	$\nu (\text{OH}) + \delta (\text{OH})$
12	4945	$\nu (\text{N-H})_b +$ Amide I
13	4878	$\nu (\text{N-H})_b +$ Amide II
14	4701	Amide B + Amide I
15	4623	Amide B + Amide II
16	4580	$\nu (\text{N-H})_b +$ Amide III
17	4529	$2 \times$ Amide I + Amide III
18	4408	$\nu_{as} (\text{CH}_3) + \delta_{as} (\text{CH}_3)$
19	4335	$\nu_s (\text{CH}_3) + \delta_{as} (\text{CH}_3)$
20	4329	$\nu_{as} (\text{CH}_2) + \delta_s (\text{CH}_3)$
21	4298	$\nu_s (\text{CH}_2) + \delta_{as} (\text{CH}_2)$
22	4243	$\nu_s (\text{CH}_3) + \delta_s (\text{CH}_3)$
23	4214	$\nu_s (\text{CH}_2) + \delta_s (\text{CH}_2)$
24	4138	$\nu_{as} (\text{CH}_3) + \text{CH}_3$ skeletal
25	4098	$\nu_{as} (\text{CH}_3) + \text{CH}_3$ rocking
26	4052	$\nu_{as} (\text{CH}_3) + \text{CH}_2$ rocking

Deuteration studies-MIR&NIR



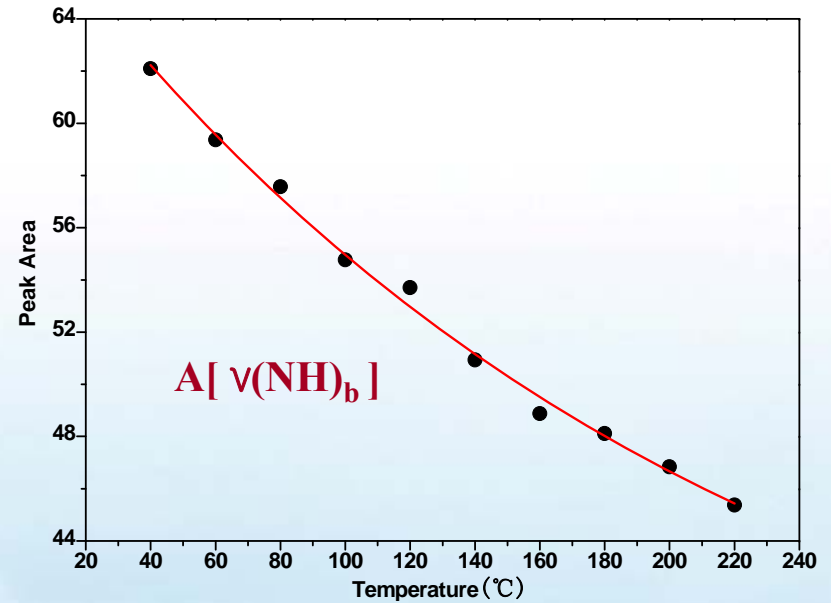
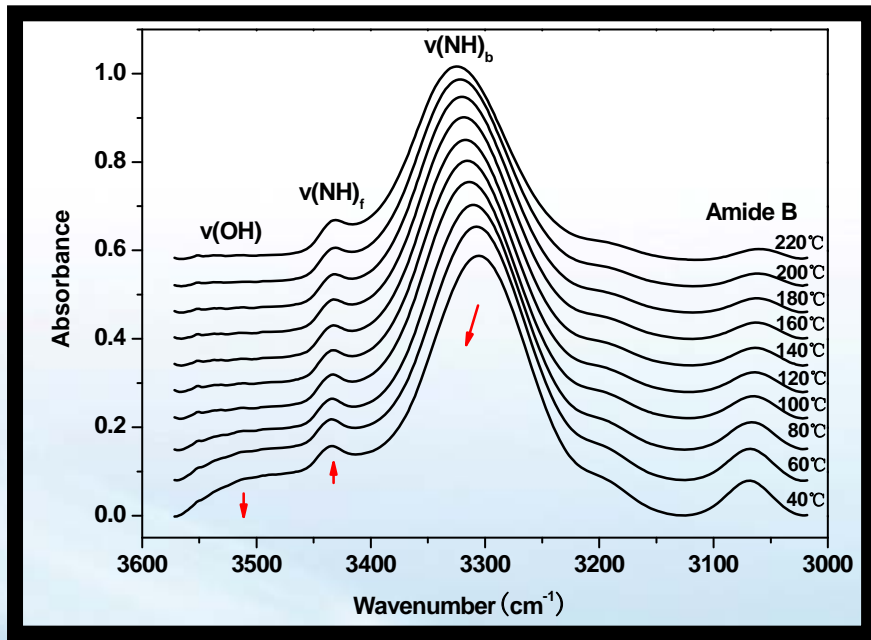
MIR Spectrum



NIR Spectrum

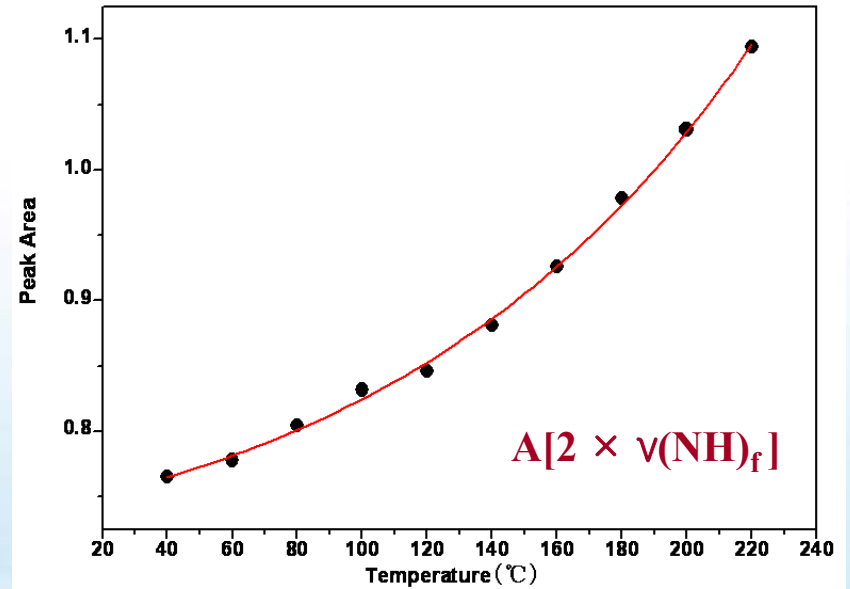
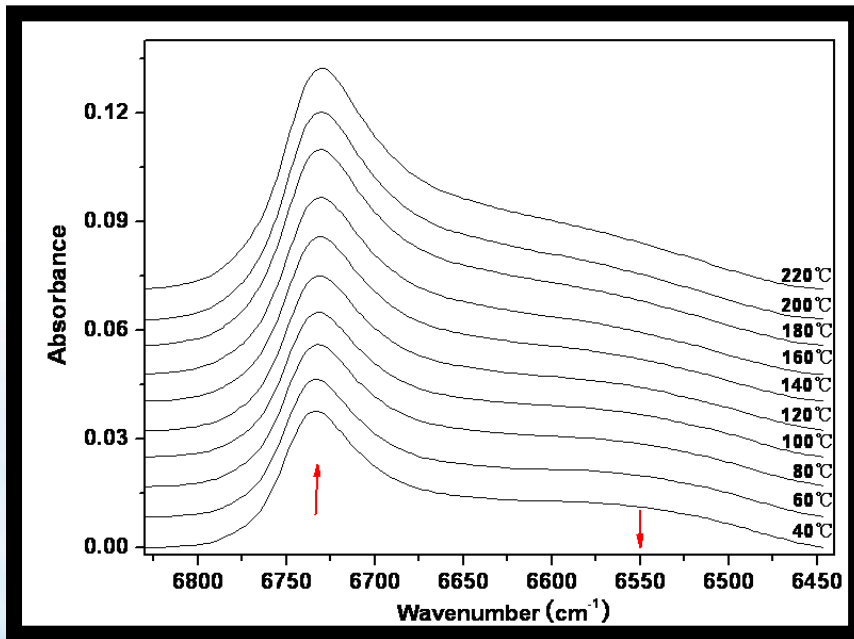
Intensity Change: Peak of Amide groups

Variable Temperature Study -MIR



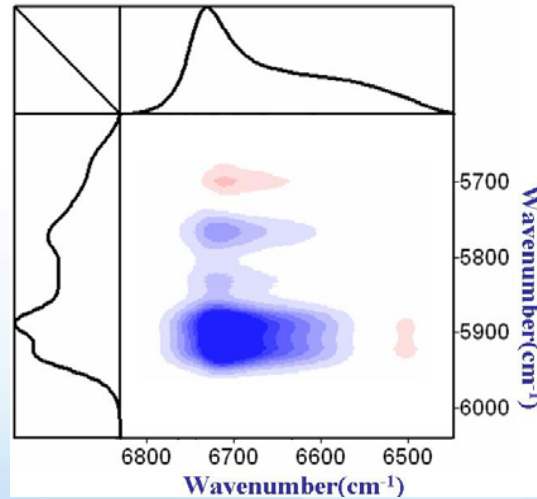
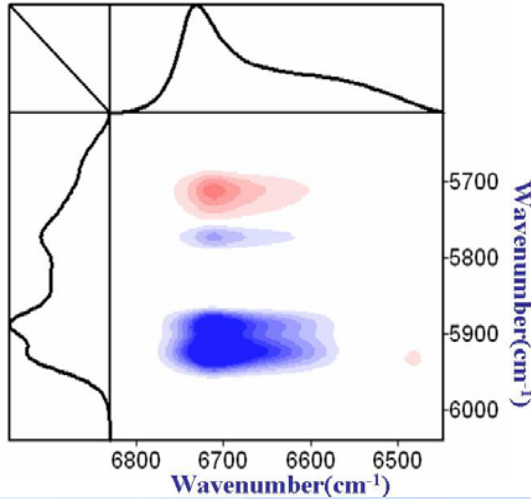
Change of NH bonding

