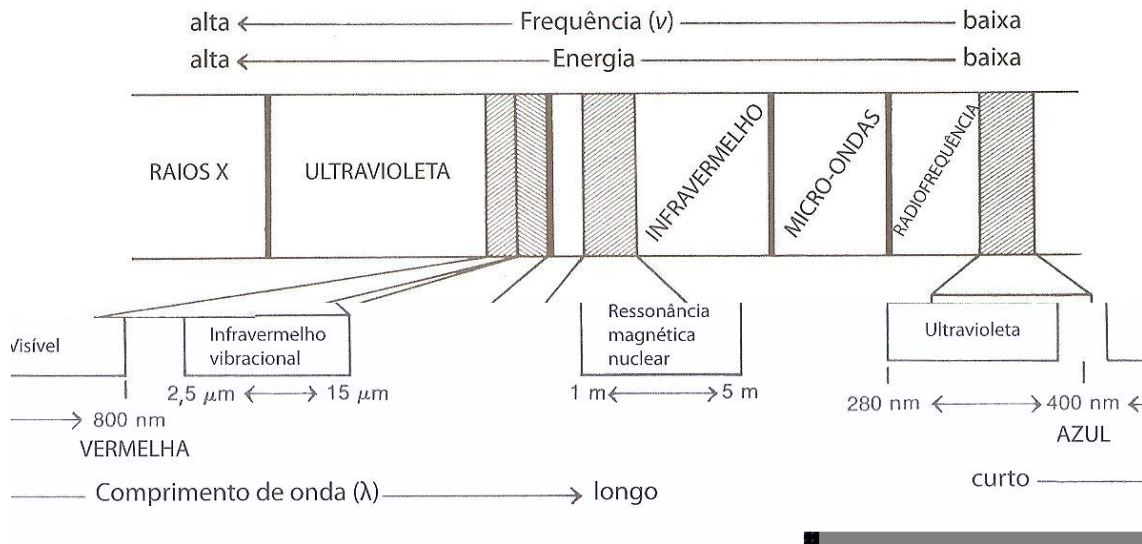


# ESPECTROMETRIA NO INFRAVERMELHO

## UMA PARTE DO ESPECTRO ELETROMAGNÉTICO



## VIBRAÇÕES DE ABSORÇÃO DE UM ÁLCOOL

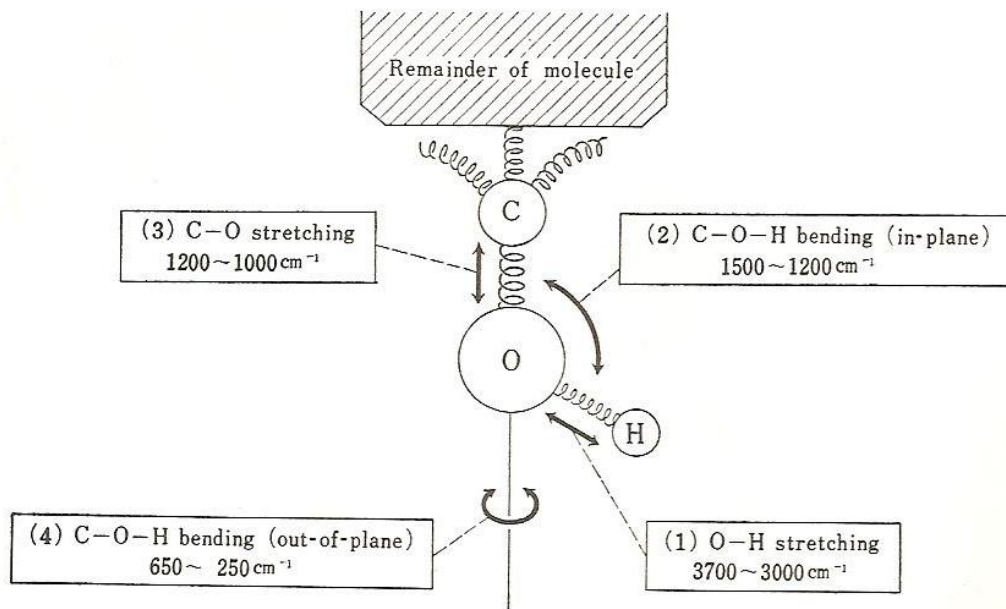
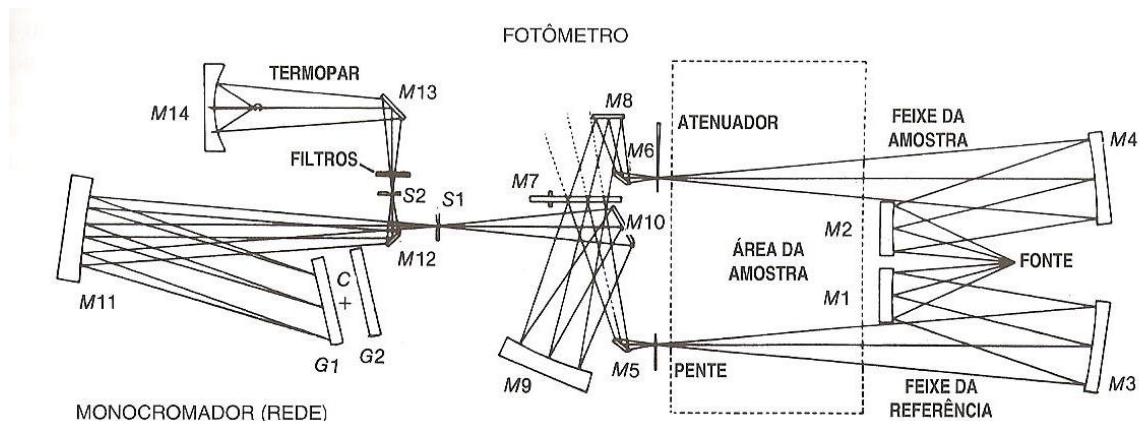


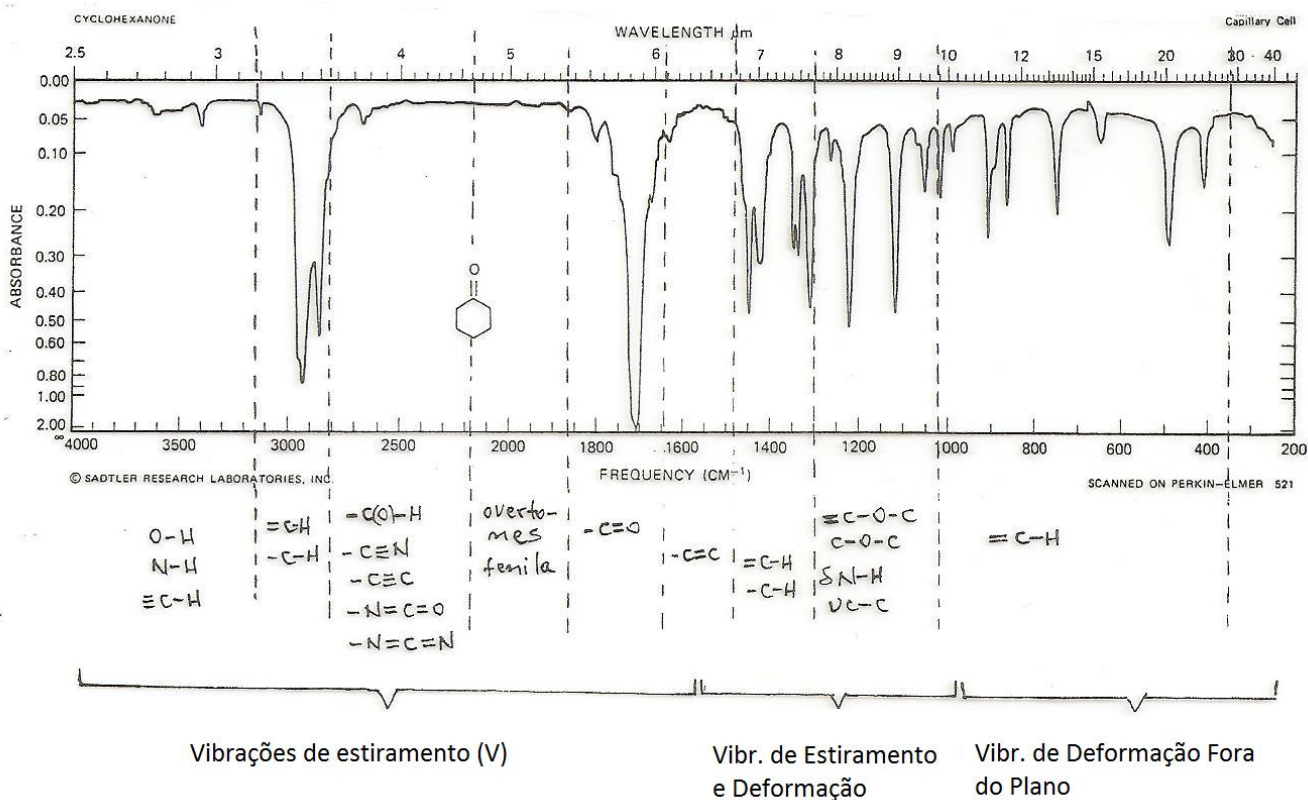
Fig. 1.2 Vibrations and absorptions of the alcoholic hydroxyl group.

