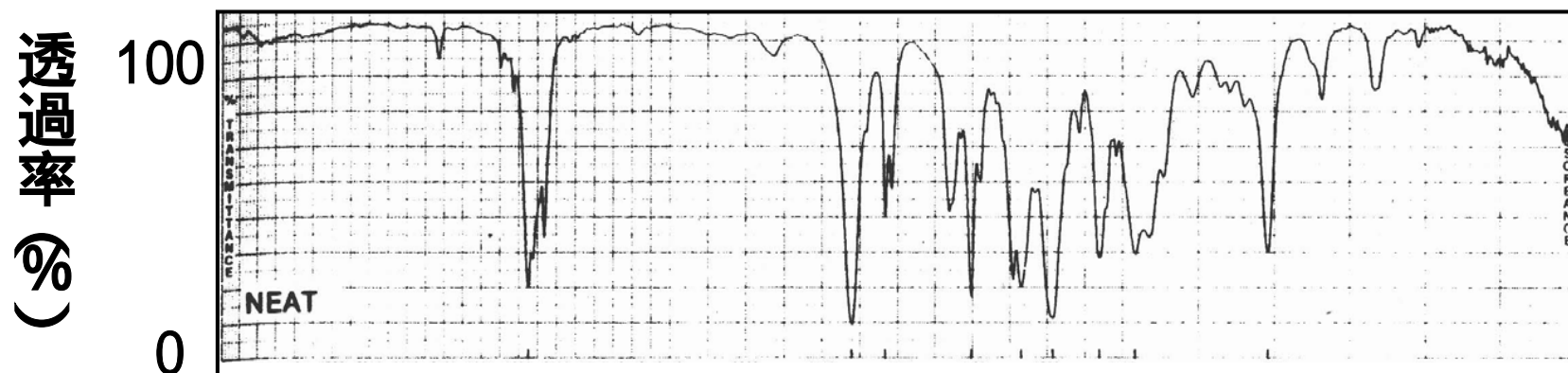


# Chap. 4 赤外分光法 (IR)

(1) **赤外線**: 電磁波  $=c/\lambda$   
 波長 大 振動数 小  
 エネルギー 小 ( $E=h\nu = hc/\lambda$ )

**波数** wavenumber  $1/\lambda$  小

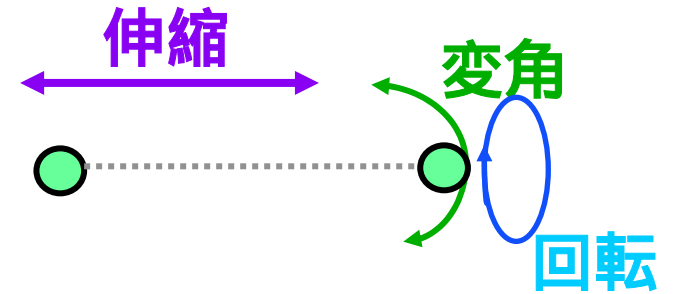
波長  $3 \times 10^{-4} \text{ cm } (\mu\text{m}) = \text{波数 } 1 / 3 \times 10^{-4} \text{ cm } (= 3333 \text{ cm}^{-1})$   
 $= \text{振動数 } 3 \times 10^{10} / 3 \times 10^{-4} \text{ cm } (= 10^{14} \text{ Hz})$



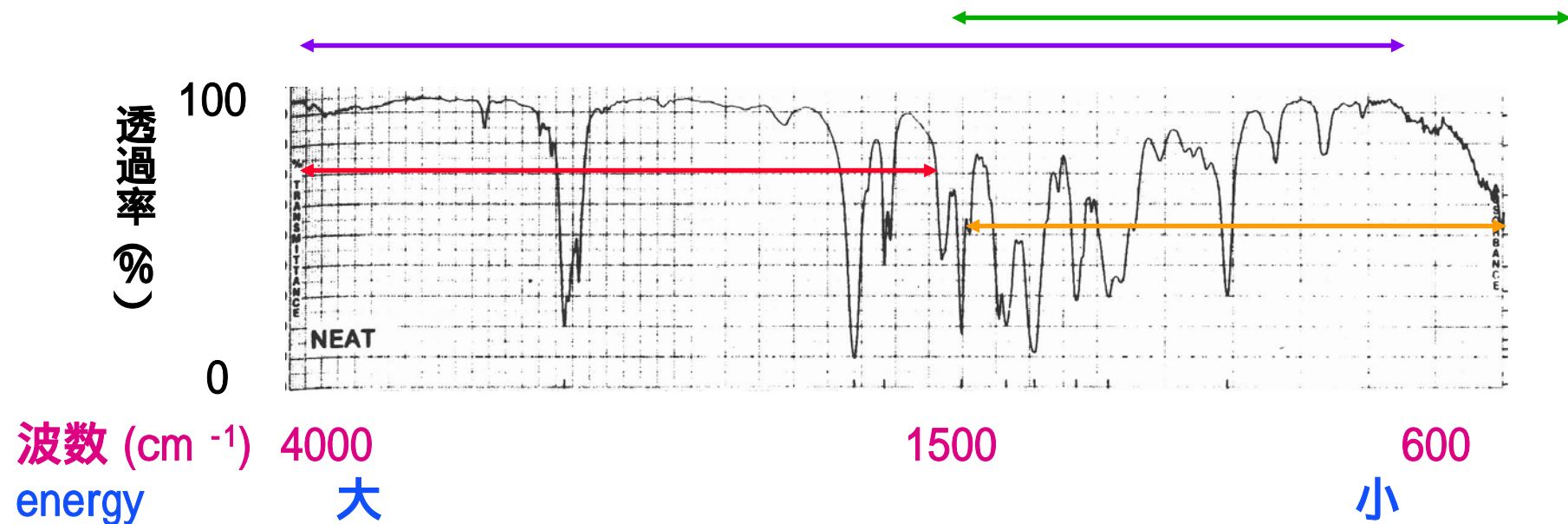
波長 (μm) 2.5 大 17  
 波数 (cm<sup>-1</sup>) 4000 小 600  
 energy 大 小

## (2) 吸収の原理： 分子の運動

- a **伸縮振動** stretching  $4000 \sim 650 \text{ cm}^{-1}$
- b **変角振動** bending  $1550 \sim 550 \text{ cm}^{-1}$
- c **回転** rotation  $< 800 \text{ cm}^{-1}$  重要でない

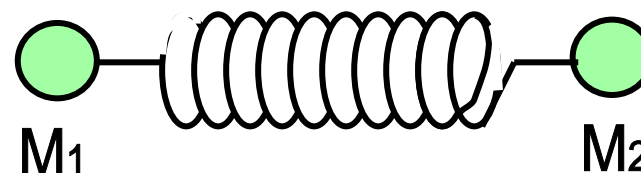


$4000 \sim 1500 \text{ cm}^{-1}$  : **官能基領域** functional group region  
 $1500 \sim 600 \text{ cm}^{-1}$  : **指紋領域** fingerprint region



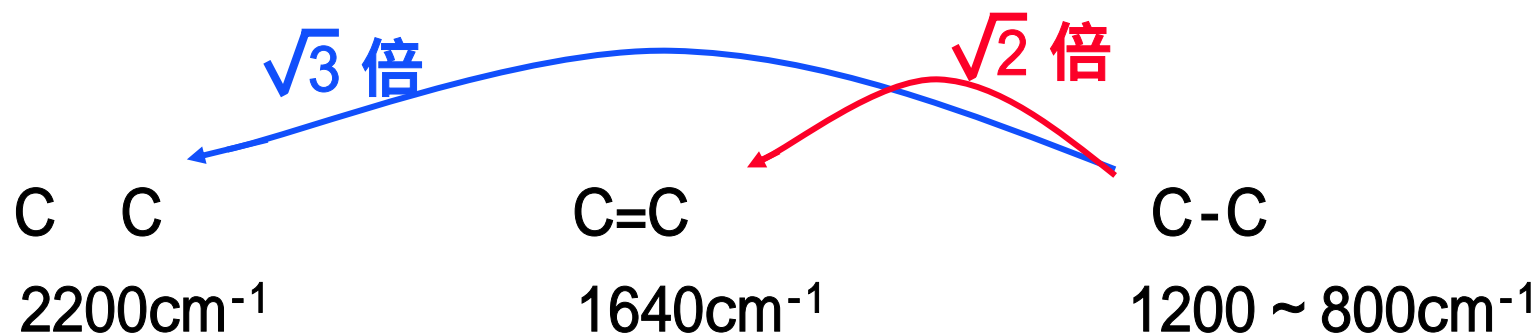
## (2) 吸収の原理： 分子の運動

伸縮運動： Hooke's Law で説明できる



$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{M_o}} \quad k: \text{force constant}$$

$$M_o = M_1 M_2 / M_1 + M_2$$



C-H	$M_o = 12 \times 1 / 12 + 1 = 0.92$	3000 ~ 2840 cm <sup>-1</sup>
C-D	$M_o = 12 \times 2 / 12 + 2 = 1.7$	2100 cm <sup>-1</sup>
C-C	$M_o = 12 \times 12 / 12 + 12 = 6.0$	1200 ~ 800 cm <sup>-1</sup>