Variable Temperature Study -NIR



Change of free NH groups

2DIR-NH groups vs. CH groups

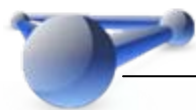


During heating,
modifications of NH >
conformational changes
of hydrocarbon chains



2008年12月7日星期日

*Application of Two-Dimensional Correlation Spectroscopy and
Perturbation Correlation Moving Window*



*Supramolecular Self-Assembly Thermodynamic Mechanism of
A Special Mesogen-Jacketed Liquid Crystalline Polymer*



Generalized Two-Dimensional Correlation Spectroscopy

Reference spectrum (average spectrum):

$$\bar{y}(v) = \frac{1}{N} \sum_{j=1}^N y(v, p_j)$$

Dynamic spectrum:

$$\tilde{y}(v, p) = \begin{cases} y(v, p) - \bar{y}(v) & \text{for } 1 \leq p \leq N \\ 0 & \text{otherwise} \end{cases}$$

Synchronous 2D correlation spectrum:

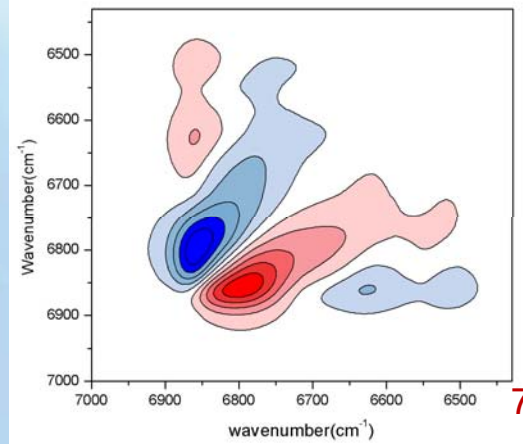
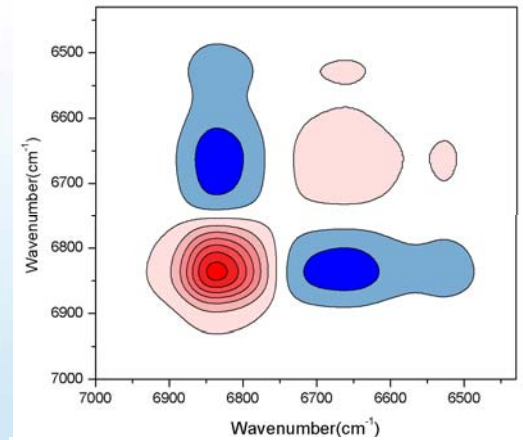
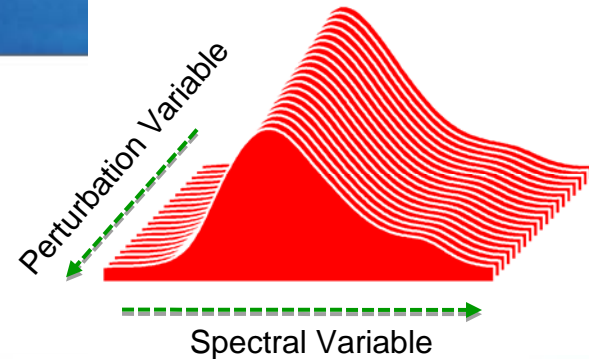
$$\Phi(v_1, v_2) = \frac{1}{N-1} \sum_{j=1}^N \tilde{y}(v_1, p_j) \cdot \tilde{y}(v_2, p_j)$$

Asynchronous 2D correlation spectrum:

$$\Psi(v_1, v_2) = \frac{1}{N-1} \sum_{j=1}^N \tilde{y}(v_1, p_j) \cdot \sum_{k=1}^N M_{jk} \cdot \tilde{y}(v_2, p_k)$$

Hilbert-Noda transformation matrix

$$M_{jk} = \begin{cases} 0 & \text{if } j = k \\ \frac{1}{\pi(k-j)} & \text{otherwise} \end{cases}$$

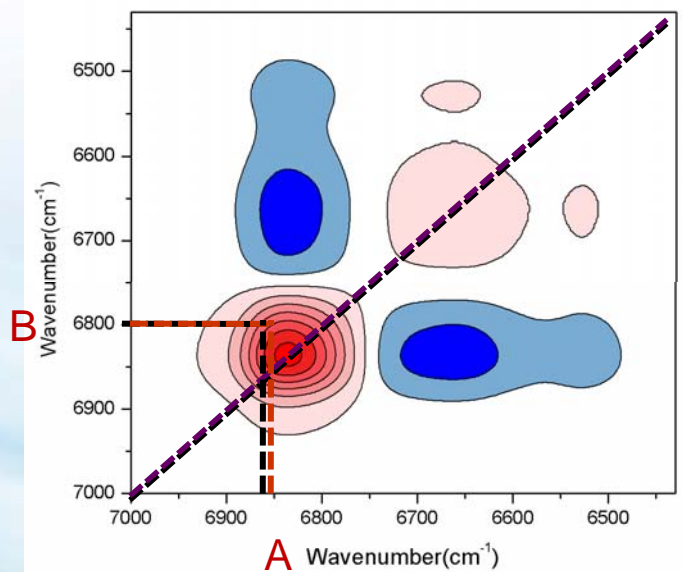


Generalized Two-Dimensional Correlation Spectroscopy

【Advantages of 2Dcos】

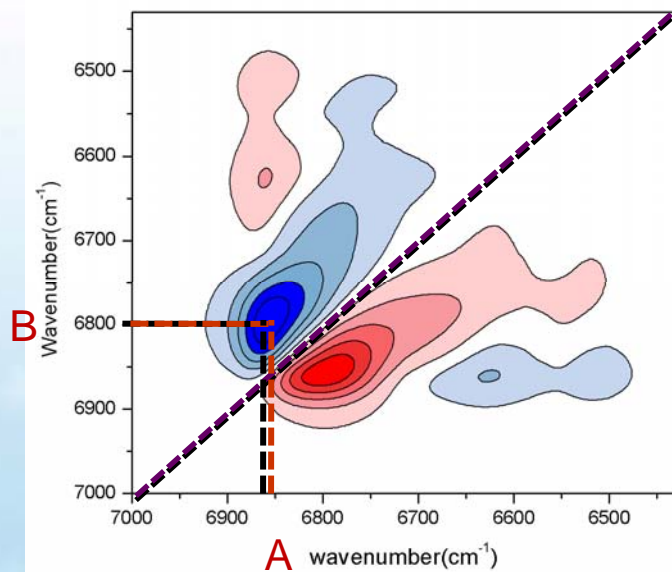
- ✂ Enhance the spectral resolution ;
- ✂ Discern the specific order taking place under perturbation. (Noda's Rule)

Synchronous Spectra (同步谱)



Synchronous → positive

Asynchronous Spectra (异步谱)



Asynchronous → negative

Conclusion: A and B both decrease (or increase);
B decreases prior to A

Contents



Generalized Two-Dimensional Correlation Spectroscopy



Perturbation Correlation Moving Window



Application

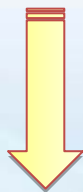
PDBVT – poly[di(butyl) vinylterephthalate]

Perturbation Correlation Moving Window



Moving Window 2D Correlation Spectroscopy (2000)