# FIGURA ESQUEMÁTICA DE UM ESPECTRÔMETRO DE INFRAVERMELHO

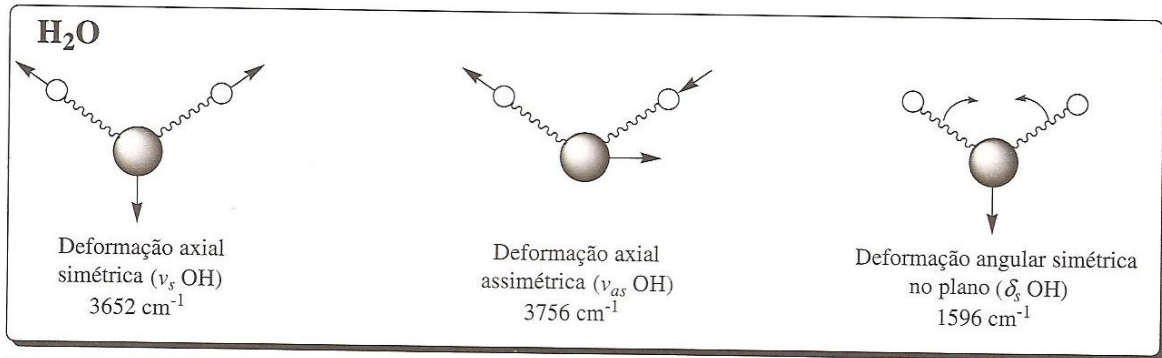


Sistema óptico de um espectrofotômetro de infravermelho de feixe duplo.

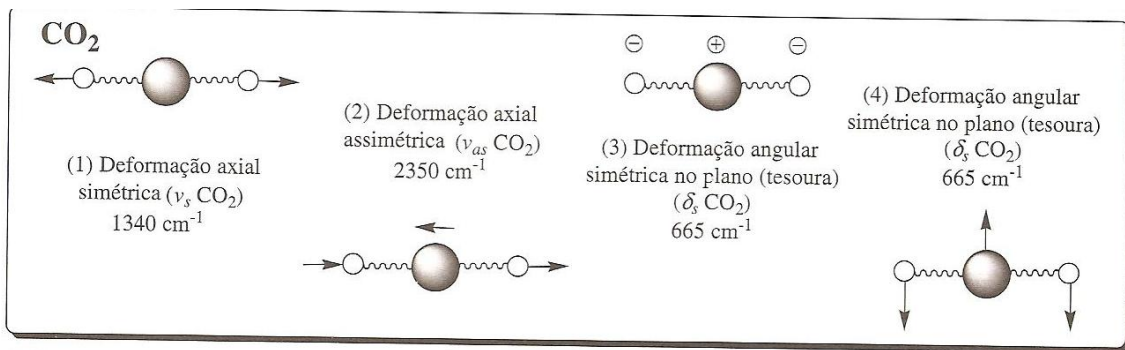
## O ESPECTRO DE INFRAVERMELHO



## VIBRAÇÕES FUNDAMENTAIS DA ÁGUA

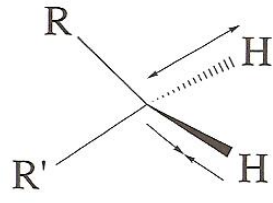
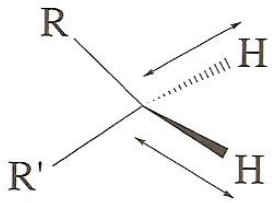


## VIBRAÇÕES FUNDAMENTAIS DO CO<sub>2</sub>

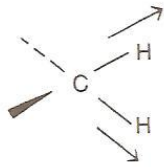


# VIBRAÇÕES FUNDAMENTAIS DE INFRAVERMELHO DO GRUPO CH<sub>2</sub>

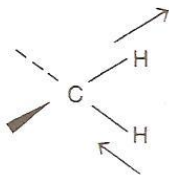
stretching vibrations



# VIBRAÇÕES FUNDAMENTAIS DE INFRAVERMELHO DO GRUPO CH<sub>2</sub>

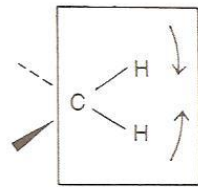


Estiramento simétrico  
(~2853 cm<sup>-1</sup>)

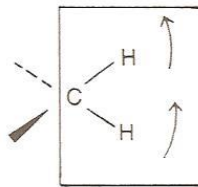


Estiramento assimétrico  
(~2926 cm<sup>-1</sup>)

## VIBRAÇÕES DE ESTIRAMENTO



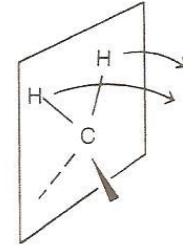
Scissoring  
(~1450 cm<sup>-1</sup>)



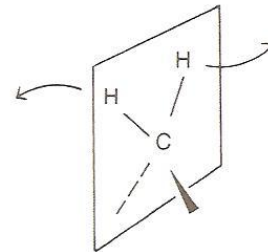
Rocking  
(~720 cm<sup>-1</sup>)

NO PLANO

## VIBRAÇÕES DE DOBRAMENTO



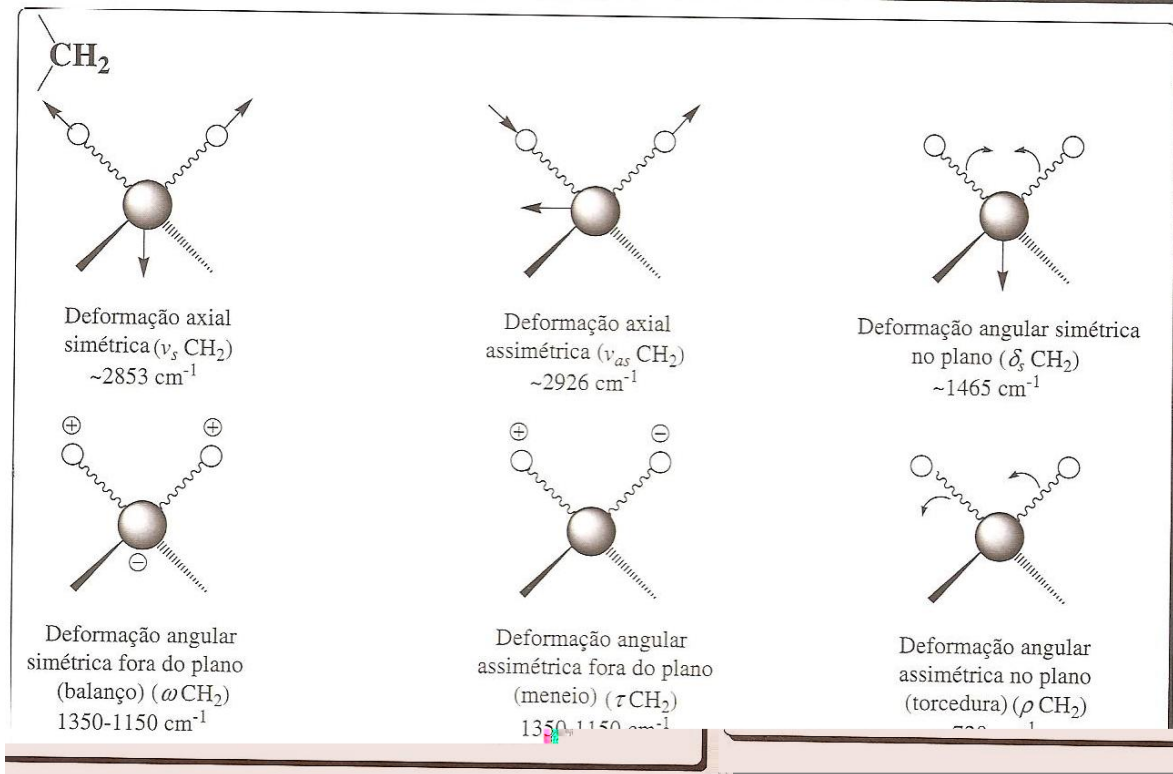
Wagging  
(~1250 cm<sup>-1</sup>)



Twisting  
(~1250 cm<sup>-1</sup>)

FORA DO PLANO

## VIBRAÇÕES FUNDAMENTAIS DE INFRAVERMELHO DO GRUPO CH<sub>2</sub>



## CÁLCULO DAS VIBRAÇÕES DE ESTIRAMENTO

Eq. DE HOOKE

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{f}{\frac{M_x M_y}{M_x + M_y}}}$$

$\nu$  = freq. vibracional

$c$  = veloc. da luz

$f$  = const. de força da ligação (dinas/cm)

$M_x, M_y$  = massas dos átomos  $x$  e  $y$  (em gramas).