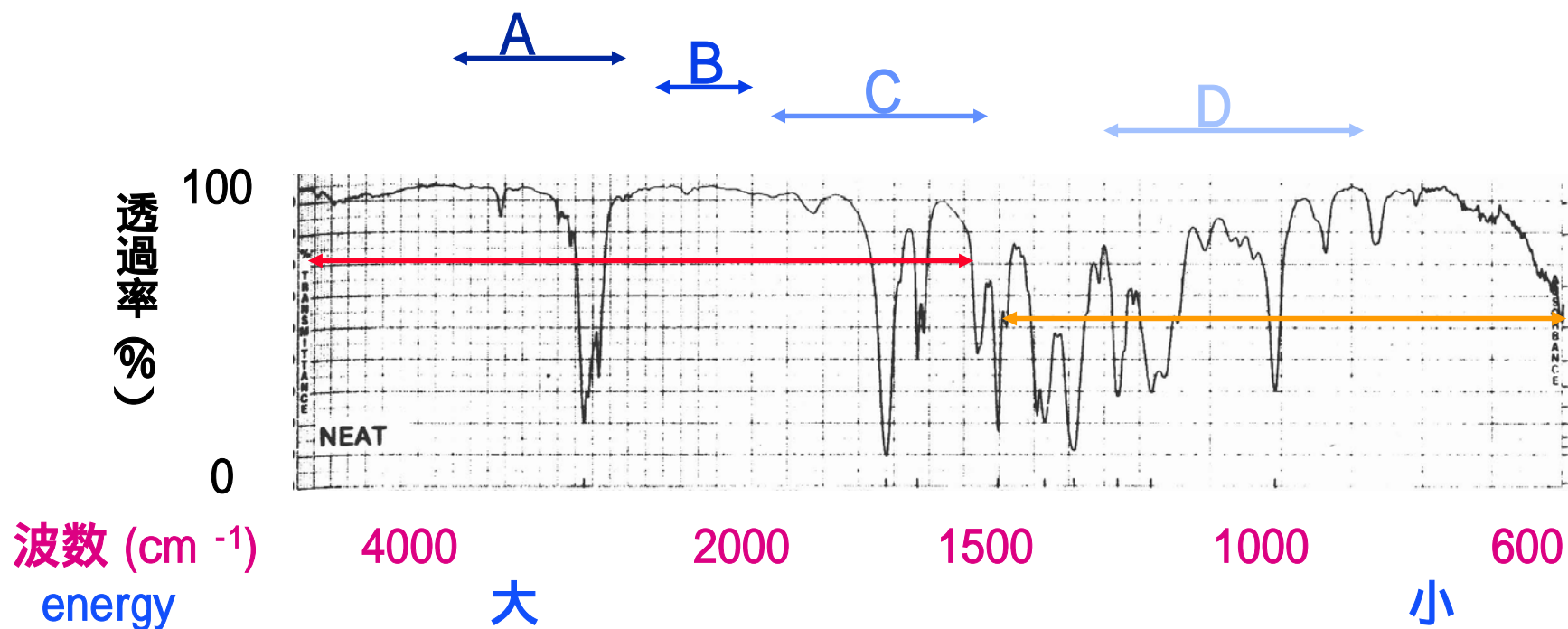
C-H > C-D >> C-C



## (2) 吸収の原理： 分子の運動

### Stretching (伸縮) による吸収

A)	C-H, O-H, N-H	3800 ~ 2700	cm <sup>-1</sup>
B)	C=C, C≡C, N≡N	2300 ~ 2000	cm <sup>-1</sup>
C)	C=O, C=N, N=O	1900 ~ 1500	cm <sup>-1</sup>
D)	C-C, C-O, C-N	1300 ~ 800	cm <sup>-1</sup>



## (2) 吸収の原理: 分子の運動

波長            大   エネルギー            小  
                  =  $c/$           振動数            小          **波数**  $1/$             小  
                                ニュー                                吸収極大  $\sim_{\text{max}} (\text{cm}^{-1})$

倍音振動: 基準振動の2倍、3倍、...の波数での吸収

結合音振動: 2つの基準振動の波数の和での吸収

## (3) 測定方法

液体試料 KBr板で挟む (**薄膜法、NEAT、Film法**)

固体試料

1. KBrと混合し、高圧下で錠剤化 (**KBr法**)
2. 流動パラフィンと混合し、KBr板で挟む (**Nujor法**)

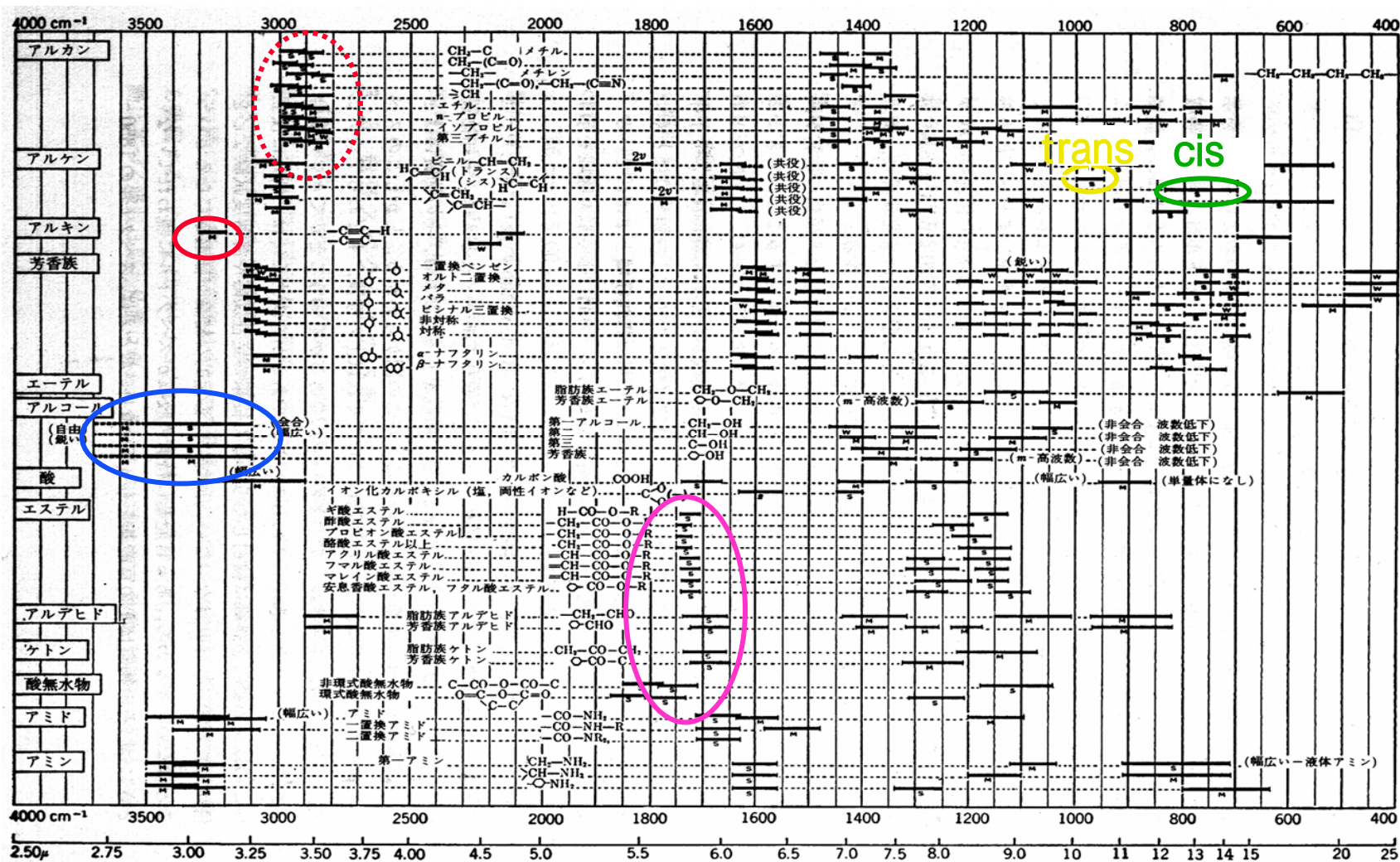
テキスト 図3.4 (a)

3. 有機溶媒の溶液 (**液体セル法**)