M. Thomas and H. Richardson, *Vib. Spectrosc.*, 24, 137-146, (2000).



⌘ search for the transition points



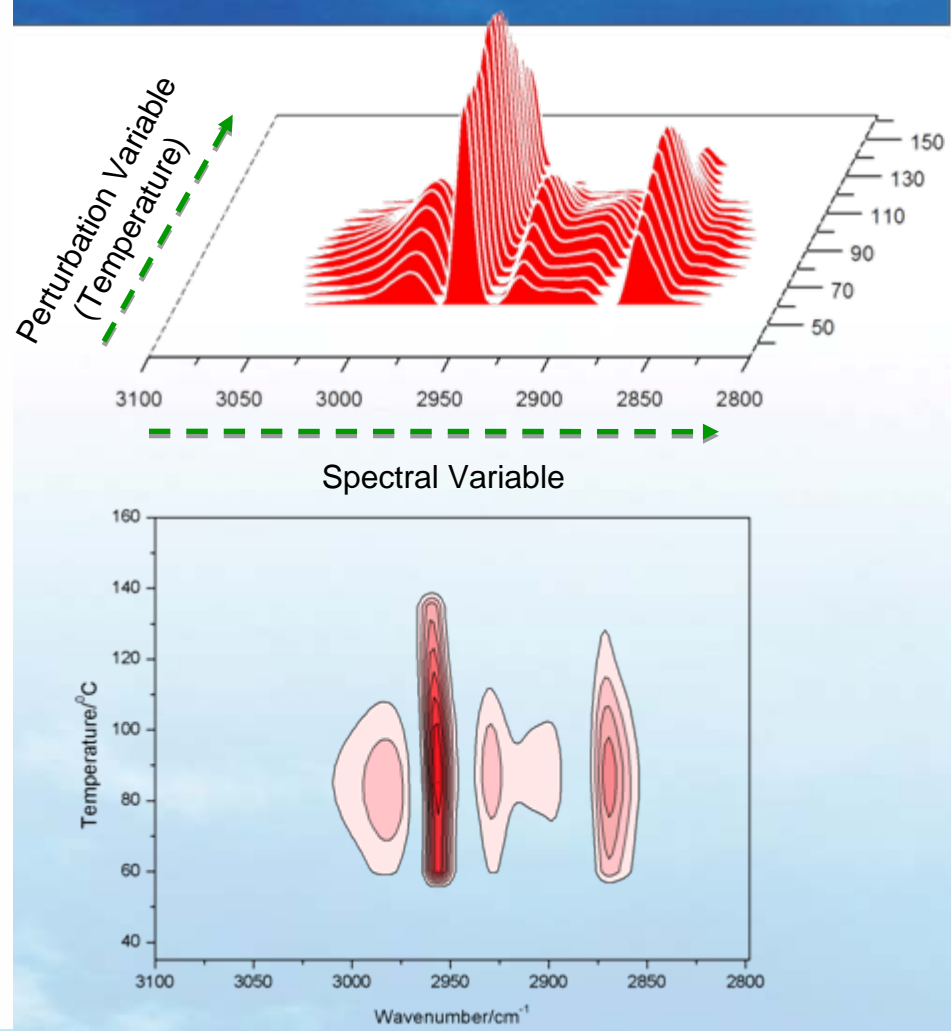
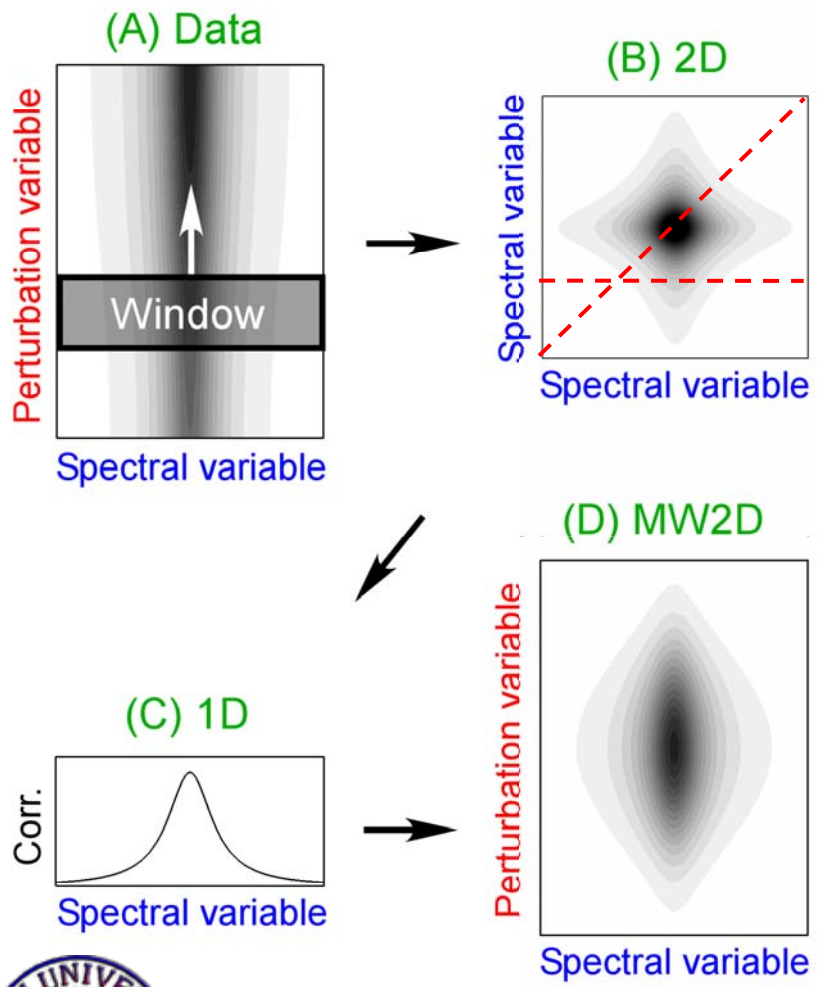
Perturbation Correlation Moving Window 2D Correlation Spectroscopy (2006)

Shigeaki Morita, et al., *Appl. Spectrosc.*, 60, 398-406, (2006).

⌘ search for the transition points

⌘ monitor complicated spectral variations along perturbation variable

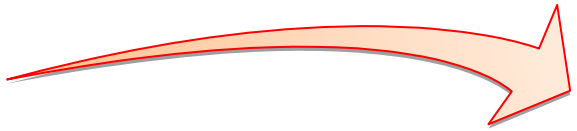
Perturbation Correlation Moving Window



Acquisition of Moving Window Spectra

Perturbation Correlation Moving Window

Introduce external perturbation variable into correlation equations



【MW2D】

MW2D (based on an auto-correlation):

$$\Omega_j(v, p_j) = \frac{1}{2m} \sum_{J=j-m}^{j+m} \tilde{y}_j^2(v, p_J)$$

MW2D (based on horizontal slice spectra):

$$\Omega_{\Phi,j}(v, p_j) = \frac{1}{2m} \sum_{J=j-m}^{j+m} \tilde{y}_j(v, p_J) \cdot \tilde{y}_j(v_c, p_J)$$

$$\Omega_{\Psi,j}(v, p_j) = \frac{1}{2m} \sum_{J=j-m}^{j+m} \tilde{y}_j(v, p_J) \cdot \sum_{K=j-m}^{j+m} M_{JK} \cdot \tilde{y}_j(v_c, p_K)$$

【PCMW2D】

PCMW2D (synchronous):

$$\Pi_{\Phi,j}(v, p_j) = \frac{1}{2m} \sum_{J=j-m}^{j+m} \tilde{y}(v, p_J) \cdot \tilde{p}_J \sim \left(\frac{\partial y}{\partial p} \right)_v$$

PCMW2D (asynchronous):

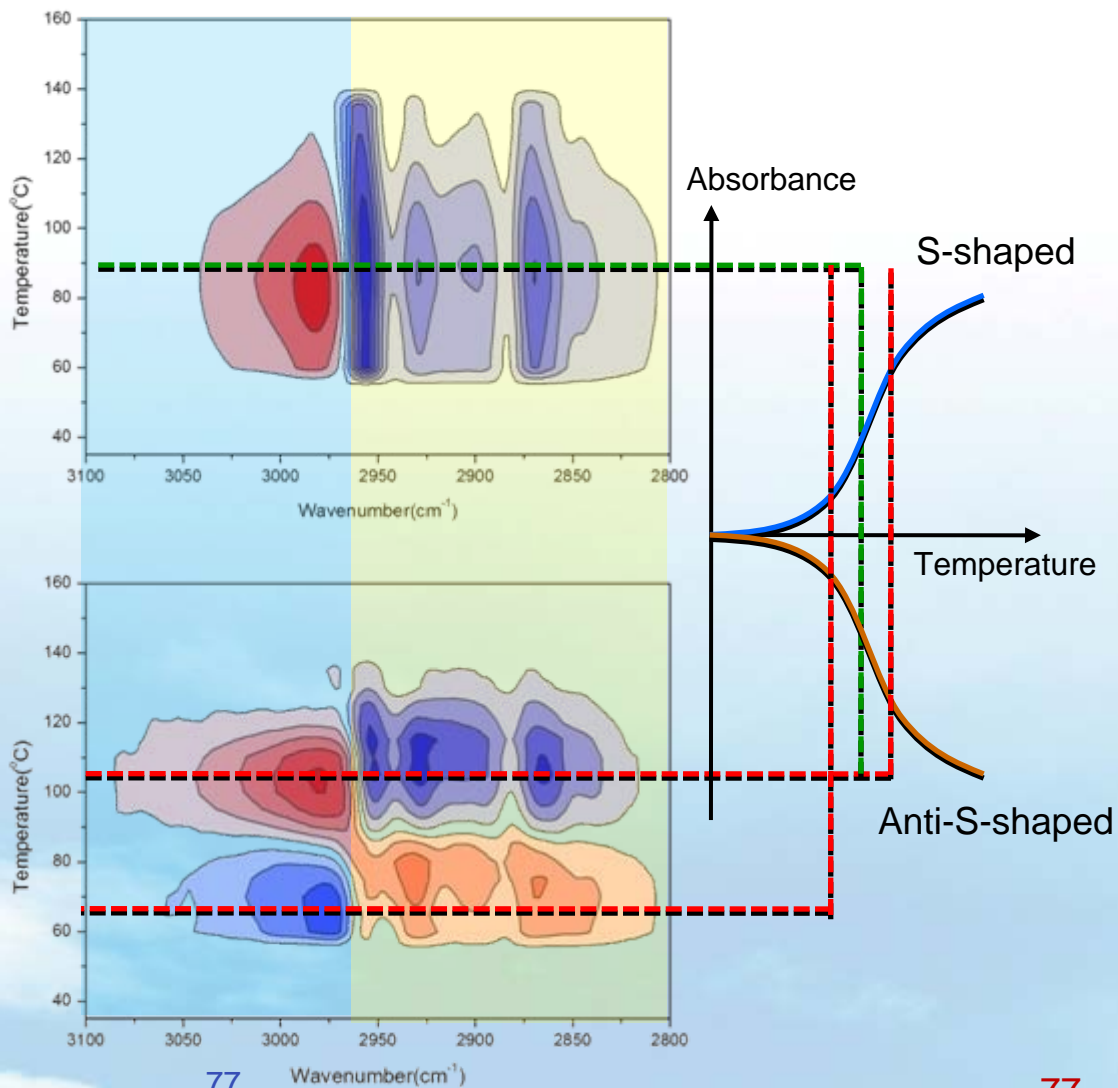
$$\Pi_{\Psi,j}(v, p_j) = \frac{1}{2m} \sum_{J=j-m}^{j+m} \tilde{y}(v, p_J) \cdot \sum_{K=j-m}^{j+m} M_{JK} \cdot \tilde{p}_K \sim - \left(\frac{\partial^2 y}{\partial p^2} \right)_v$$