$\pi$  = 3,1416

$f = 5 \times 10^5$  dinas/cm  $\rightarrow$  ligação simples  
 $= 10 \times 10^5$  " "  $\rightarrow$  " duplas  
 $= 15 \times 10^5$  " "  $\rightarrow$  " triplas

$$M_c = 19,8 \times 10^{-24} \text{ g}$$
$$= 1,64 \times 10^{-24} \text{ g}$$

TABLE 1 ALKANES  
(Non-diagnostic bands in italics)

Group	Band (cm <sup>-1</sup> )	Intensity (mole <sup>-1</sup> ·l·cm <sup>-1</sup> )	Assignment	Remarks	Figs.	
1) -CH <sub>3</sub>	2960	s 70	<i>ν</i> <sub>as</sub> CH <sub>3</sub>	C=C-CH <sub>3</sub> moved to higher frequency	(31)	
	2870	m 30	<i>ν</i> <sub>s</sub> CH <sub>3</sub>	2830~2815 ( <i>ε</i> <sup>a</sup> 35~75) in R-OMe, Ar-OMe[1]		(66)
				2820~2730 ( <i>ε</i> <sup>a</sup> 15~21) in -NMe, [2] lacking in -NEt.		(47)
	1460	m 15	<i>δ</i> <sub>as</sub> CH <sub>3</sub>	2820~2710 in methylenedioxy[3] C=C-CH <sub>3</sub> moved to higher frequency and split into doublet	(2)	
	1380	m 15	<i>δ</i> <sub>s</sub> CH <sub>3</sub>	Doublet in <i>gem</i> -dimethyl groups (see 5~7). See also (11)~(13). Shift on attachment to other atoms depends on electronegativity and C-X bond distance, e.g., -SCH <sub>3</sub> (1330), CH <sub>3</sub> I (1250), -SiCH <sub>3</sub> (1255), -BCl <sub>3</sub> (1322±7). [3a]	(2)	
2) -CH <sub>2</sub> -	2925	s 75	<i>ν</i> <sub>as</sub> CH <sub>2</sub>	1445 in cyclopentanes, 1450 in cyclohexanes. See also (14)~(15). Sometimes doublet in solid state. Present when <i>n</i> ≥ 4. Higher with smaller <i>n</i> . Pr 743~734; Et 790~770. -CH <sub>2</sub> - also has wag and twist band at ca. 1300 ( <i>ε</i> <sup>a</sup> 1). Solid state spectra of long chain with terminal polar group (acids, esters, amides) show regular series of bands at 1350~1180 (CH <sub>2</sub> wag).	(2)	
	2850	s 45	<i>ν</i> <sub>s</sub> CH <sub>2</sub>			
	1470	m 8	CH <sub>2</sub> scissor			
	725~720[4]	s 3	(CH <sub>2</sub> ) <sub>n</sub> rock			
3) $\begin{array}{c}   \\ -\text{C}-\text{H} \\   \end{array}$	2890	w	<i>ν</i> CH	Of no practical use.		
	1340	w	<i>δ</i> CH	Of no practical use.		
4) -(CH <sub>2</sub> ) <sub>4</sub> -O-	742~734		CH <sub>2</sub> rock	Corresponds to 720 band of (2).		
5) $\begin{array}{l} \text{CH}_3 \\ \diagup \\ \text{C}-\text{CH}- \\ \diagdown \\ \text{CH}_3 \end{array}$	1170	s Weaker than the 1380 ( <i>ε</i> <sup>a</sup> 15) doublet	skeletal	Doublet at 1380 suggests <i>gem</i> -dimethyl group; identification of this group then made by skeletal vibration (5)~(7).	(10)	
	1145			1145 band is shoulder on 1170 band.		
6) $\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{C}- \\   \\ \text{CH}_3 \end{array}$	1255	s "	"	Position more constant than 1210 band.		
	1210	s "	"	Absorption also at 930~925.		
7) quat. C $\begin{array}{c} \text{CH}_3 \\   \\ -\text{C}- \\   \\ \text{CH}_3 \end{array}$	1215	s "	"	Position of 1195 band more constant; 1215 band forms shoulder on 1195 band.	(20), (40)	
	1195	s "	"			
8) $\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\   \quad   \\ \text{R} \quad \text{H} \\   \\ \text{C} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \end{array}$ [5]	3070±10	m	<i>ν</i> <sub>as</sub> CH <sub>2</sub>	Lacking when ring carries no CH <sub>2</sub> .	(42)	
	3005±5	m	<i>ν</i> <sub>as</sub> CH			
	1020~1005	m 20~80	skeletal	Confirmatory only; often absent or obscured by other strong bands (hydroxyl, ether, etc.).		
	860					



## TABELA DE INTENSIDADES DAS BANDAS

TABLE 2.1 INTENSITIES

Intensity	$\epsilon^a$
very strong (vs)	200
strong (s)	75-200
medium (m)	25-75
weak (w)	5-25
very weak (vw)	0-5

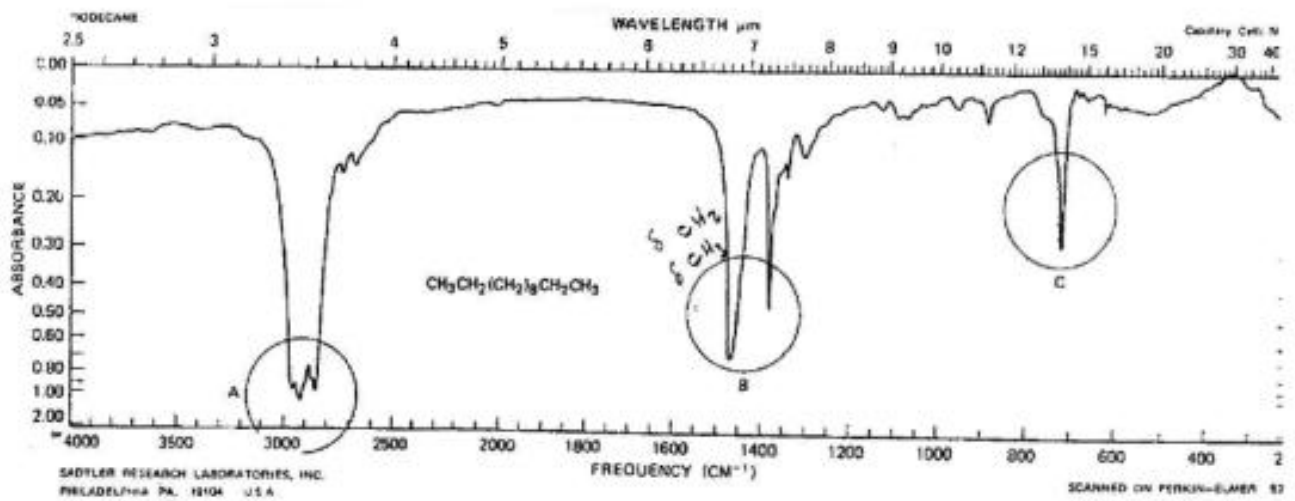


Figure 8. A. C-H stretch:  $2962\text{ cm}^{-1}$  ( $3.38\ \mu\text{m}$ )  $\nu_{\text{as}}\ \text{CH}_3$ ,  $2872\text{ cm}^{-1}$  ( $3.48\ \mu\text{m}$ )  $\nu_{\text{s}}\ \text{CH}_3$ ,  $2926\text{ cm}^{-1}$  ( $3.43\ \mu\text{m}$ )  $\nu_{\text{as}}\ \text{CH}_2$ ,  $2853\text{ cm}^{-1}$  ( $3.51\ \mu\text{m}$ )  $\nu_{\text{s}}\ \text{CH}_2$ . B. C-H bend:  $1465\text{ cm}^{-1}$  ( $6.83\ \mu\text{m}$ )  $\delta_{\text{s}}\ \text{CH}_2$ ,  $1450\text{ cm}^{-1}$  ( $6.90\ \mu\text{m}$ )  $\delta_{\text{as}}\ \text{CH}_2$ ,  $1375\text{ cm}^{-1}$  ( $7.28\ \mu\text{m}$ )  $\delta_{\text{s}}\ \text{CH}_3$ . C.  $\text{CH}_2$  rock:  $722\text{ cm}^{-1}$  ( $13.9\ \mu\text{m}$ )  $\rho\ \text{CH}_2$ .

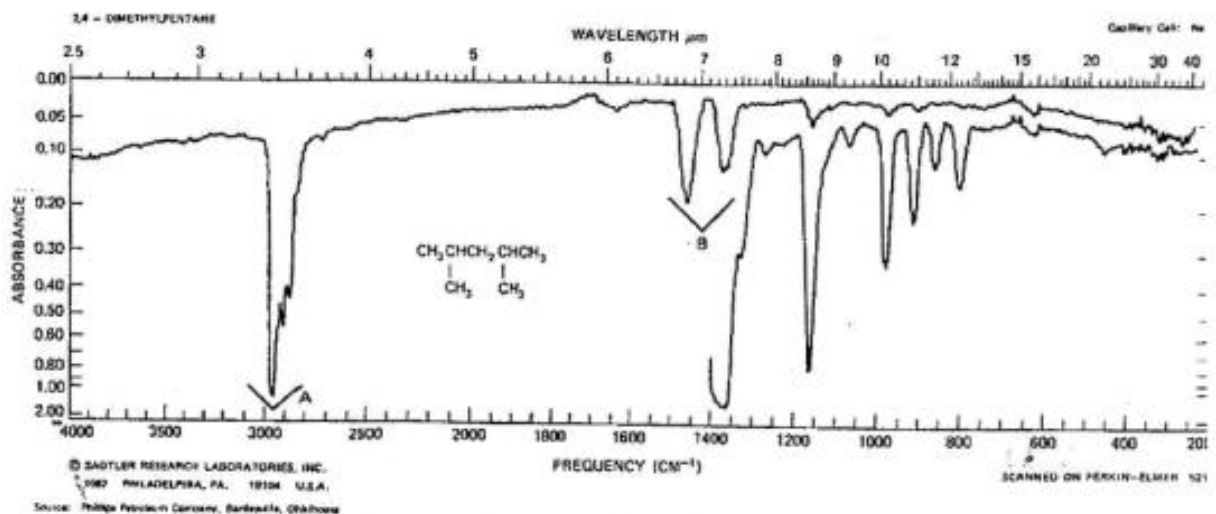


Figure 9. A. C-H stretch (see Figure 8). B. C-H bend (see Figure 8). There is an unresolved gem-dimethyl band for  $1385\text{--}1395\text{ cm}^{-1}$ . Compare the weak methylene rocking band(s) ( $800\text{--}1000\text{ cm}^{-1}$ ) to that for Figure 8. (A. see absorption C in Figure 16.)