# (4) 官能基の特性吸収帯

プリント IR-1

吸収極大  $\sim_{\max}$  (  $\text{cm}^{-1}$  ) 強度: s m w

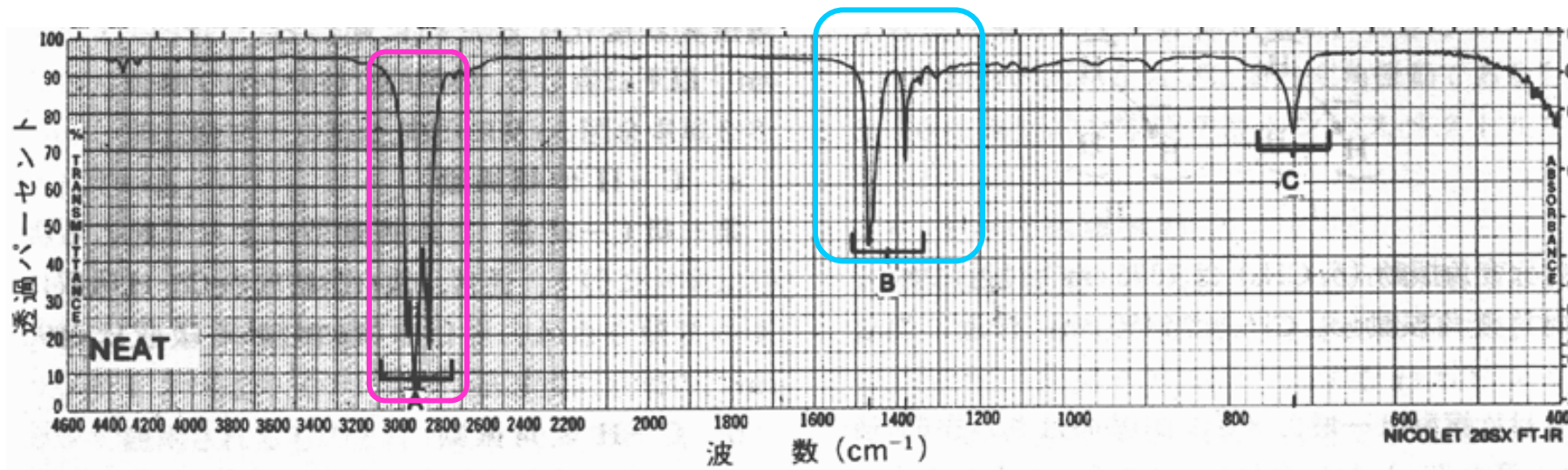


## (4) 官能基の特性吸収帯

プリント IR-2

A) 炭化水素の吸収帯 吸収極大  $\tilde{\nu}_{\max}$  (  $\text{cm}^{-1}$  )

A-1. 直鎖alkane (dodecane)



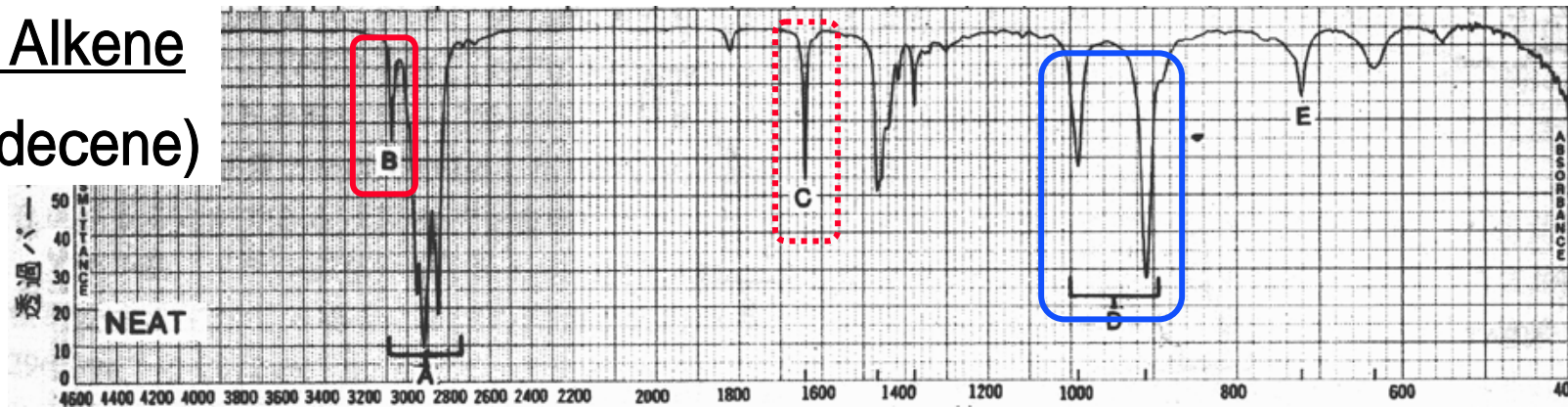
C-H伸縮 2962  $\text{cm}^{-1}$  CH<sub>3</sub>逆(非)対称伸縮 2924  $\text{cm}^{-1}$  CH<sub>2</sub>逆対称伸縮  
2872  $\text{cm}^{-1}$  CH<sub>3</sub>対称伸縮 2853  $\text{cm}^{-1}$  CH<sub>2</sub>対称伸縮

C-H変角 1467, 1450, 1378, 721  $\text{cm}^{-1}$

## (4) 官能基の特性吸収帯

プリント IR-2

### A-2. Alkene (1-decene)

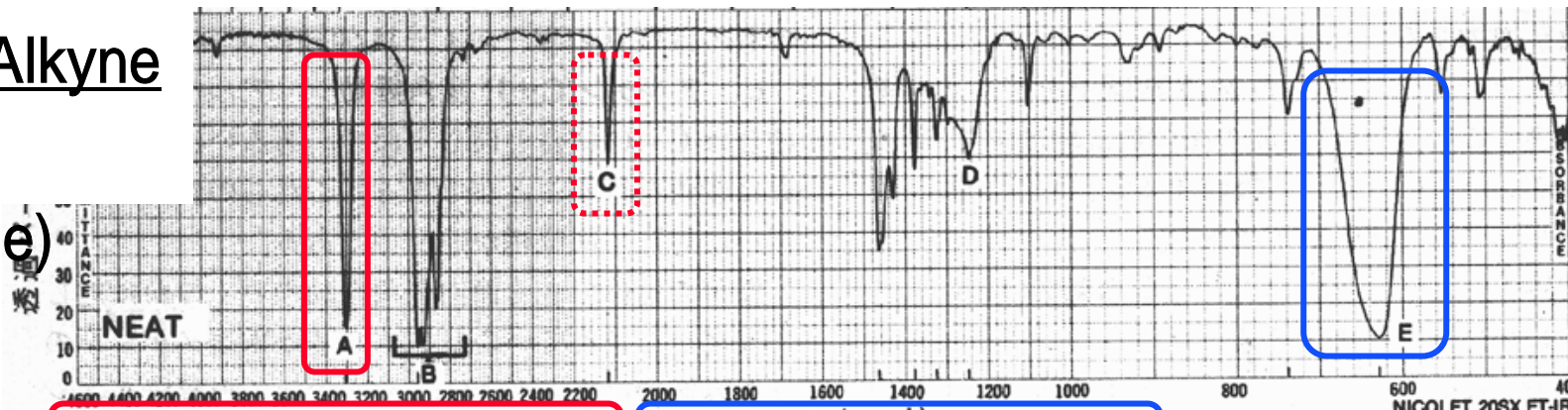


=C-H伸縮 3049 cm<sup>-1</sup>

=C-H変角 991 cm<sup>-1</sup>, 910 cm<sup>-1</sup>

C=C伸縮 1642 cm<sup>-1</sup>(1置換), [2置換以上だと1670 cm<sup>-1</sup>]

### A-3. Alkyne (1-hexyne)



C-H伸縮 3310 cm<sup>-1</sup>

C-H変角 630 cm<sup>-1</sup>, 1250 cm<sup>-1</sup>(倍音振動)

C≡C伸縮 2119 cm<sup>-1</sup>



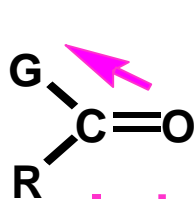
## (4) 官能基の特性吸収帯

### B) カルボニル化合物

C=O伸縮 ( $\sim_{\max}$  1870 ~ 1540  $\text{cm}^{-1}$ ) 1715 $\text{cm}^{-1}$ が基本

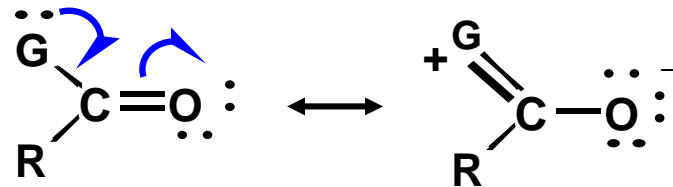
構造決定に有効

#### B-1. 隣接置換基と共役の影響



Inductive effect

誘起効果



Resonance effect

電子吸引基 結合の長さを減少  $f$  が大  $\sim_{\max}$  が大

G: F ( $1869\text{cm}^{-1}$ ), Cl ( $1815 \sim 1785\text{cm}^{-1}$ ),

OH (単量体 $1760\text{cm}^{-1}$ ), OR ( $1750 \sim 1735\text{cm}^{-1}$ )