Perturbation Correlation Moving Window

【Rules of PCMW2D】

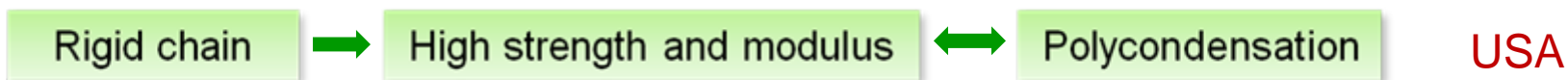
Synchrono us	Asynchrono us	Spectral Change
+	+	
+	0	
+	-	
0	+	
0	0	
0	-	
-	+	
-	0	

(In the case of liner increment perturbation)



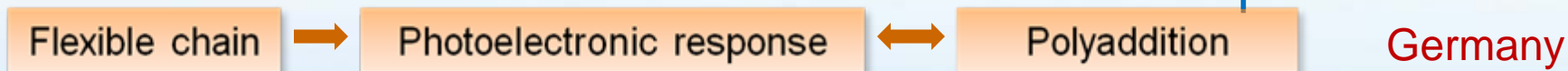
Supramolecular Self-Assembly Thermodynamic Mechanism of PDBVT

Main chain LCP

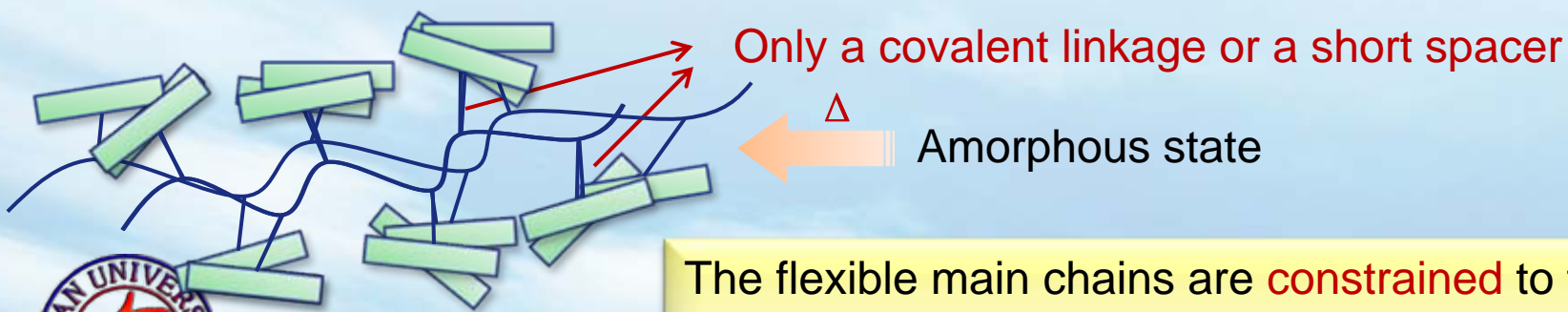


Mesogen-Jacketed LCP

Side chain LCP



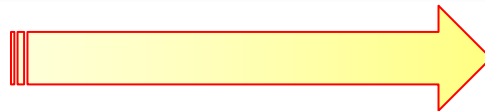
Molecular structure of MJLCP



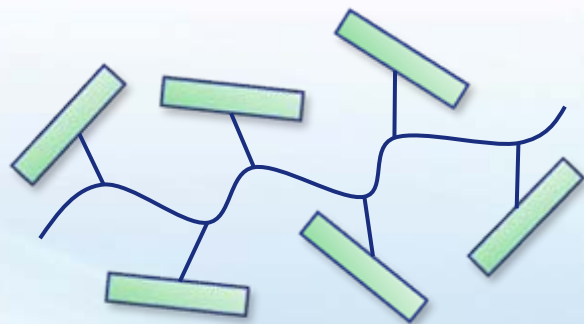
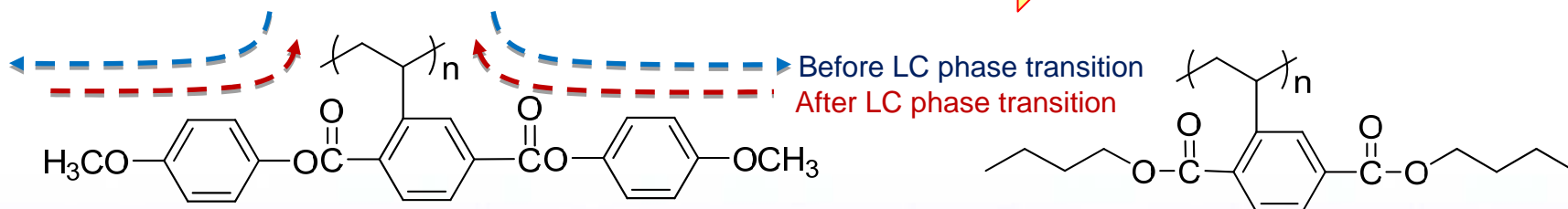
The flexible main chains are **constrained** to take an extended chain conformation

Supramolecular Self-Assembly Thermodynamic Mechanism of PDBVT

PMPCS



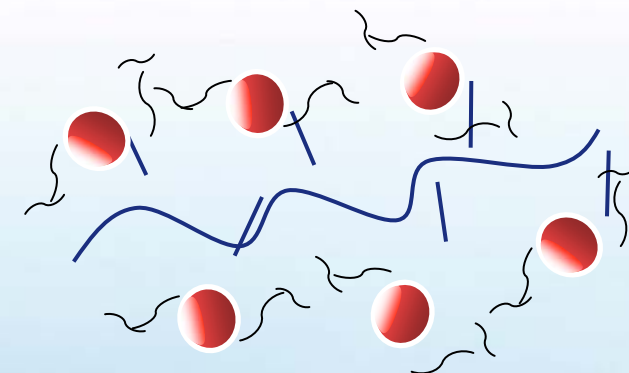
PDBVT



Rigid side groups



Nematic phase



Flexible side groups

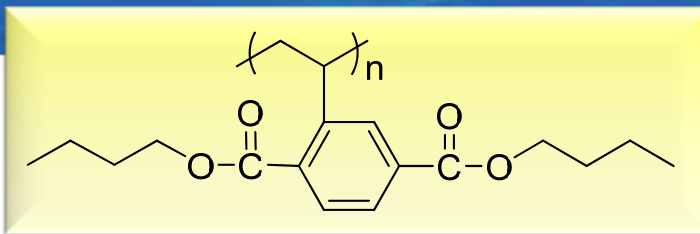


Mechanism?

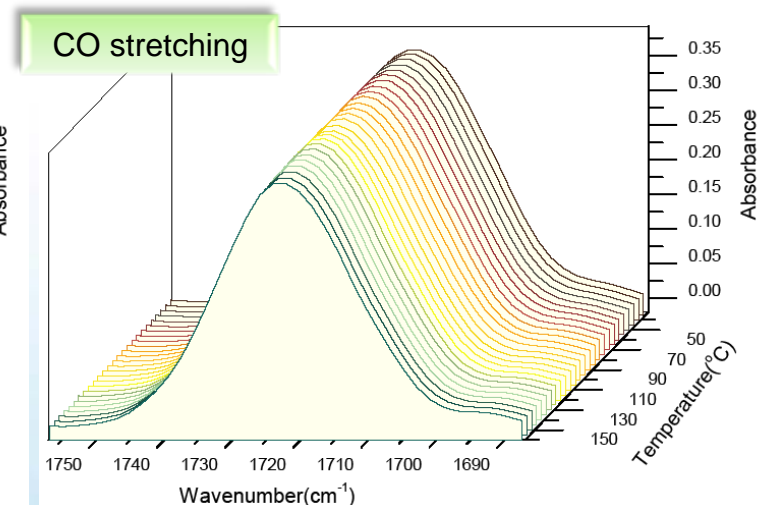
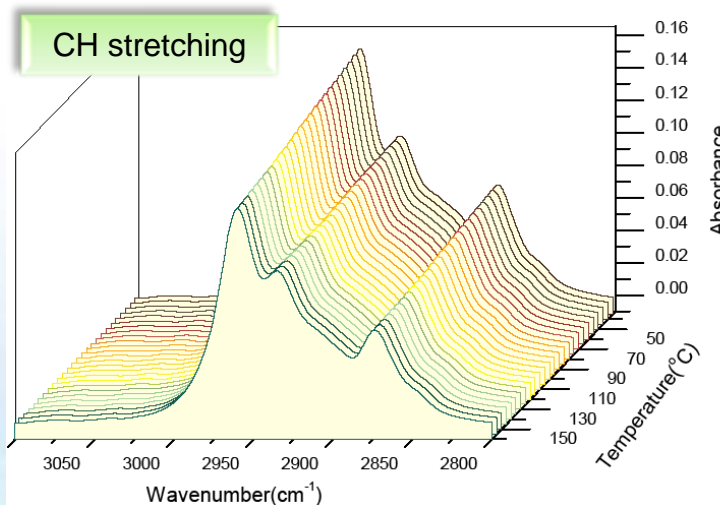
2D hexagonal columnar phase

1. Shen, Y.; Wu, P. Y.; Noda, I.; Zhou, Q. F. *J. Phys. Chem. B* **2005**, 109, 6089-6095.
2. Yin, X. Y.; Wan, X. H.; Cheng, S. Z. D.; Zhou, Q. F. *J. Am. Chem. Soc.* **2003**, 125, 6854.