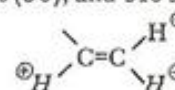
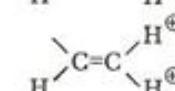
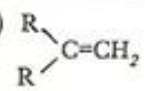
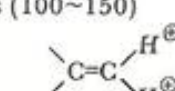
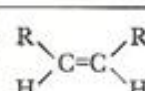
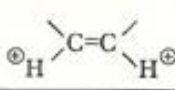
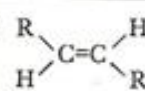
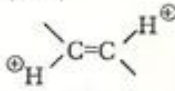
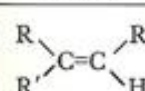
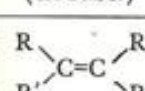
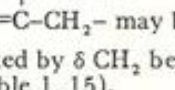
CH stretching frequencies **TABLE 2 ALKENES** (Non-diagnostic bands in italics)  
( $\epsilon^a$  in parentheses)

1) =CH <sub>2</sub>	3080, m (30) 2975, m	$\nu_{as}$ CH <sub>2</sub> $\nu_s$ CH <sub>2</sub>	2975 band overlaps with alkane absorption. Bands higher than 3000 suggest presence of unsaturated =CH- (alkenes, aromatics).
2) =CH-	3020, m	$\nu$ CH <sub>2</sub>	

Substitution type ( $\epsilon^a$  in parentheses)

## ALCENOS (Continuação)

Substitution type ( $\epsilon^a$  in parentheses)

Type	Overtone of $\delta$ CH (out-of-plane)	$\nu$ C=C	$\delta$ CH (in-plane)	$\delta$ CH (out-of-plane)	Figs.
3) R/CH=CH <sub>2</sub> (term. vinyl)	1860~1800 m (30)	1645, m (40)	1420, m (10~20) Same region as in Table 1, 14~16. 1300, m~w	990 s (50), and 910 s (110); 990  910 	(5), (19) (24)
4)  (term. methylene)	1800~1750 m (30)	1655, m (35)	1415, m (10~20) Same region as in Table 1, 14~16.	890 s (100~150) 	(3), (20)
5)  (cis)		1660, m (10)	1415, m (10~20)	730~675 m (40), ambiguous and variable. 	(5), (6)
6)  (trans)		1675, w (2)		965 s (100) 	(5)
7)  (tri-subst.)		1670, w~m		840~800 s (40). Vibration of single H; not as useful as others.	(3), (19)
8)  (tetra-subst.)		1670, w Intensified if bonded directly to O or N.		No out-of-plane bending (H absent), but  may be detected by $\delta$ CH <sub>2</sub> bending (Table 1, 15).	

## ALCENOS (Continuação)

Conjugated double bonds			
Group	$\nu$ C=C	$\delta$ CH (out-of-plane)	Figs.
9) Diene	1650 and 1600	Position not affected much by conjugation. The <i>trans</i> 965 band is sometimes shifted to 990. The <i>cis</i> band is usually found at 720, occasionally as a group of bands.	④
10) Triene	1650 and 1600; sometimes only one band; sometimes additional shoulder on 1650 band.	<i>trans-cis-trans</i> and <i>cis-trans-trans</i> systems have bands at 990 s, 960 m, and 720.	⑤
11) Polyene	Broad band at 1650~1580.	990~970 if <i>trans</i> -double band present.	⑥
12) Enones	— see Table 8 (p. 16).		

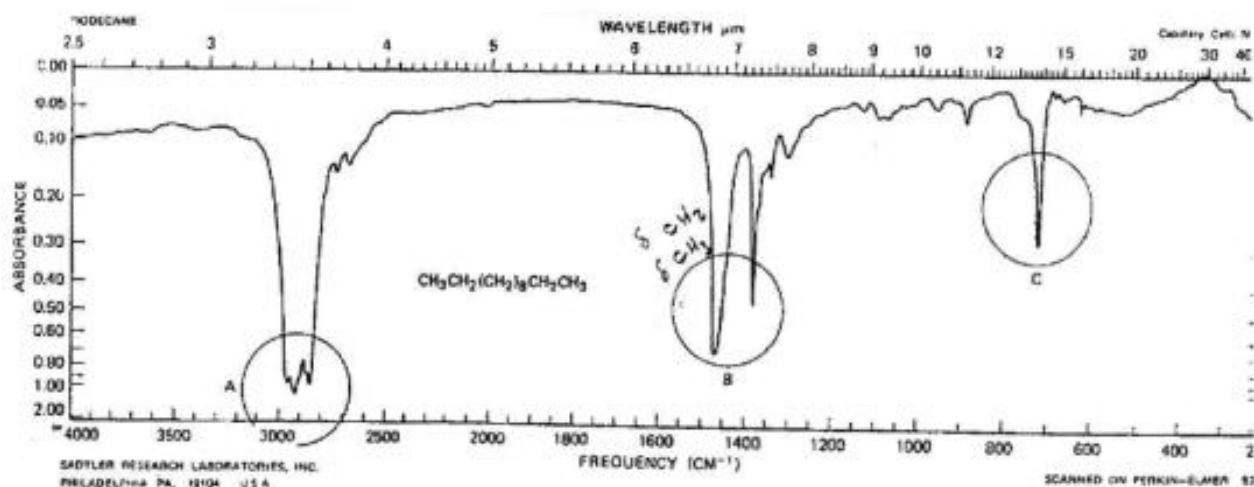


Figure 8. A. C-H stretch:  $2962\text{ cm}^{-1}$  ( $3.38\ \mu\text{m}$ )  $\nu_{\text{as}}\ \text{CH}_3$ ,  $2872\text{ cm}^{-1}$  ( $3.48\ \mu\text{m}$ )  $\nu_{\text{s}}\ \text{CH}_3$ ,  $2926\text{ cm}^{-1}$  ( $3.43\ \mu\text{m}$ )  $\nu_{\text{as}}\ \text{CH}_2$ ,  $2853\text{ cm}^{-1}$  ( $3.51\ \mu\text{m}$ )  $\nu_{\text{s}}\ \text{CH}_2$ . B. C-H bend:  $1465\text{ cm}^{-1}$  ( $6.83\ \mu\text{m}$ )  $\delta_{\text{s}}\ \text{CH}_2$ ,  $1450\text{ cm}^{-1}$  ( $6.90\ \mu\text{m}$ )  $\delta_{\text{as}}\ \text{CH}_2$ ,  $1375\text{ cm}^{-1}$  ( $7.28\ \mu\text{m}$ )  $\delta_{\text{s}}\ \text{CH}_3$ . C.  $\text{CH}_2$  rock:  $722\text{ cm}^{-1}$  ( $13.9\ \mu\text{m}$ )  $\rho\ \text{CH}_2$ .

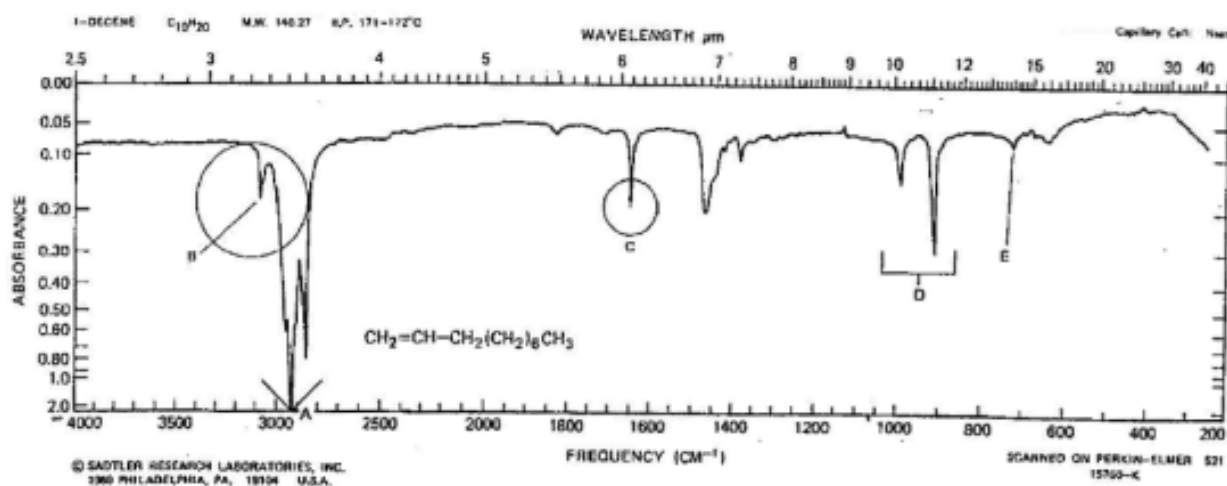


Figure 10. A. C-H stretch (see Figure 8). Note olefinic C-H stretch (B) at  $3049\text{ cm}^{-1}$  ( $3.28\ \mu\text{m}$ ). C. C=C stretch,  $1645\text{ cm}^{-1}$  ( $6.08\ \mu\text{m}$ ), see Table III of Appendix D. D. Out-of-plane C-H bend:  $986\text{ cm}^{-1}$  ( $10.14\ \mu\text{m}$ ), (olefinic)  $907\text{ cm}^{-1}$  ( $11.03\ \mu\text{m}$ ). E. (methylenic rock)  $720\text{ cm}^{-1}$  ( $13.89\ \mu\text{m}$ ).