共鳴効果

共鳴 二重結合性を減少  $f$  が小  $\sim_{\max}$  が小

G: NH<sub>2</sub> ( $1695 \sim 1650\text{cm}^{-1}$ ), SR ( $1720 \sim 1690\text{cm}^{-1}$ )

C=C、フェニル基との共役

電子の非局在化

二重結合性を減少

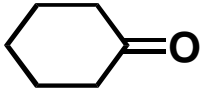
テキスト 図3.11

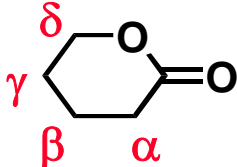
## (4) 官能基の特性吸収帯

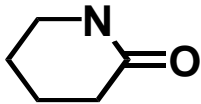
### B-2. 環のひずみの影響

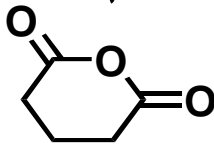
環のサイズ	ketone	lactone	lactam	anhydride
4	1780	1820 $\beta$	1750	-
5	1745	1770 $\gamma$	1710	1850, 1786
6	1715	1740 $\delta$	1689	1820, 1754

~ max



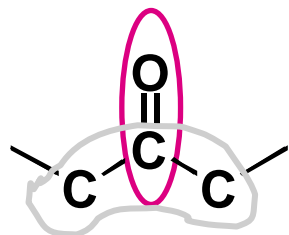






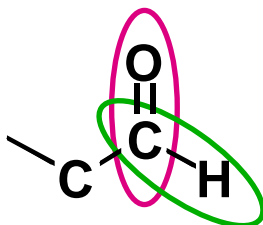
### B-3. 各化合物の特性吸収

1725 ~ 1705 s



1300 ~ 1100 m

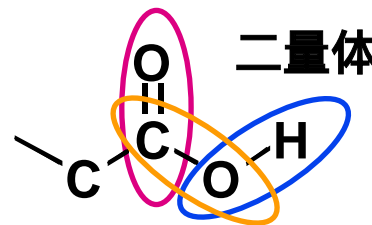
1740 ~ 1720 s



stre. 2900 ~ 2700 m  
bend. 1390 m

テキスト 図3.7 (b)

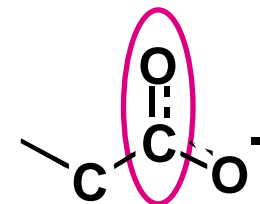
1725 ~ 1700 s



1320 ~ 1210 s

stre. 3300 ~ 2500 broad m  
bend. 1440 ~ 1395, 920 m

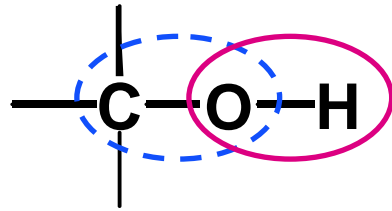
1650 ~ 1550 s  
1400 m



## (4) 官能基の特性吸収帯

### C) アルコール

テキスト 図3.7 (a)



stretching ( $> 3000 \text{ cm}^{-1}$ )

bending ( $1420 \sim 1330 \text{ cm}^{-1}$ )

stretching ( $1260 \sim 1000 \text{ cm}^{-1}$ )

#### C-1. O-H伸縮 水素結合の影響を強く受ける。

freeな水酸基 (稀薄溶液) :  $3600 \text{ cm}^{-1}$  (s, sharp)

テキスト 図3.6

水素結合 分子間 :  $3550 \sim 3200 \text{ cm}^{-1}$  (m, broad)

濃度依存性

分子内 :  $3100 \text{ cm}^{-1}$  (s, broad)

濃度に依存しない

#### C-2. C-O伸縮

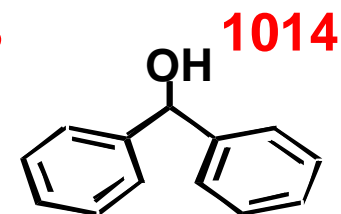
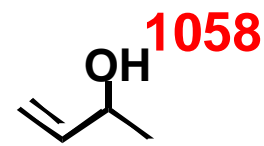
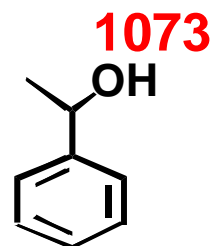
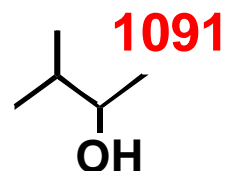
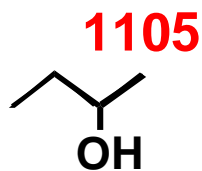
隣接のC-C伸縮と結合  
 $3^\circ > 2^\circ > 1^\circ$  飽和 >

複雑化

-不飽和

直鎖 >

-枝分かれ

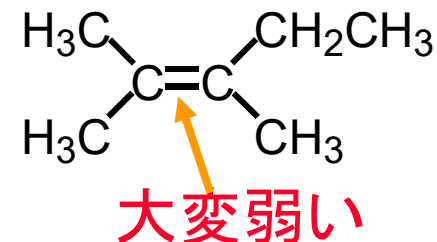
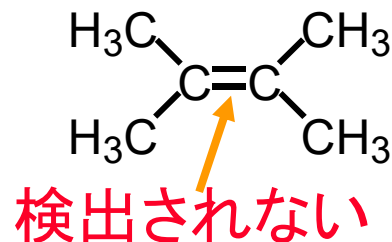
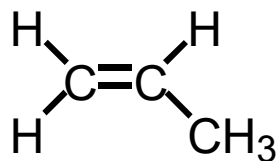


## (5) 検出できない振動

吸収の強度： 双極子モーメントの変化の大きさに依存

極性、吸収強度  $\overset{\delta-}{\text{O}}-\overset{\delta+}{\text{H}} > \text{N}-\text{H} > \text{C}-\text{H}$

C=Cの伸縮



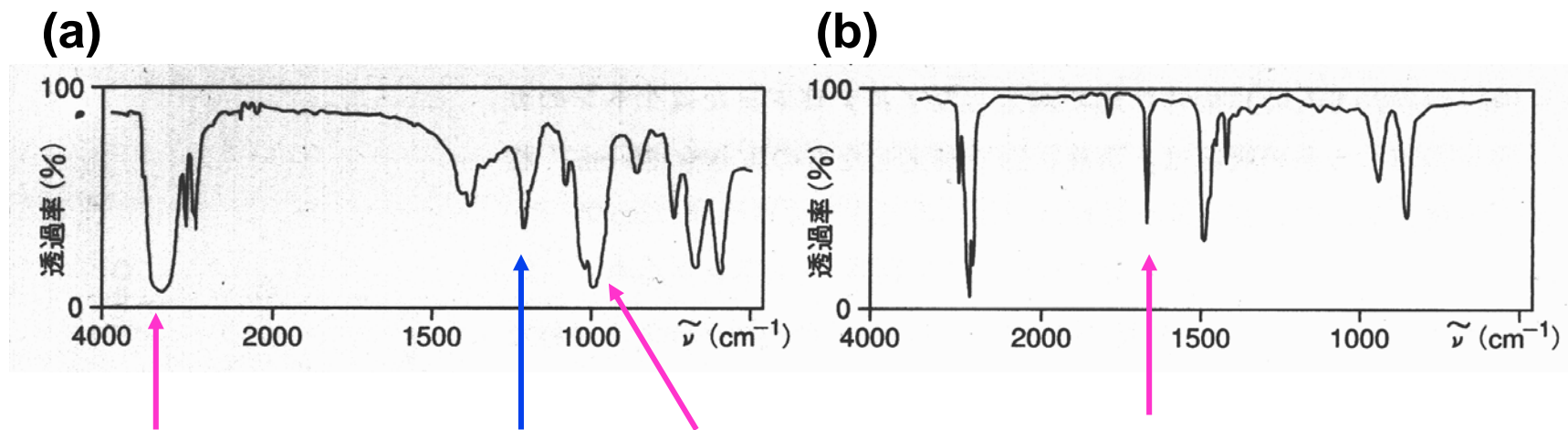
IRの吸収をしない結合を含むものはどれか？

acetone, 1-butyne, 2-butyne, H<sub>2</sub>, H<sub>2</sub>O, Cl<sub>2</sub>, ethene

# Chap. 4 赤外分光法 (IR)

テキスト p. 45

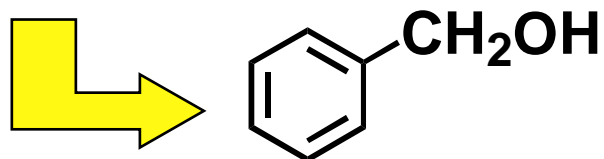
## 練習問題 3.1



O-H伸縮 3330  $\text{cm}^{-1}$   
O-H変角 1210  $\text{cm}^{-1}$   
C-O伸縮 1020  $\text{cm}^{-1}$