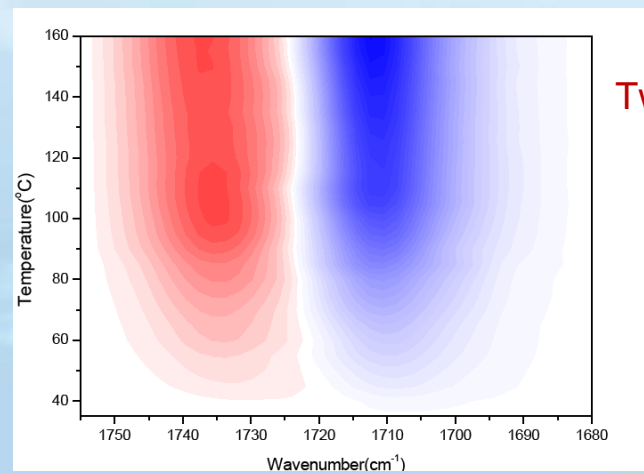
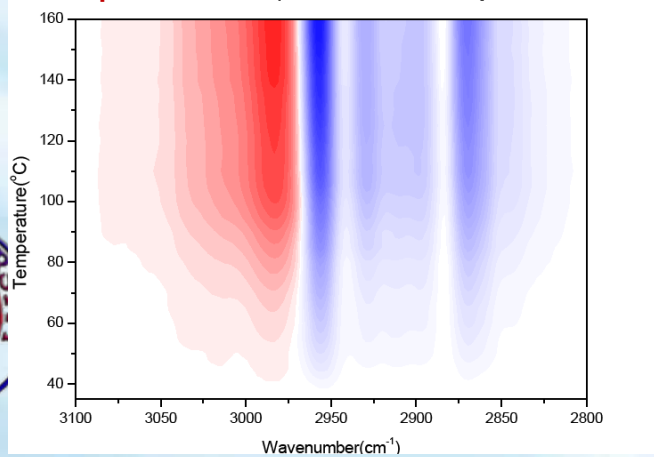
Supramolecular Self-Assembly Thermodynamic Mechanism of PDBVT



【Conventional IR spectra】



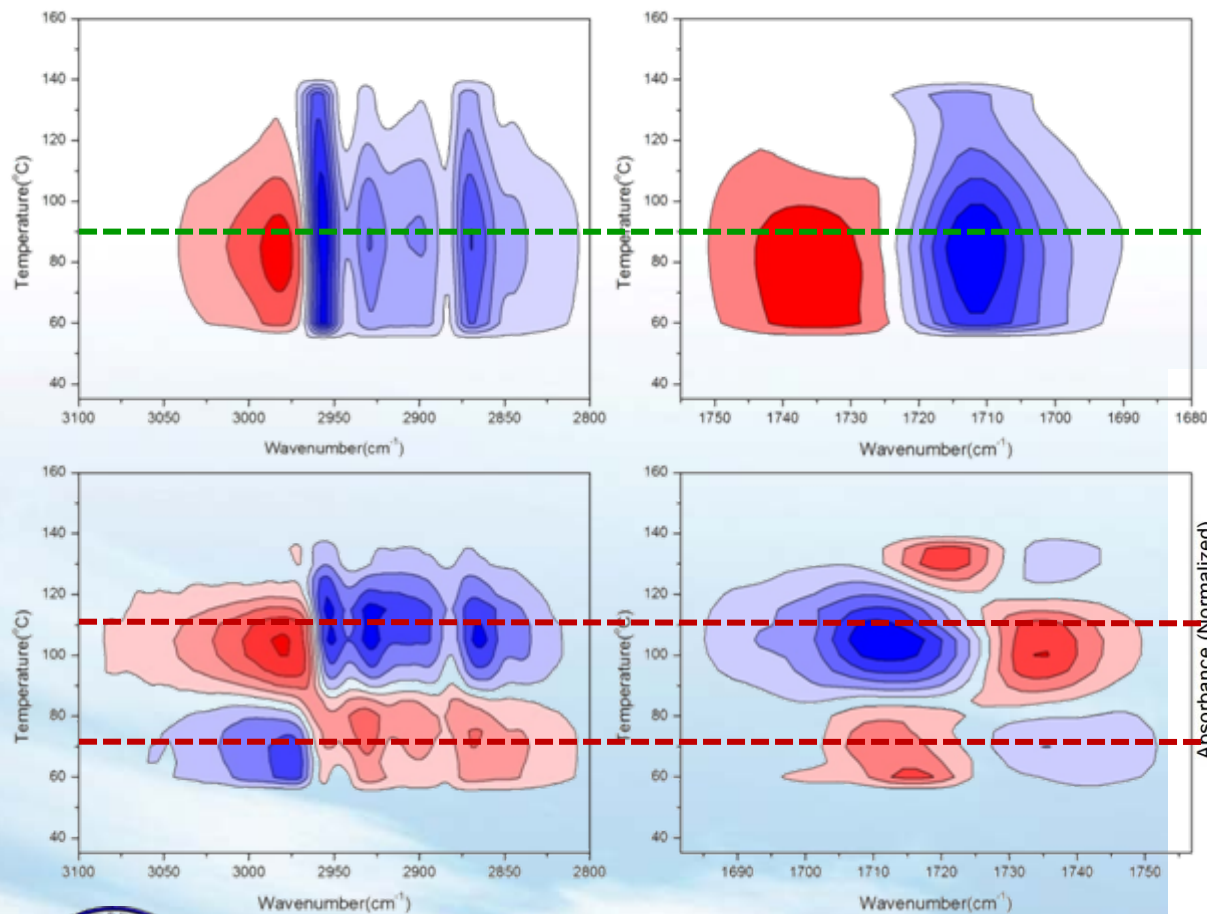
【Differential spectra】 (reference spectrum: 35 °C)



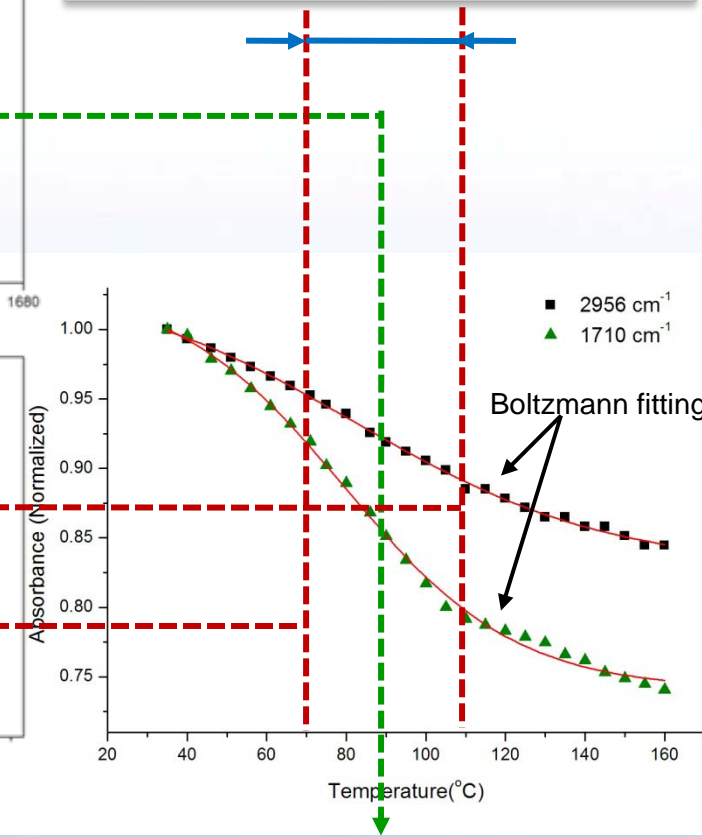
Two splitting bands

Supramolecular Self-Assembly Thermodynamic Mechanism of PDBVT

【Perturbation Correlation Moving Window】



LC phase development: 70~110 °C



DSC: no observable LC phase transition
 WAXD: 100 °C

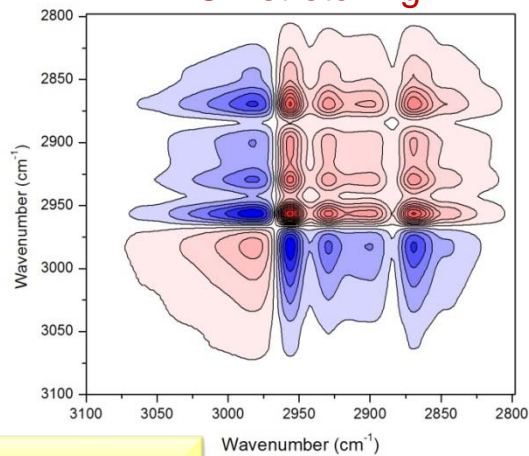
LC phase transition: ≈ 90 °C

Supramolecular Self-Assembly Thermodynamic Mechanism of PDBVT

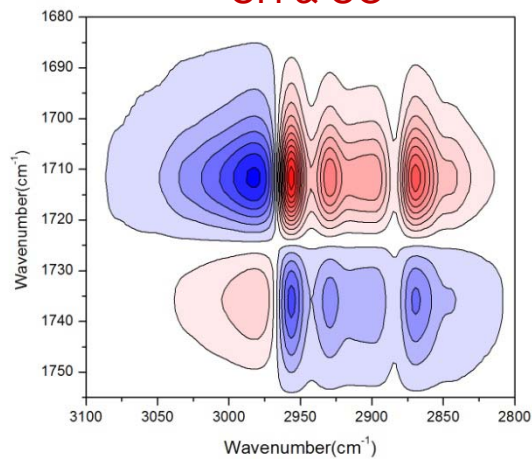
【2D Correlation Spectra】 (70~110 °C)