## Espectros de IV de ALCENOS

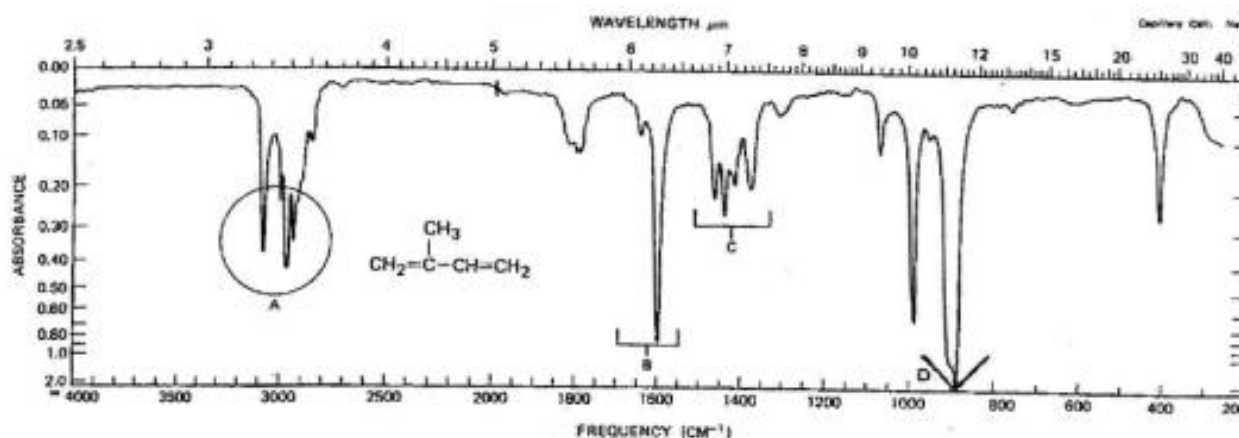


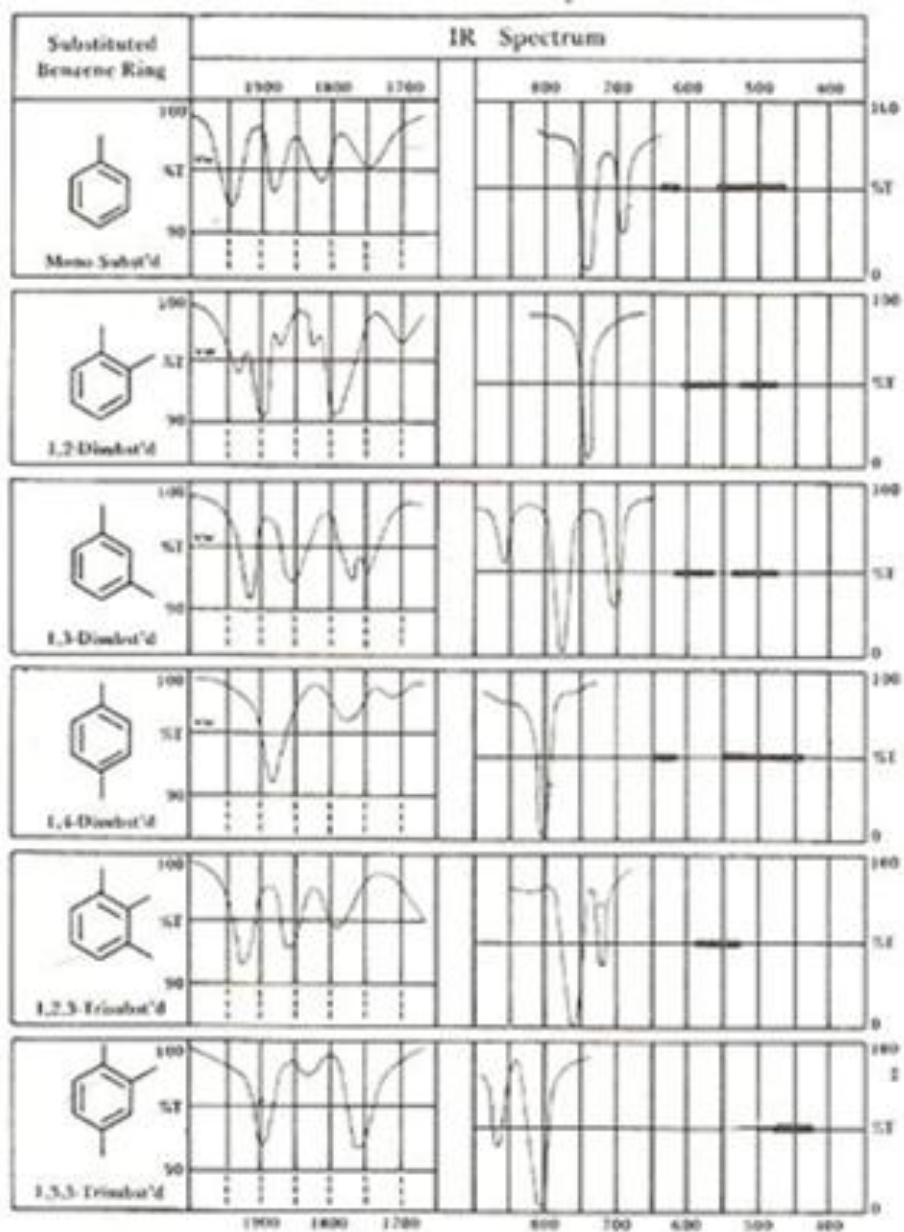
TABLE 3 AROMATICS

(Non-diagnostic bands in italics)

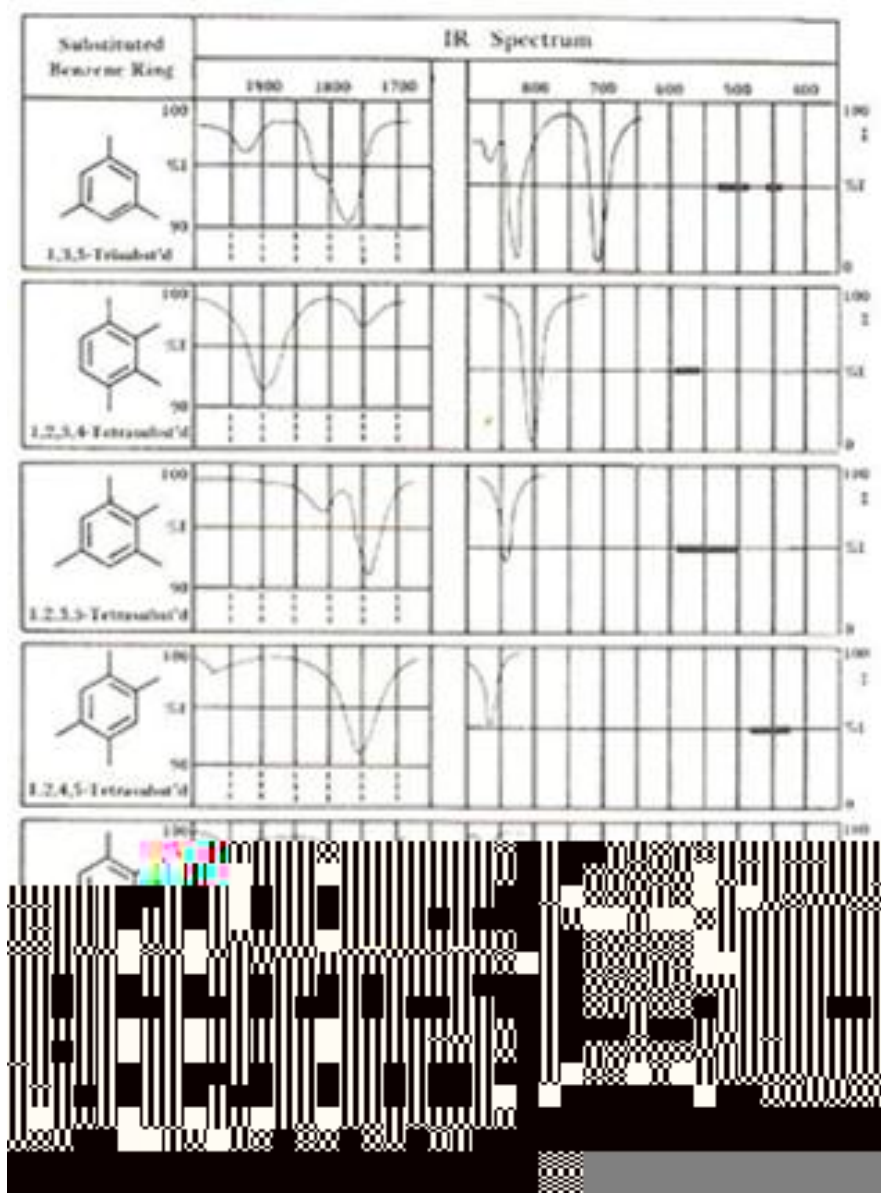
Phenyls (naphthalenes, phenanthrenes, etc., are similar)

Position	Intensity, $\epsilon^a$	Assignment	Remarks	Figs.
1) ~3030, several	less than 60	$\nu$ CH and combination	With NaCl prisms, the bands frequently appear only as a weak shoulder on the main $\nu$ CH aliph. band. In certain arom. compounds, the main absorption appears below 3000 $\text{cm}^{-1}$ .	(7), (9)
2) 2000~1660 several bands (Fig. 2.1)	w, ~5	Overtone of $\delta$ CH (out-of-plane) and combination	Group of 2 to 6 bands characteristic of substitution pattern; identified by comparison with standard curves, e.g. alkylbenzenes. Hidden by strong bands due to C=O, etc. Sample concentration should be more than ten times that of normal.	(7), (9)
3) 1600, (1580), 1500, (1450)	$\epsilon^a$ variable but usually less than 100. The 1600 $\text{cm}^{-1}$ band sometimes stronger than C=C band.	Phenyl nucleus	Variable intensity, 1500 usually stronger than 1600. In principle, 1580 band only appears when phenyl is conjugated with unsatd. groups or groups having lone pair electrons. Conj. intensifies all 3 peaks but positions not affected. 1450 $\text{cm}^{-1}$ peak overlaps with $\text{CH}_2$ band. Condensed systems absorb at 1650~1600, (1600), 1525~1450 (two) $\text{cm}^{-1}$ ; pyridines similar to phenyl group.	(7), (9) (11), (31)