C=C伸縮 1640  $\text{cm}^{-1}$

プリント IR-2  
参照



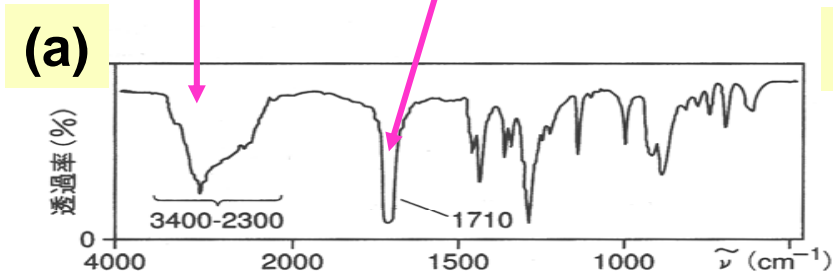
# Chap. 4 赤外分光法 (IR)

テキスト p. 46

## 練習問題 3.2

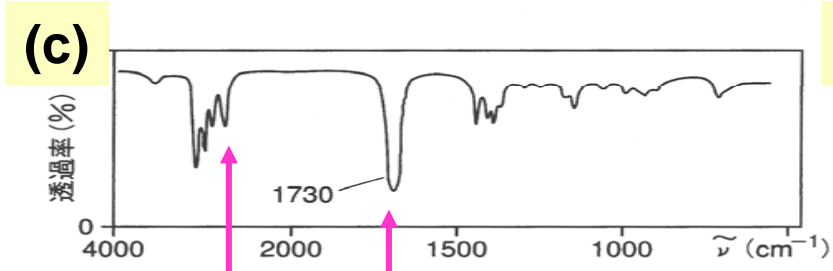
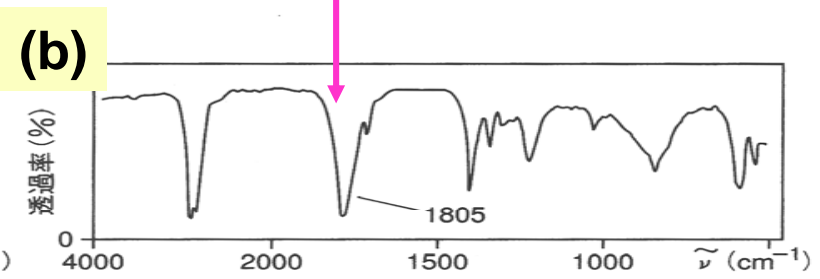
RCO<sub>2</sub>H

O-H伸縮 (broad) C=O伸縮



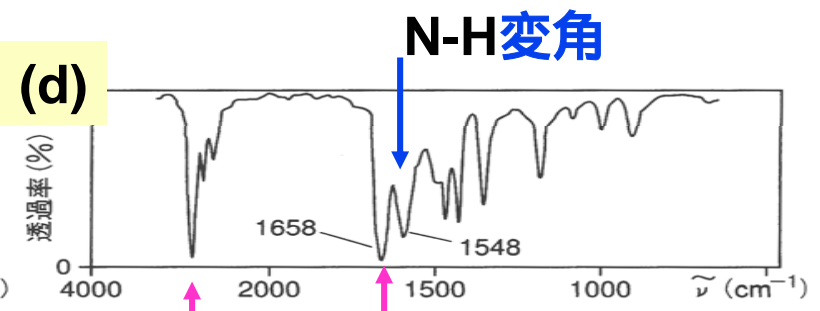
RCOCl

C=O伸縮 (ν<sub>max</sub>高)



OC-H伸縮 C=O伸縮 (ν<sub>max</sub>少し高)

RCHO

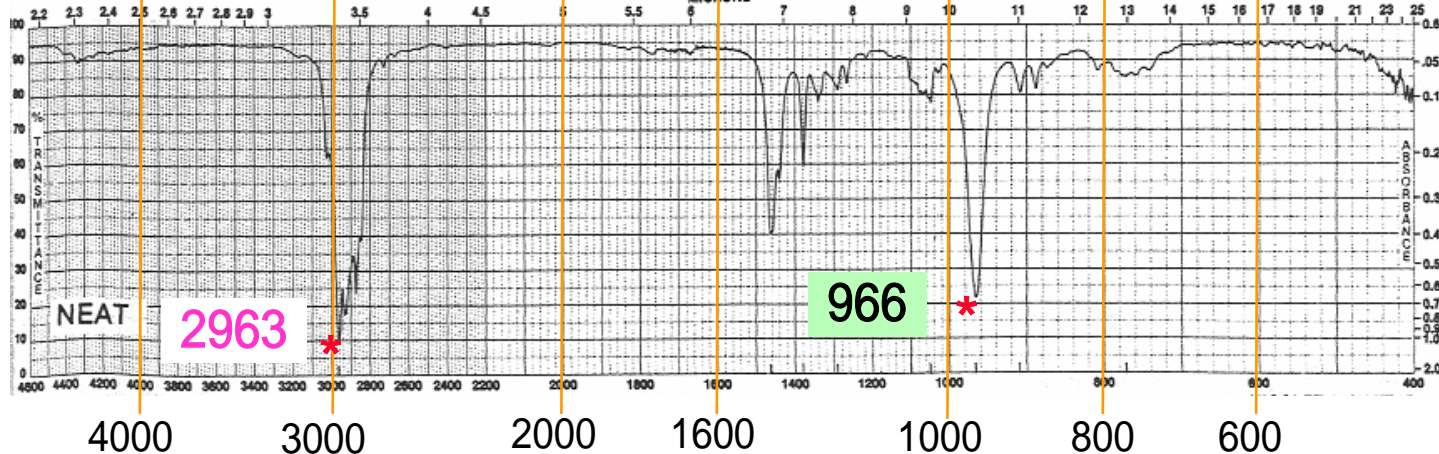
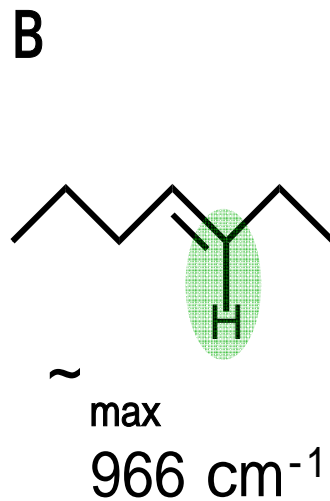
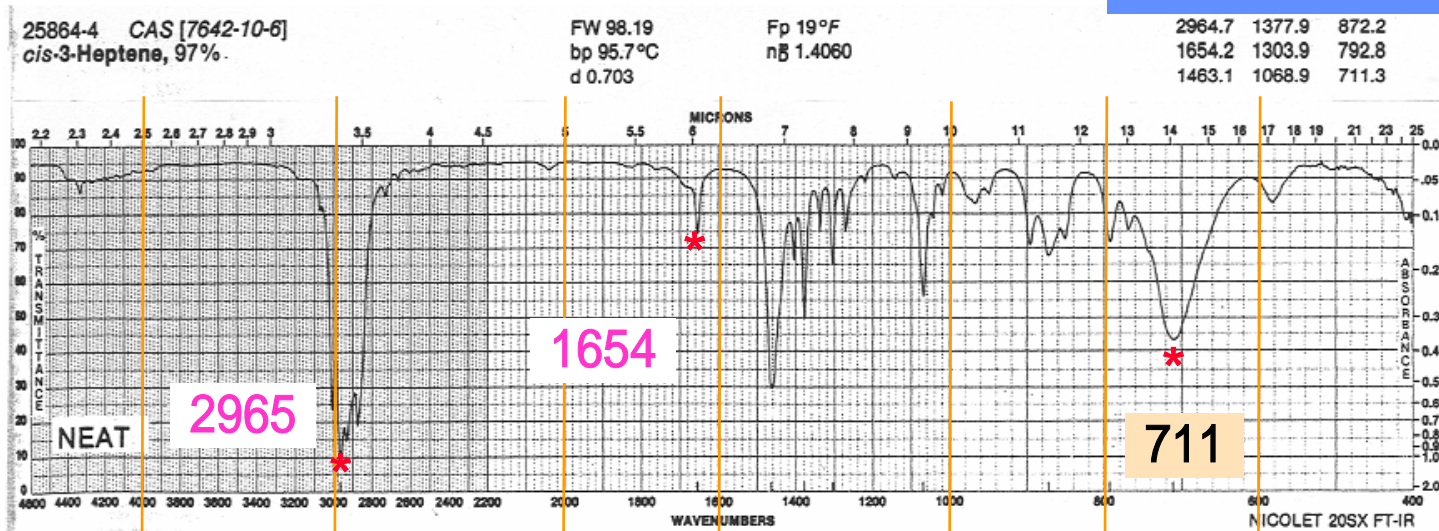
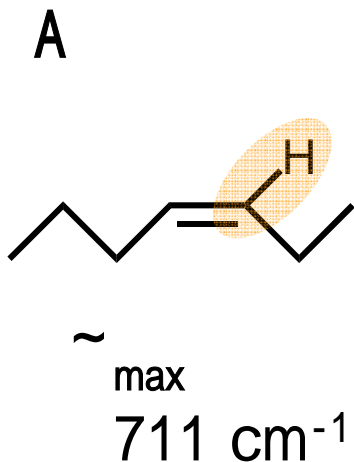