Synchronous

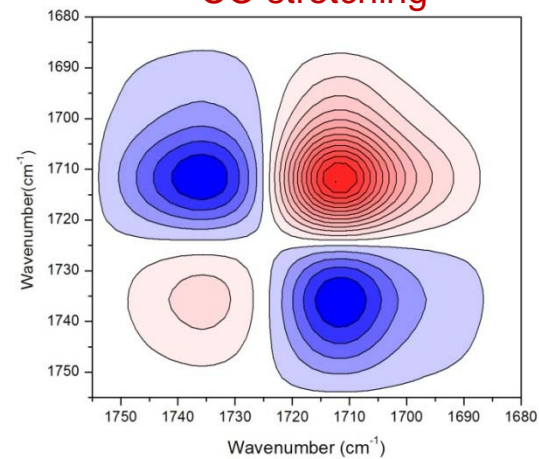
CH stretching



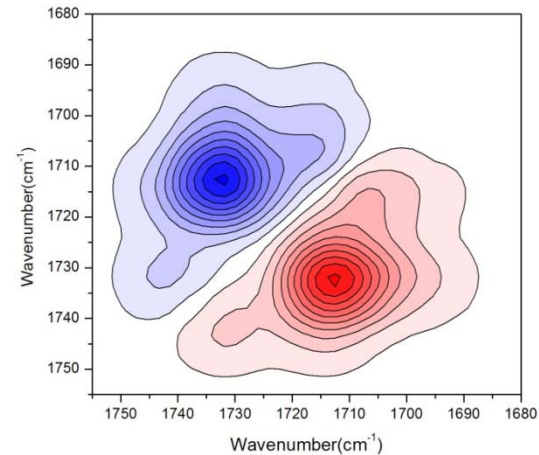
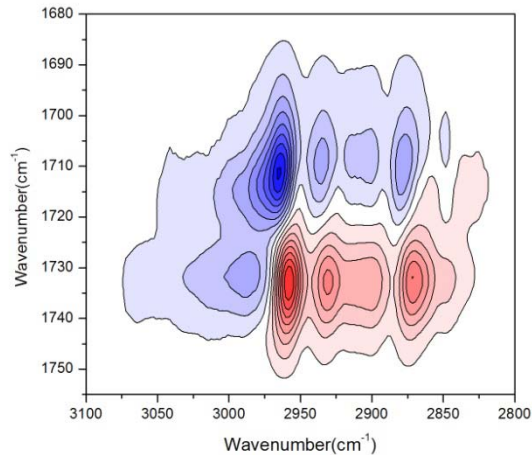
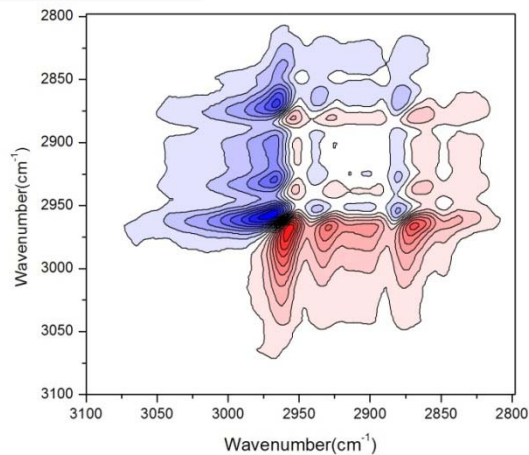
CH & CO



CO stretching



Asynchronous



Supramolecular Self-Assembly Thermodynamic Mechanism of PDBVT

Specific order (70~110 °C)



1732 > 2837 > 3041, 2987 > 1710 > 1714 > 2871 > 2958 > 2900 > 2935

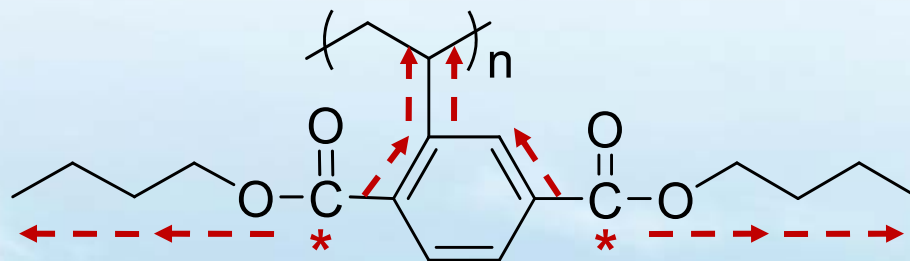


$\nu(\text{CO})(1732) > \nu_s(\text{CH}_2) > \nu_{\text{ar}}, \nu_{\text{as}}(\text{CH}_3)$ (disorder) > $\nu(\text{CO})(1710) > \nu(\text{CO})(1714) > \nu_s(\text{CH}_3)$



> $\nu_{\text{as}}(\text{CH}_3) > \nu(\text{CH}) > \nu_{\text{as}}(\text{CH}_2)$ (side chains)

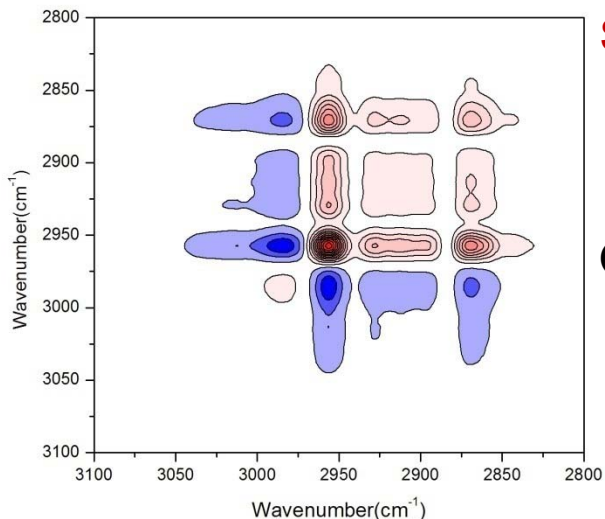
CO → CH₂ → CH₃, phenylene → CH (backbone)



Carbonyl plays a **key** role in the formation of 2D hexagonal columnar phase !

Supramolecular Self-Assembly Thermodynamic Mechanism of PDBVT

【2D Correlation Spectra】 (35~65 °C)

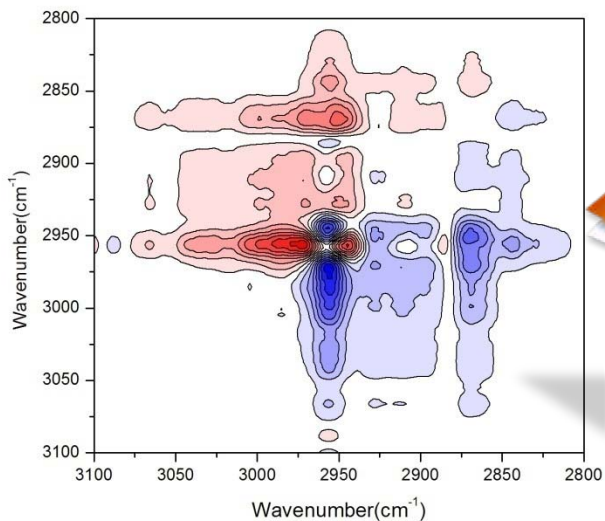
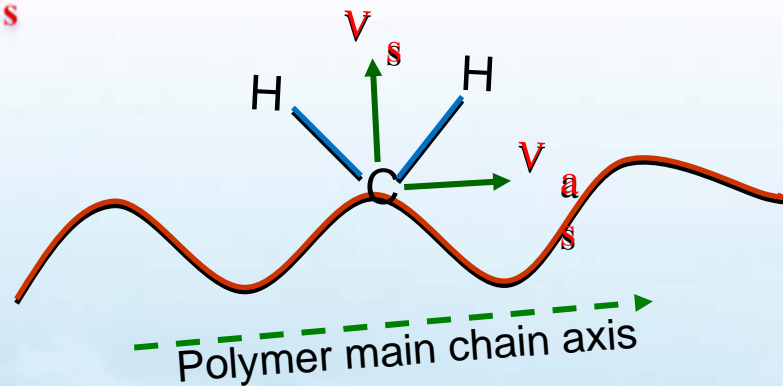


Specific order (partial)