# PADRÃO DE SUBSTITUIÇÃO BENZENOS SUBSTITUÍDOS

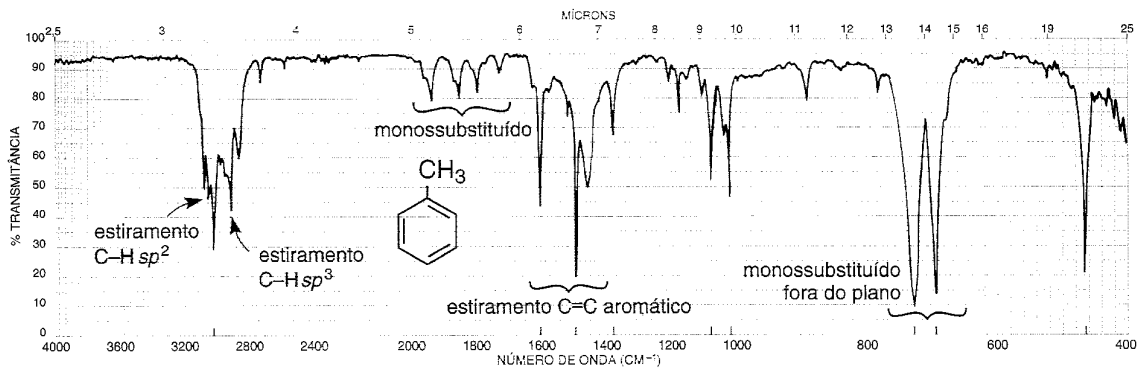


# PADRÃO DE SUBSTITUIÇÃO BENZENOS SUBSTITUÍDOS

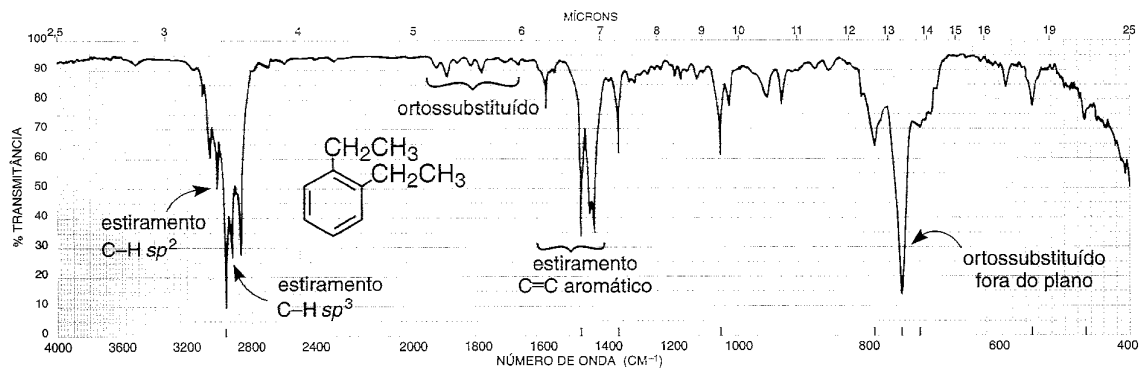




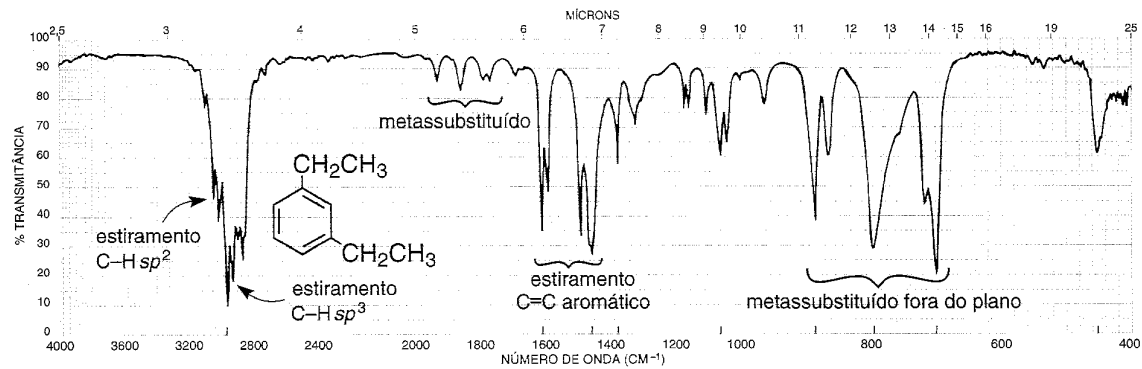
## Espectral de benzenos substituídos



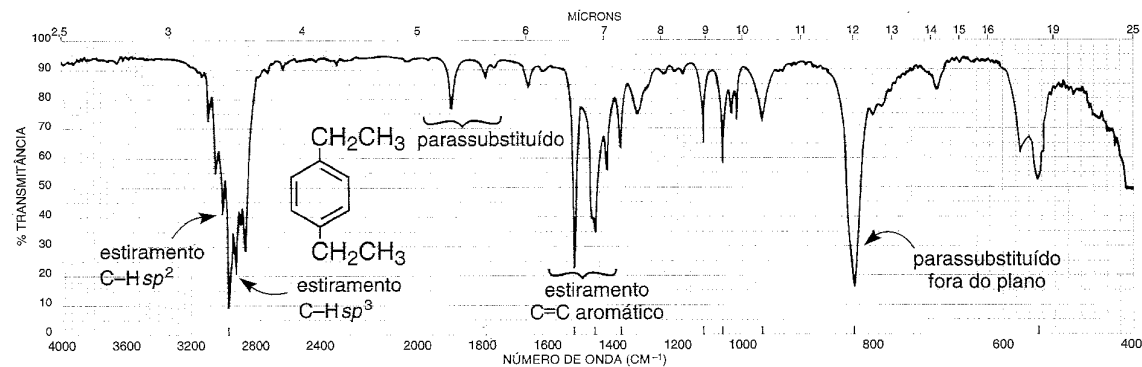
Espectro infravermelho do tolueno (líquido puro, placas de KBr).



Espectro infravermelho do *orto*-dietilbenzeno (líquido puro, placas de KBr).



Espectro infravermelho do *meta*-dietilbenzeno (líquido puro, placas de KBr).



Espectro infravermelho do *para*-dietilbenzeno (líquido puro, placas de KBr).

## DIFERENÇAS ENTRE UM ÁLCOOL E UM FENOL

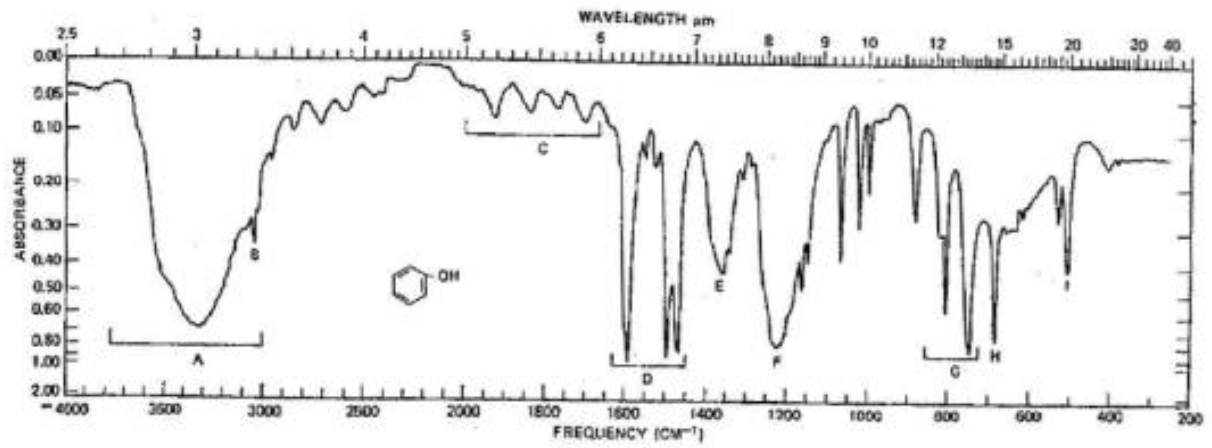
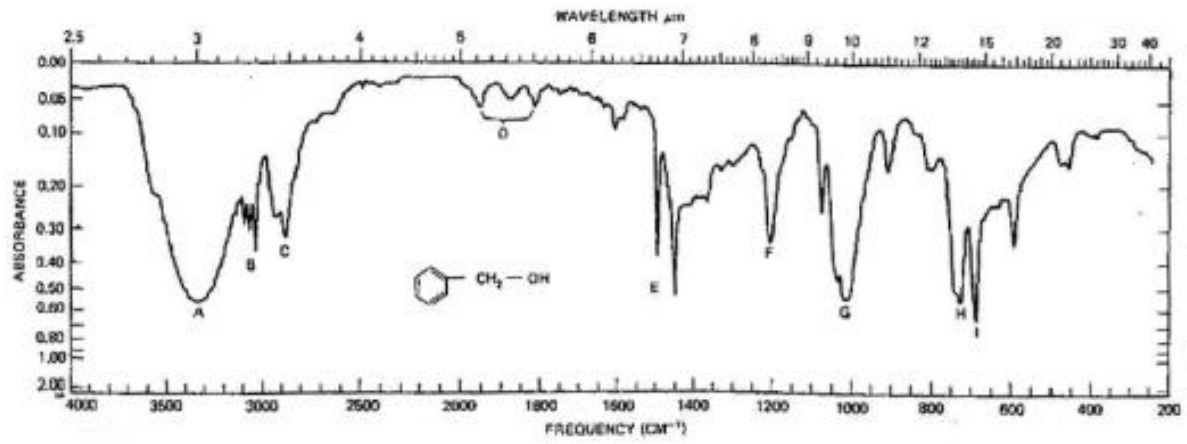


TABLE 4 X≡Y, X≡Y=Z GROUPS

Group	Band (cm <sup>-1</sup> )	ε <sup>a</sup>	Remarks	Ref.	Figs.
1) Acetylene, -C≡C-	terminal position: 2140~2100	5	sp <sup>3</sup> CH appears sharply at 3300 cm <sup>-1</sup> , ε <sup>a</sup> 100. ≡C-H also shows bending at 700~600, and occasionally its overtone at 1300~1200 cm <sup>-1</sup> .	1	(16), (16)
	central: 2260~2190 1330±5	1	Completely absent when symmetry is high. Medium to weak, sharp. CH <sub>2</sub> wag of C≡C-CH <sub>2</sub> -.		