N-H変角 C=O伸縮 (ν<sub>max</sub>低) N-H伸縮

RCONH<sub>2</sub>

# IRスペクトル集

プリント IR-3

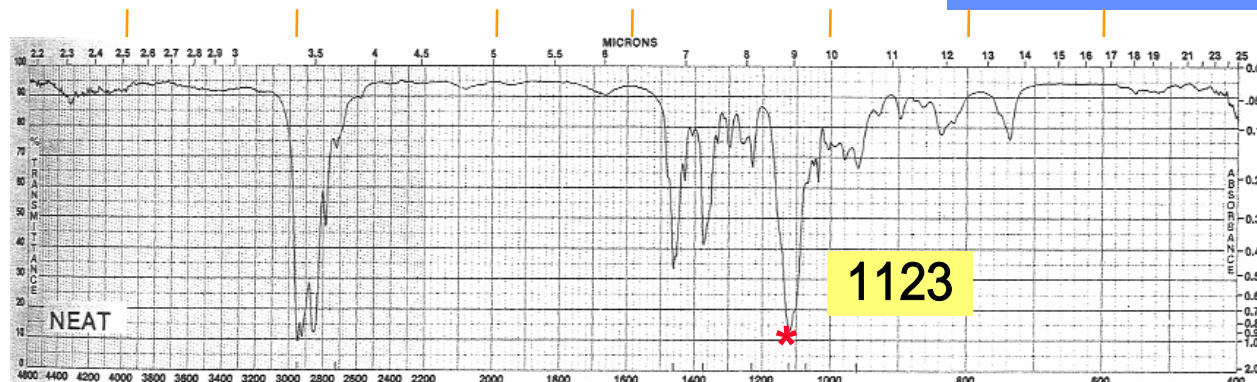
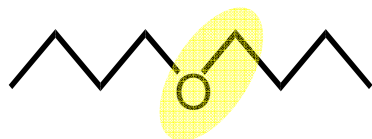


参考: テキスト 図3.10 (b)

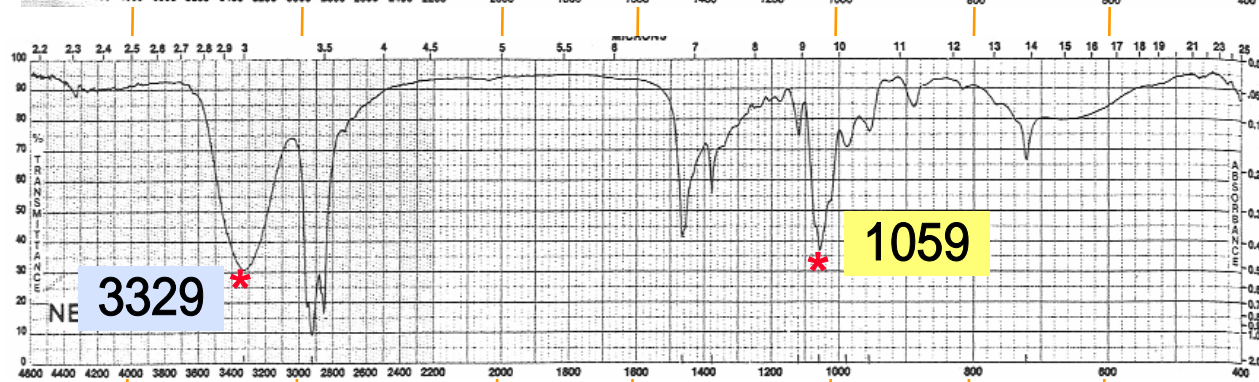
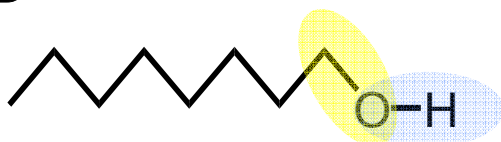
# IRスペクトル集

プリント IR-3

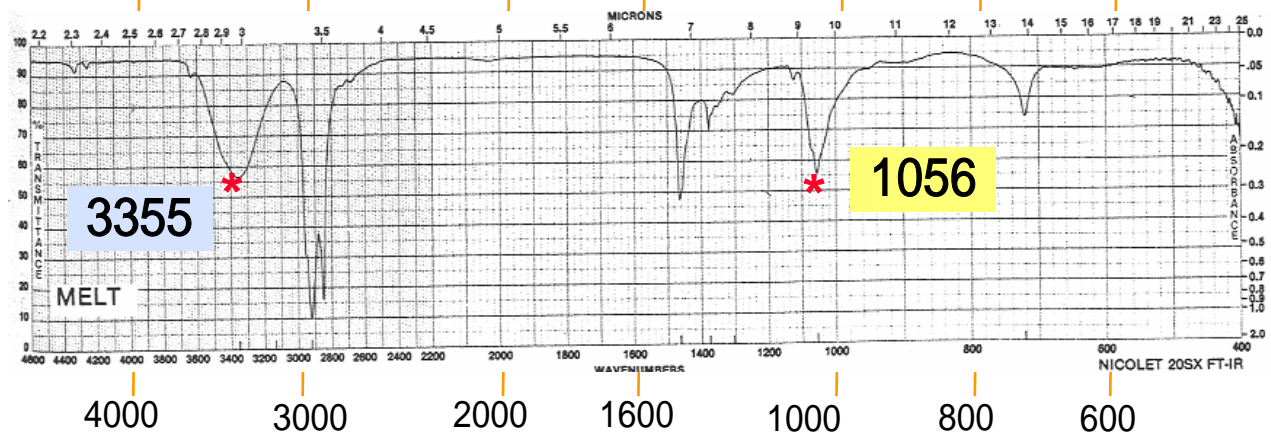
C



D



E



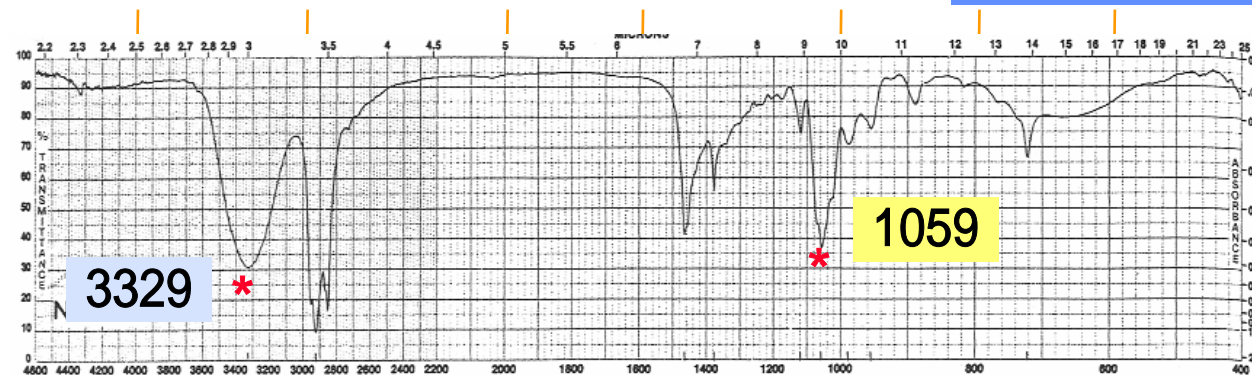
参考: テキスト 図3.7 (a)