$\nu_{as}(\text{CH}_3) (2956) > \nu_s(\text{CH}_3) (2870)$

$\nu_{as}(\text{CH}_2) (\text{backbone}) (2913) > \nu_{as}(\text{CH}_2) (\text{side chains}) (2931) > \nu_s(\text{CH}_2) (2840)$

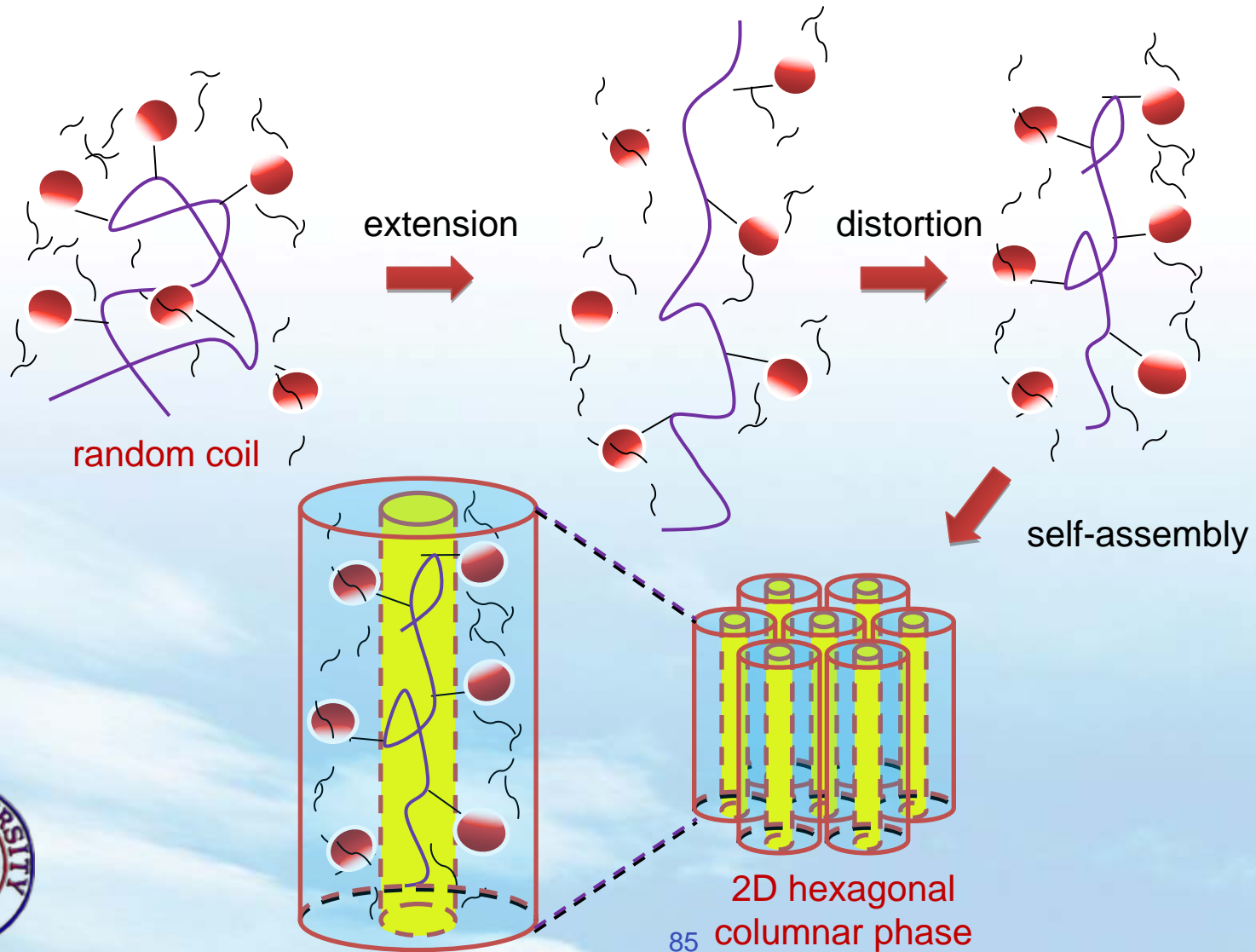
$\nu_{as} > \nu_s$



The backbone and flexible side chains extended vertically before it twisted laterally preparing for the formation of 2D hexagonal columnar phase !

Supramolecular Self-Assembly Thermodynamic Mechanism of PDBVT

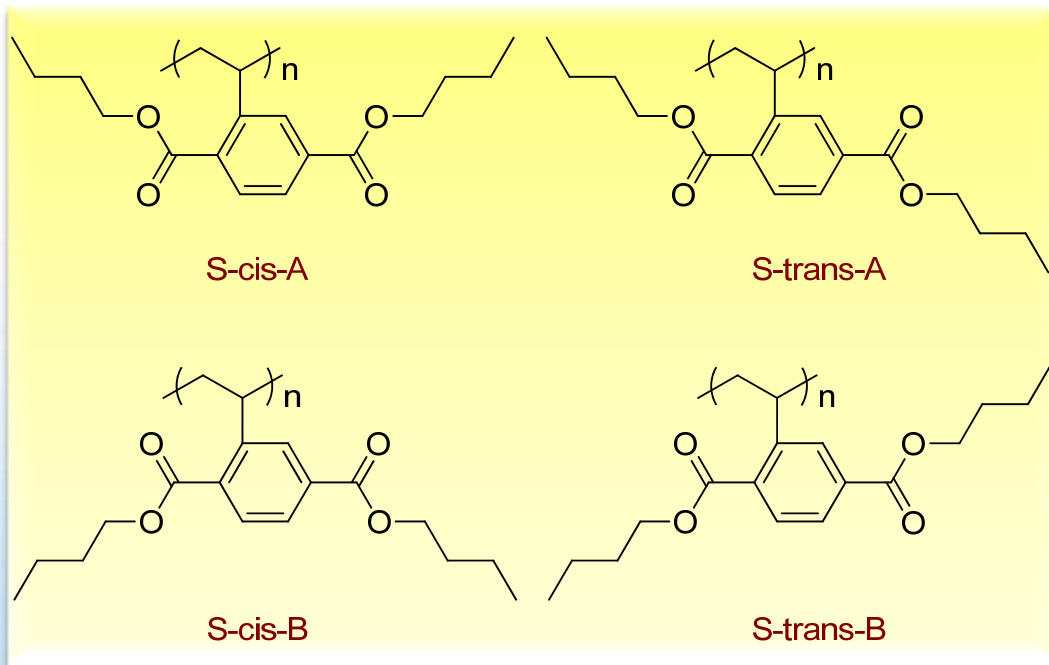
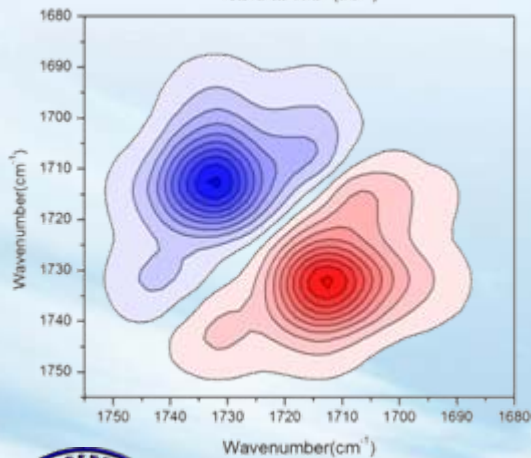
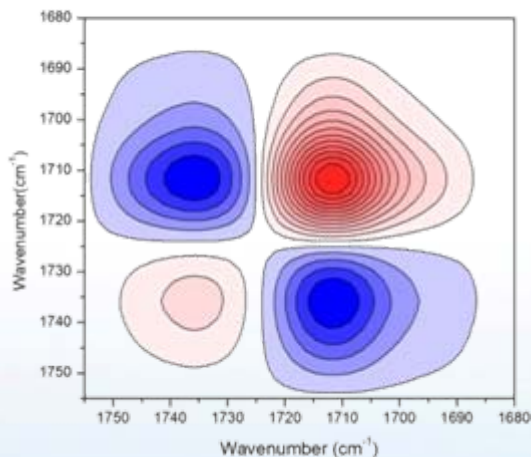
【Mechanism】



Supramolecular Self-Assembly Thermodynamic Mechanism of PDBVT

【CO splitting phenomenon】

Four splitting peaks: 1707, 1712, 1731, 1741



Further investigations

- 🌿 The assignment of four splitting peaks to different conformers
- 🌿 The influence of carbonyl conformation transition on the formation of 2D hexagonal columnar phase



【Acknowledge】

NSFC



Acknowledgement: NSFC(20425415)