Espectros de IV de ALCINOS

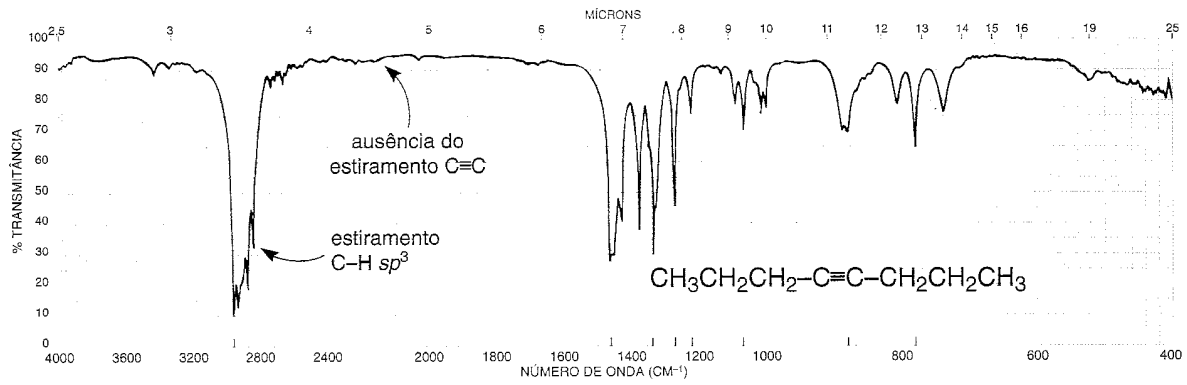
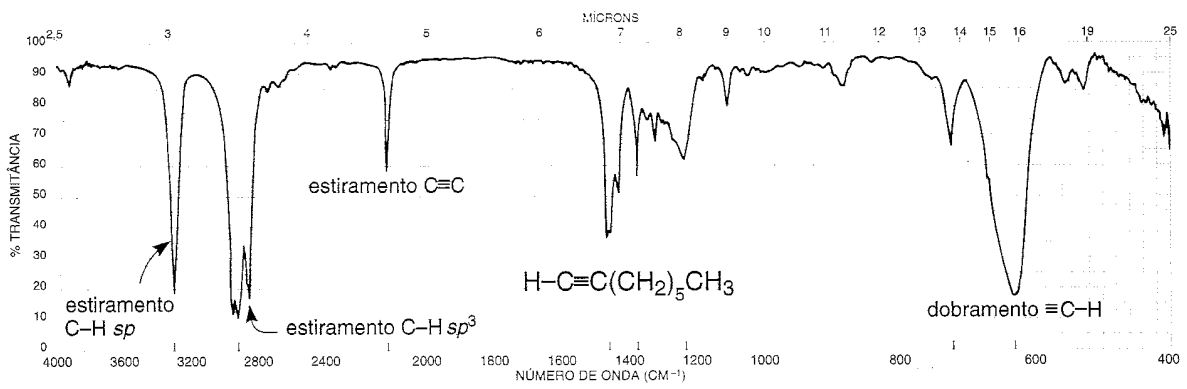


TABLE 4 X=Y, X=Y=Z GROUPS

2) Nitrile, -C≡N	2260~2210	Variable, 10~150	The lower wave-number region indicated is observed when conjugated to other unsatd. groups or when contained in cyanamide (N-CN) group.  Alkali metal salts show very intense bands ( $\epsilon_a 10^4 \sim 10^5$ ) for the carbanion at 2100~2050. Position varies with counter ion and physical state.	2 3  18	(13)
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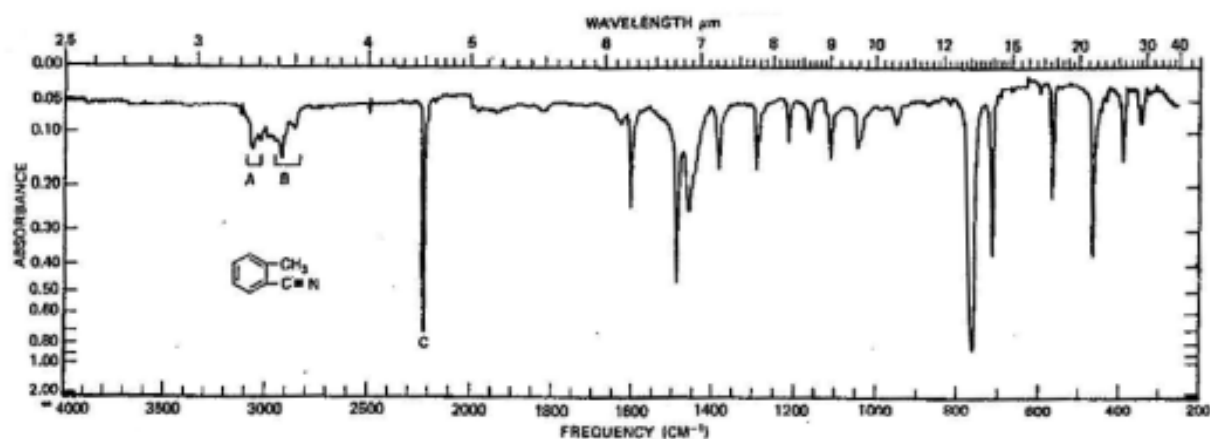
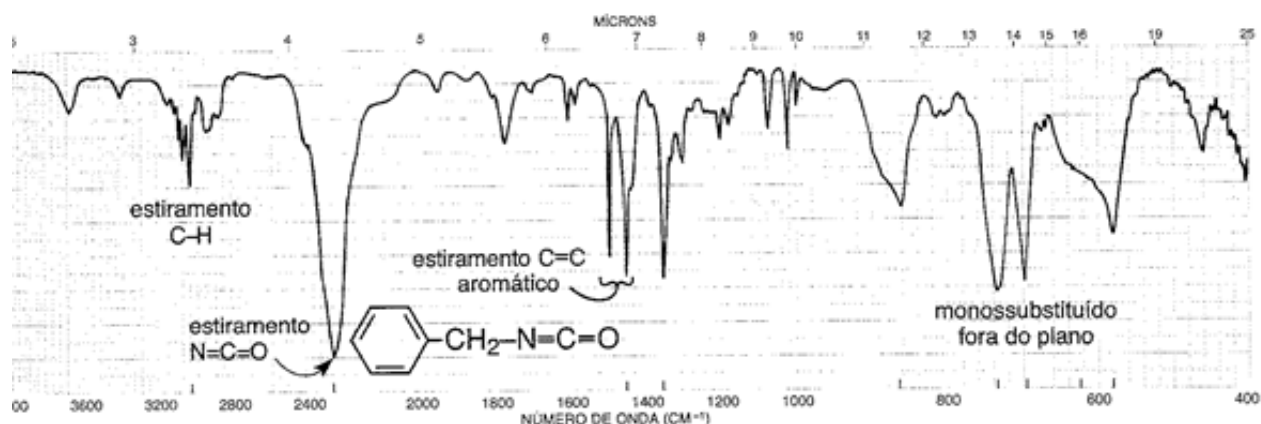


TABLE 4 X=Y, X=Y=Z GROUPS

6) Isocyanate, -N=C=O	2275~2250  1350	1500~2000	Extremely strong, position not affected by conj.  No practical value because of weak intensity and overlapping with CH <sub>2</sub> peak.	8,9	(11)
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Espectro infravermelho de isocianato de benzila (líquido puro, placas de KBr).