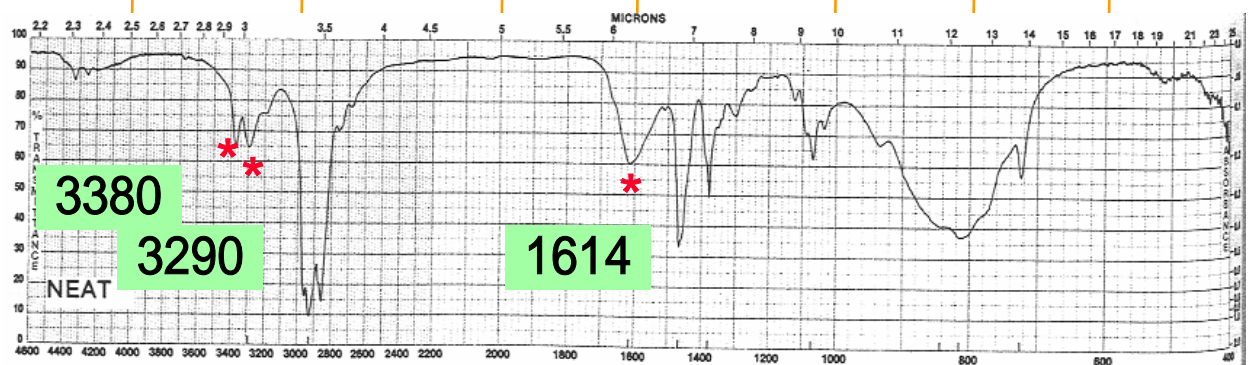
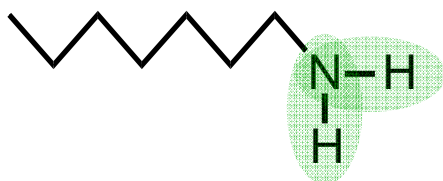
# IRスペクトル集

プリント IR-4

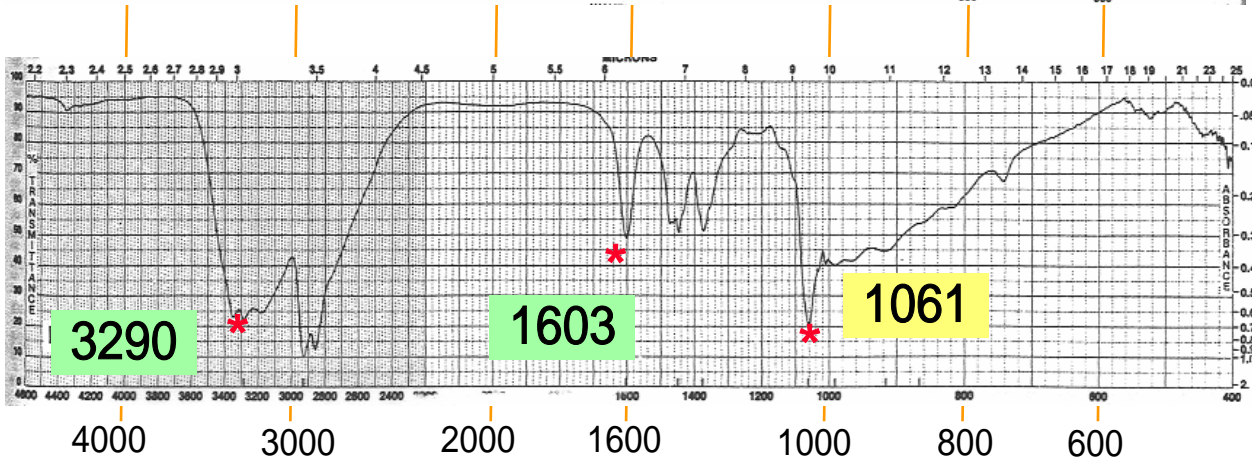
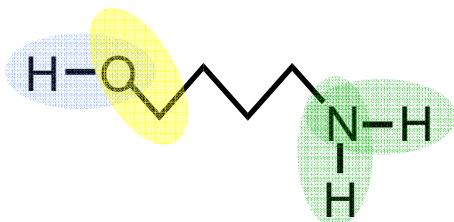
D



F



G

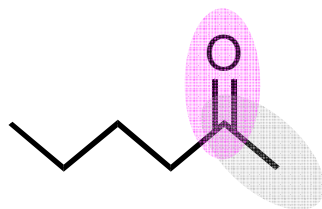


参考: テキスト 図3.7 (a)

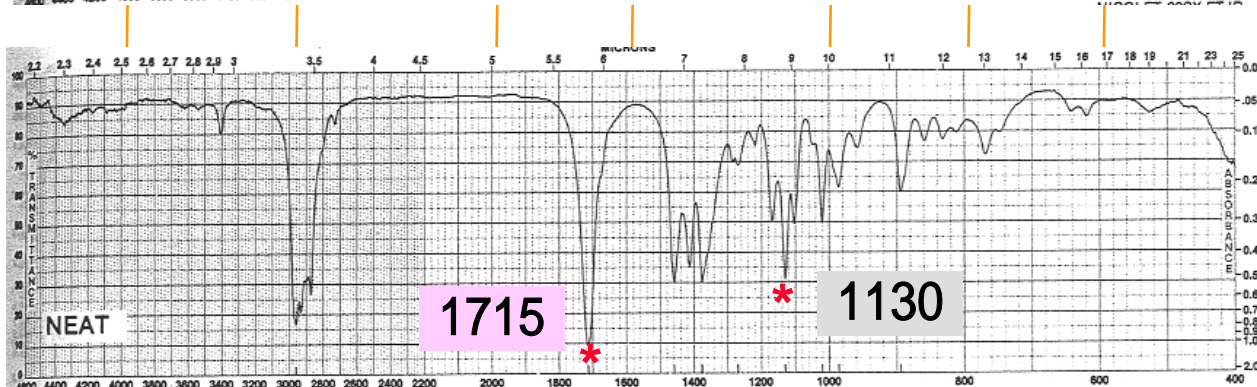
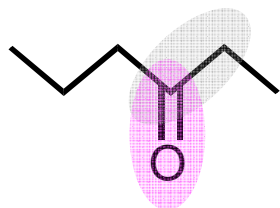
# IRスペクトル集

プリント IR-4

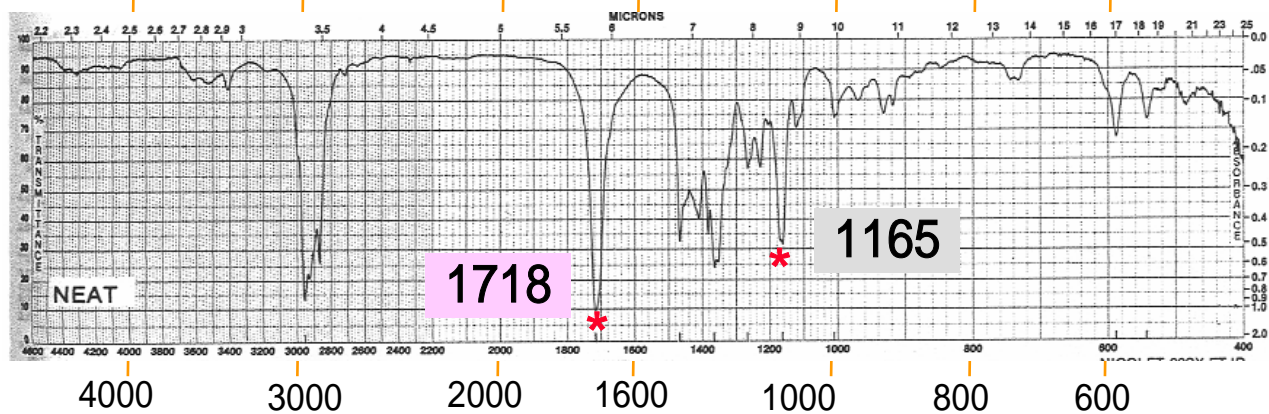
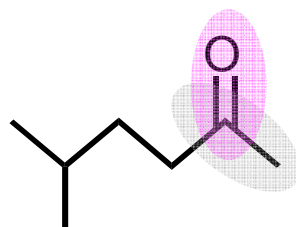
H



I



J

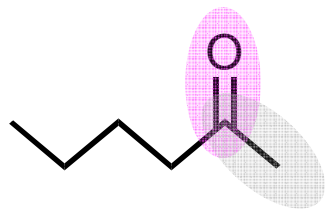


参考: テキスト 図3.14 (a, b)

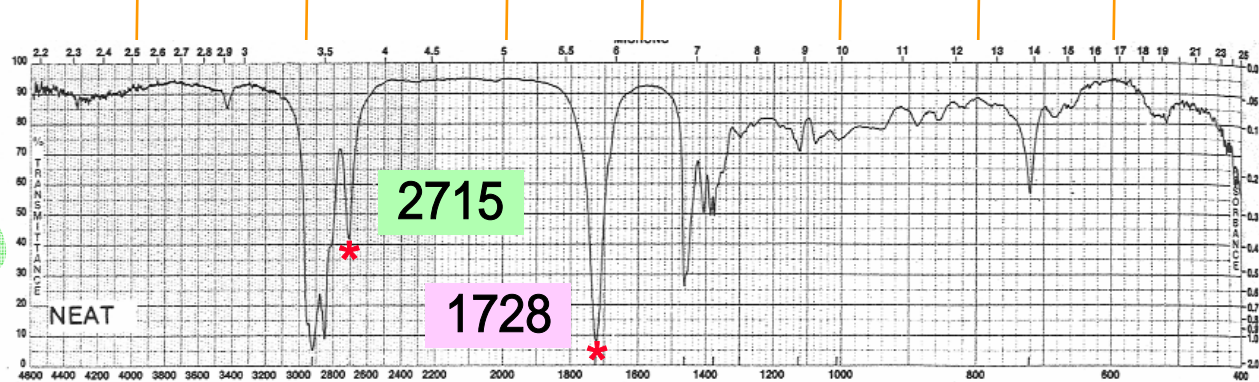
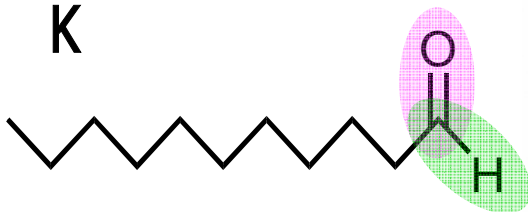
# IRスペクトル集