Professor H. W. Siesler

and Dr. Isao Noda for helpful discussion

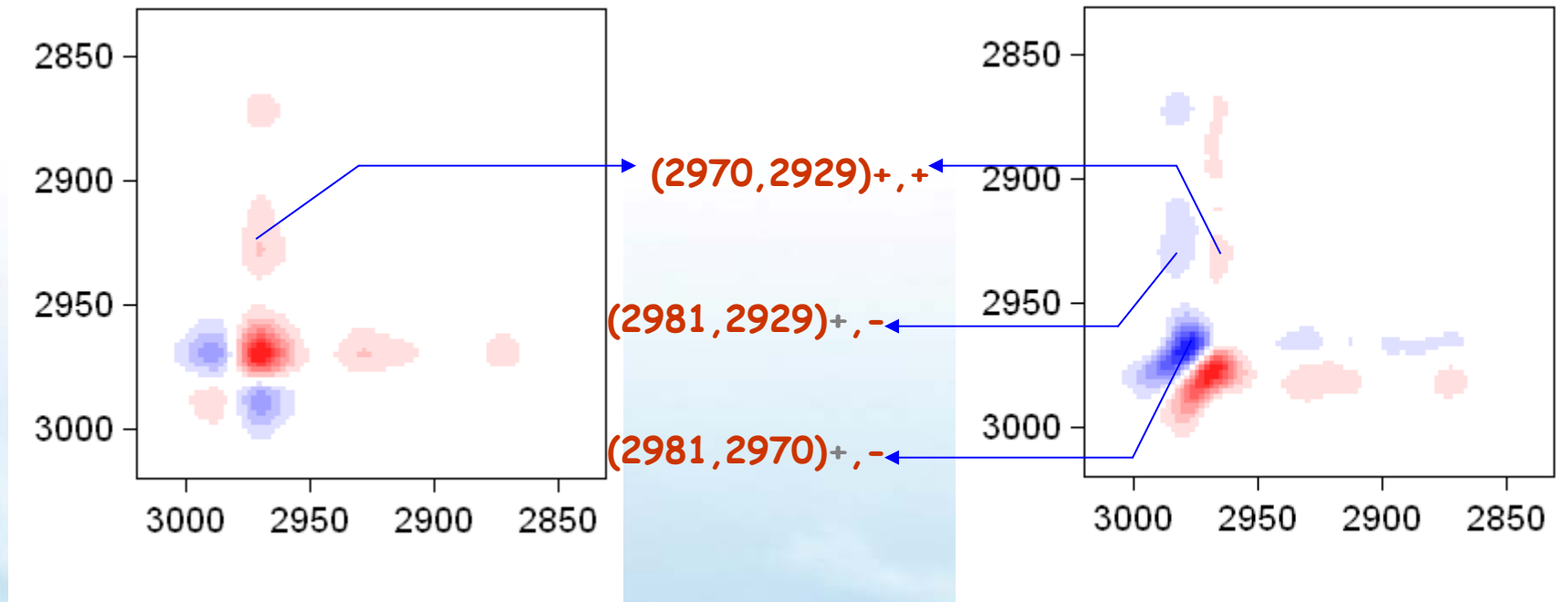




Thank You !



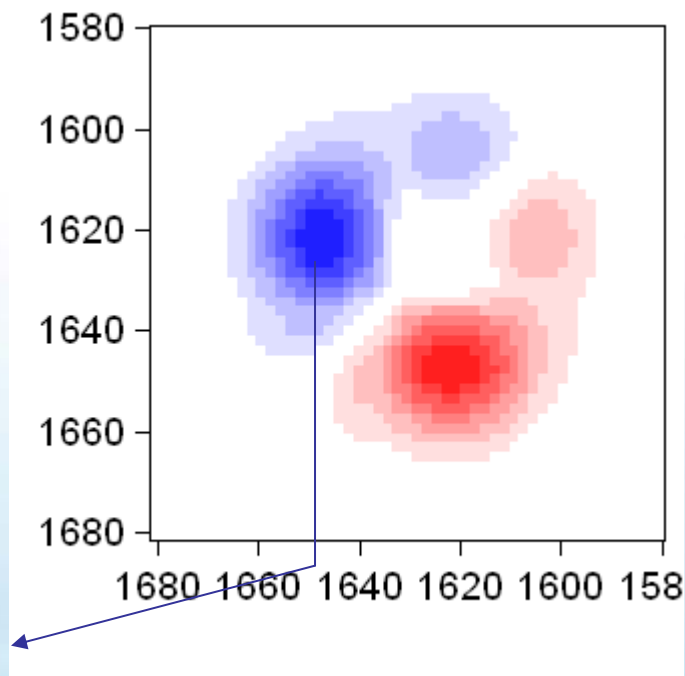
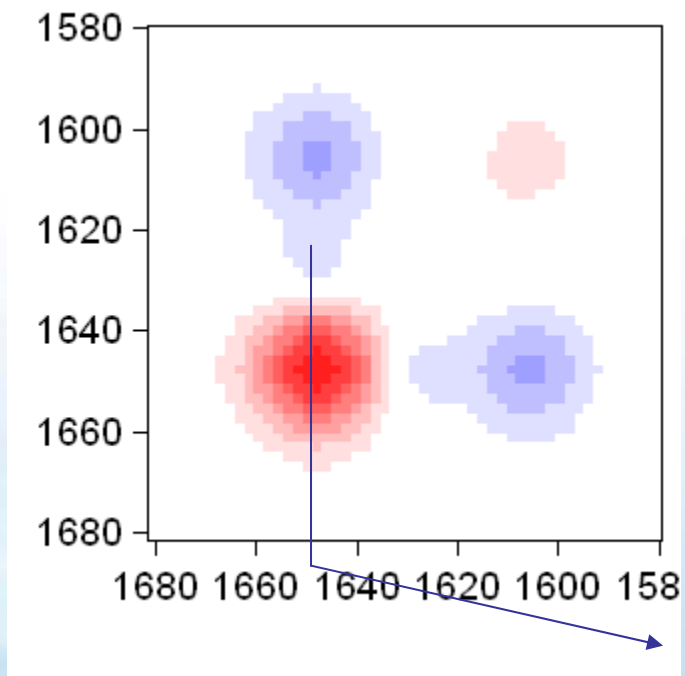
Investigation of CH Bands during cooling- 2DIR



2970 > 2929 > 2981

CH₃ with less water > main-chain $\nu_{as}(\text{CH}_2)$ > CH₃ with more water

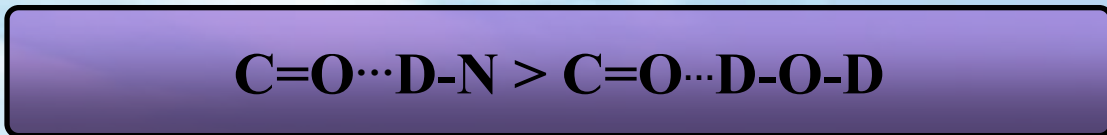
Investigation of Amide I Band during cooling- 2DIR



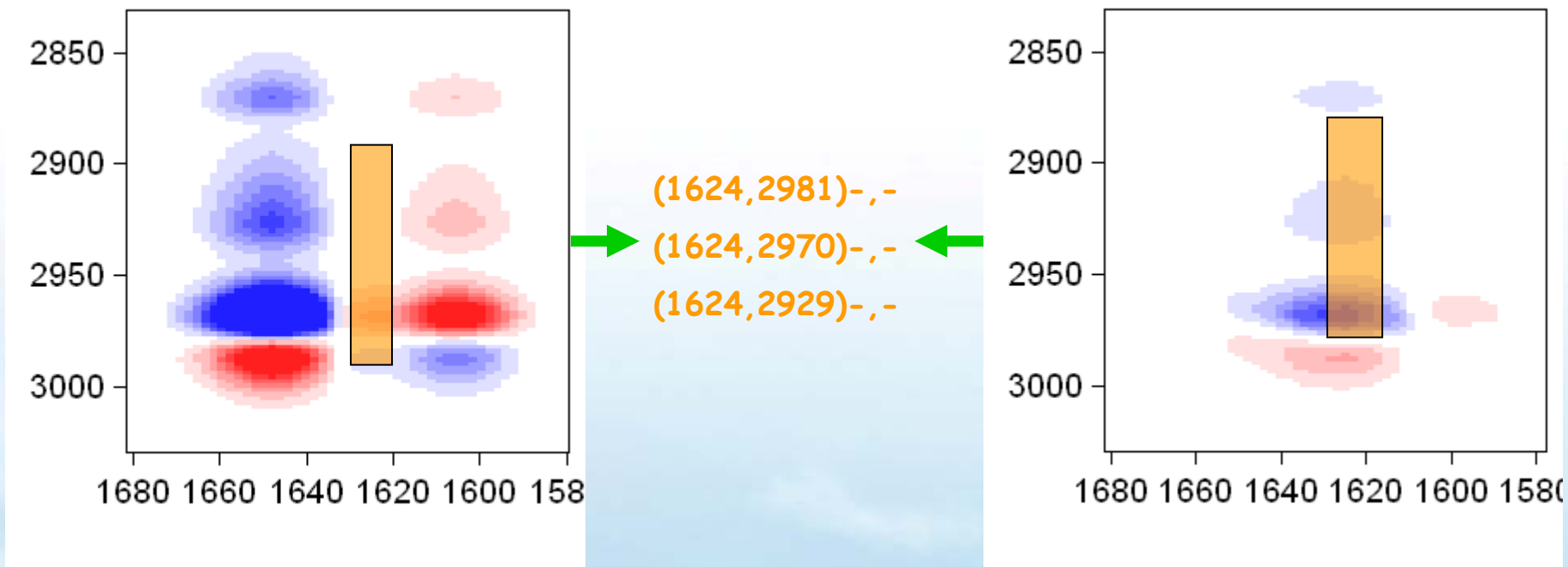
(1649, 1624)-, -



1649 > 1624



Investigation of CH vs. Amide I region in cooling-2DIR



1649 > 1624 > 2970 > 2929 > 2981

**C=O with D-N > C=O with water > CH₃ with less water
 > main-chain ν as(CH₂) > CH₃ with more water**



Dynamics mechanism of PNIPAM 20wt% D₂O solution during cooling

C=O with D-N > N-D with water > C=O with water

> CH₃ with less water > main-chain $\nu_{as}(\text{CH}_2)$ > CH₃ with more water