プリント IR-5

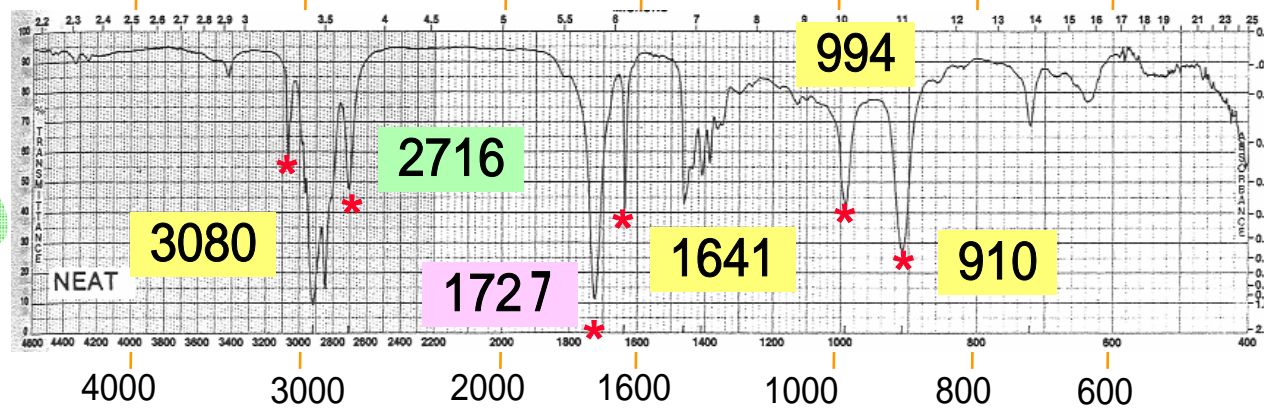
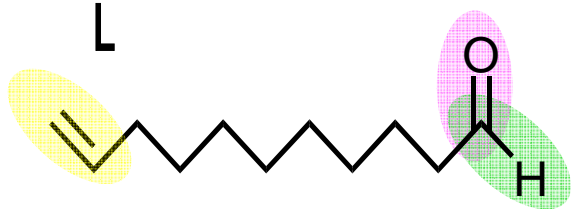
H



K



L

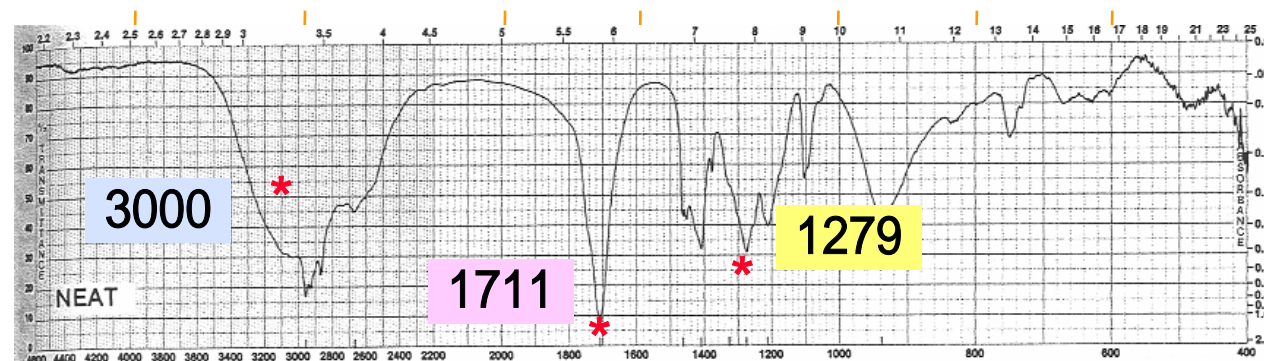
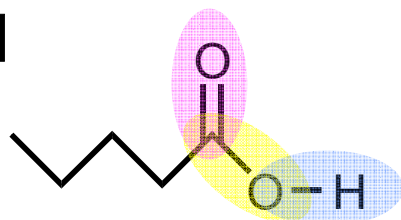


参考: テキスト 図3.11 (a, b)

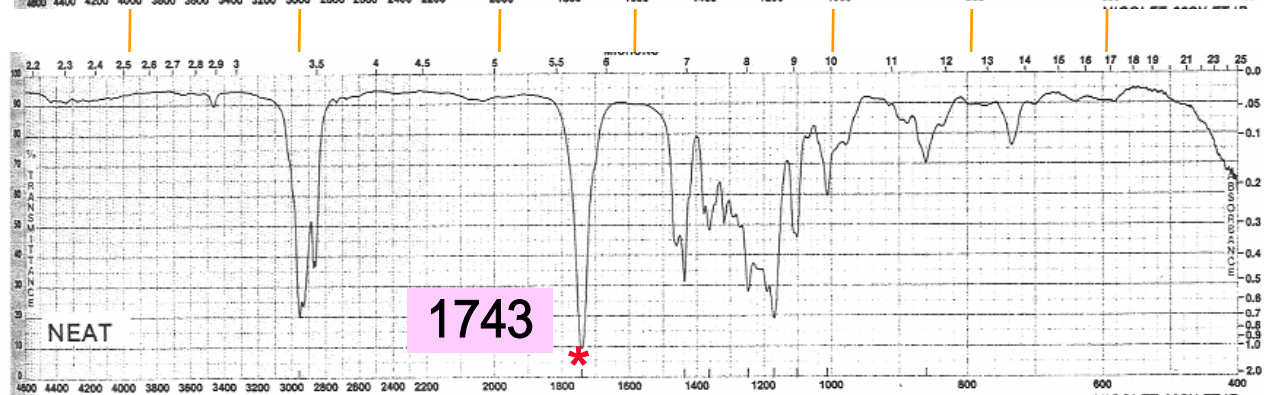
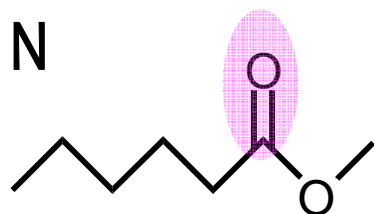
# IRスペクトル集

プリント IR-5

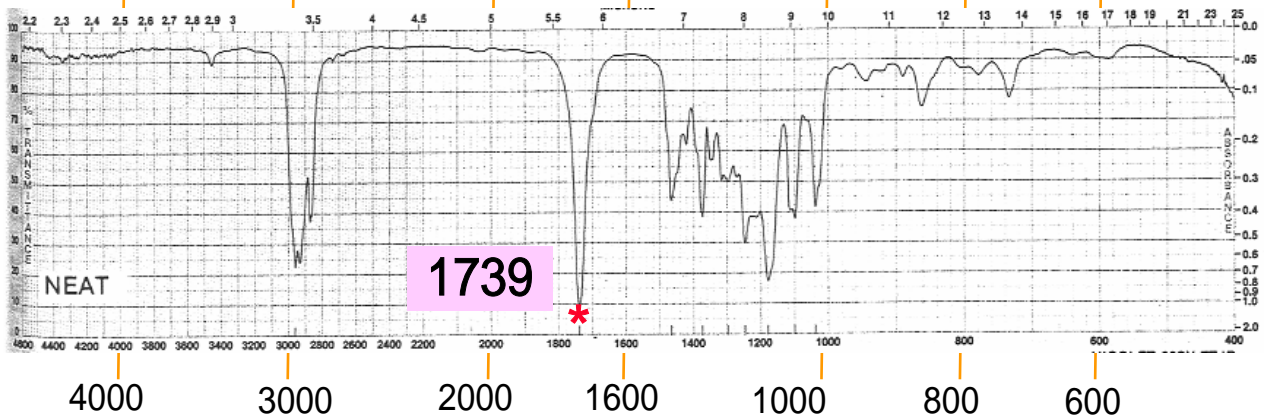
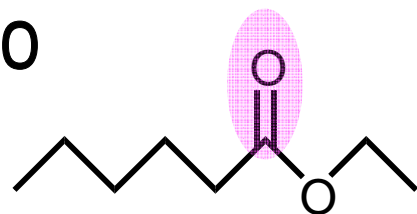
M



N



O



参考: テキスト 図3.7 (b)