TABLE 4 X=Y, X=Y=Z GROUPS

9) Thiocyanate, -S-C=N	{ aliphatic: 2140 { aromatic: 2175~2160 { aliphatic: 2140~1990 { aromatic: 2130~2040	Stronger than isocyanates	Integrated intensity has been measured.  Somewhat broad, frequently split or accompanied by shoulders. Other bands: aliph. 1090 (s), arom. 1250 (w) and 930 cm <sup>-1</sup> (s). [12]	12,	(14)
Isothiocyanate, -N=C=S				13,	

TABLE 4 X=Y, X=Y=Z GROUPS

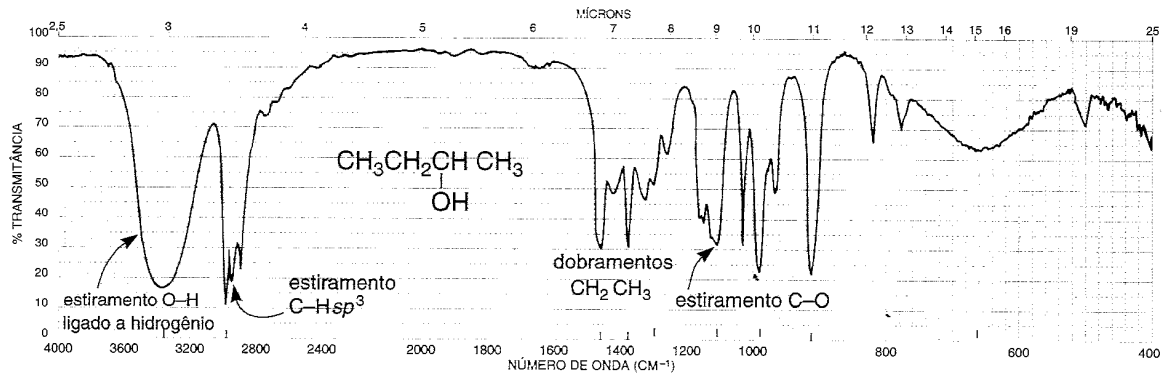
8) Azide, -N <sub>3</sub>	2160~2095  1340~1180		ν <sub>2,3</sub> strong; aromatics usually split due to Fermi resonance with C-N, Δν~60 cm <sup>-1</sup> .  ν <sub>1</sub> , weak.	11,9	(15)
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TABLE 5 ALCOHOLS AND PHENOLS

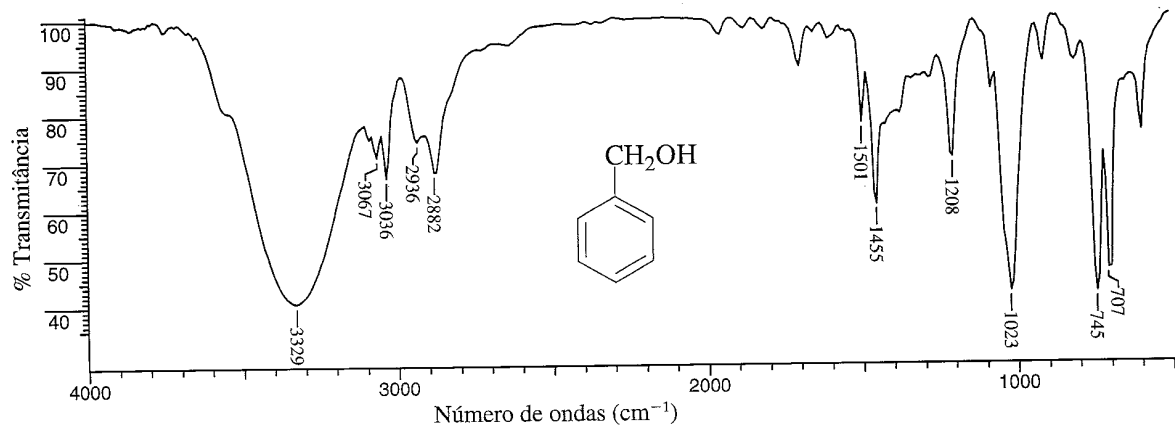
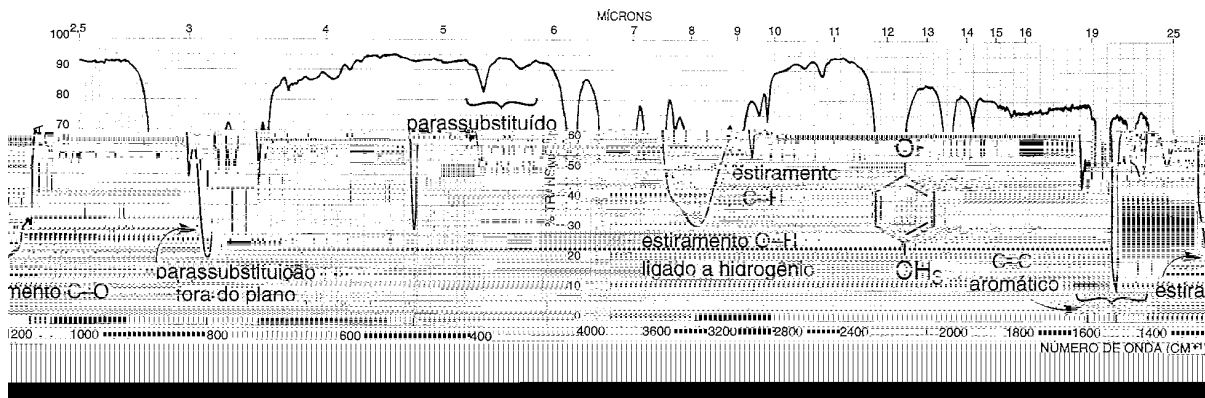
Table 5a O-H Stretching vibration

State of OH	cm <sup>-1</sup>	e <sup>a</sup>	Shape	Remarks	Figs.
Free (monometric)	3640~3610	30~100	sharp	Data measured in so-called non-polar (CCl <sub>4</sub> , CHCl <sub>3</sub> , etc.*) dilute solutions.	(18)
1) { p-OH s-OH t-OH phenolic OH	3640 3630 3620 3610	70 60~50 45		Water absorption at 3710 cm <sup>-1</sup> when solution is damp.	(26)
2) -O-O-H, hydroperoxide	3560~3530[1]				
Intermol. H-bond 3) dimeric	3600~3500		rather sharp	Usually hidden in polymeric band ( <i>vide infra</i> ) unless polymer formation is hindered by steric hindrance. Absorptions arising from H-bond with polar solvents such as ethers, ketones, and amines also appear in this region.	(18)
4) polymeric	3400~3200	strong	broad	With solids and liquids, this broad absorption is the only one observed; in dilute solutions, accompanied by monomer band. Free and assoc. ν NH of amines and amides also appear at 3500~3200 cm <sup>-1</sup> . First overtone of ν C=O (ca. 1720 cm <sup>-1</sup> ) also appears at 3500~3400 cm <sup>-1</sup> , but can be differentiated because of low intensity, e <sup>a</sup> < 10. Water of crystallization: also at 3600~3100 cm <sup>-1</sup> , but not so strong and somewhat narrower; also weak band at 1640~1615 cm <sup>-1</sup> (H-O-H bending vibration).	(19), (22) (84)

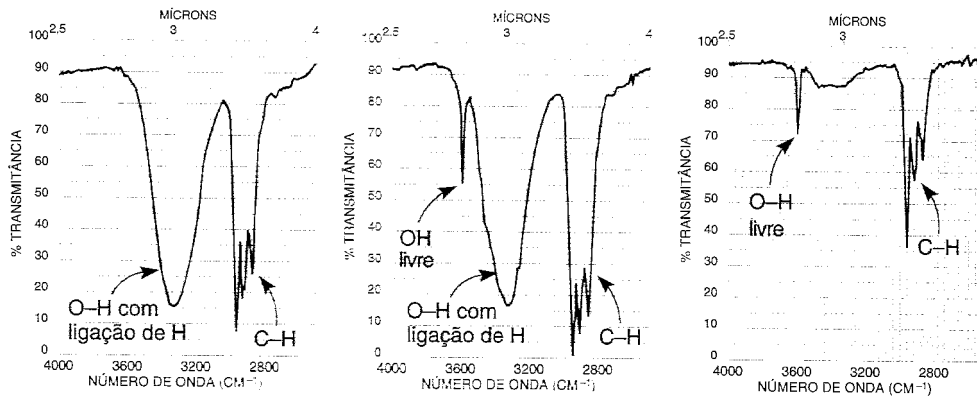
# Espectros de IV de ÁLCOIS e FENOL



Espectro infravermelho de 2-butanol (líquido puro, placas de KBr).



## Influência da diluição no estiramento de ÁLCOOIS



Região do estiramento O—H. (a) Apenas O—H com ligação de hidrogênio (líquido puro), (b) O—H livre e com ligação de hidrogênio (solução diluída) e (c) O—H livre e com ligação de hidrogênio (solução muito diluída).

## Influência de ligações de hidrogênio intramoleculares em O-H e C=O

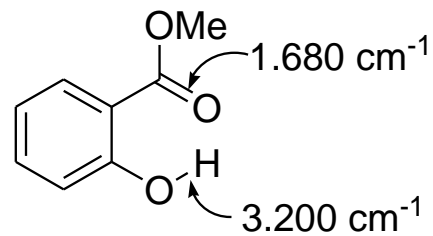
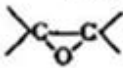
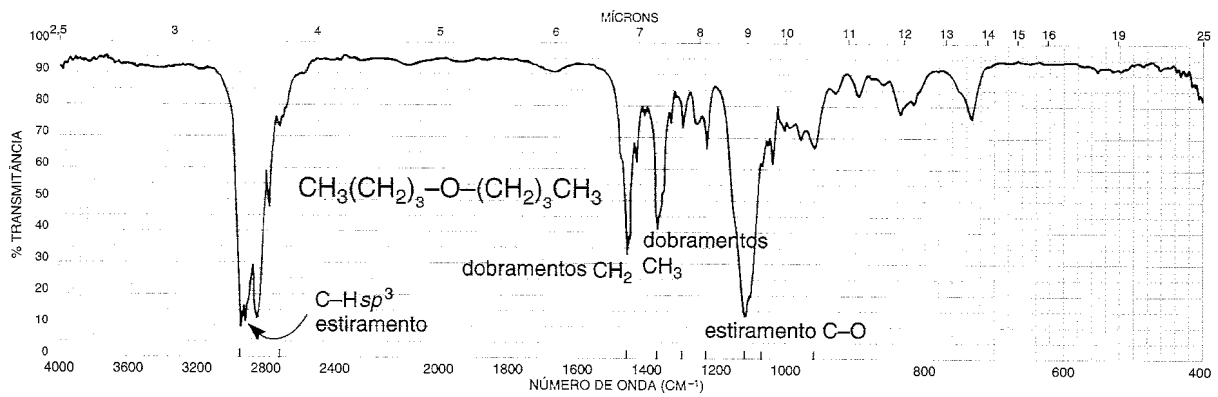




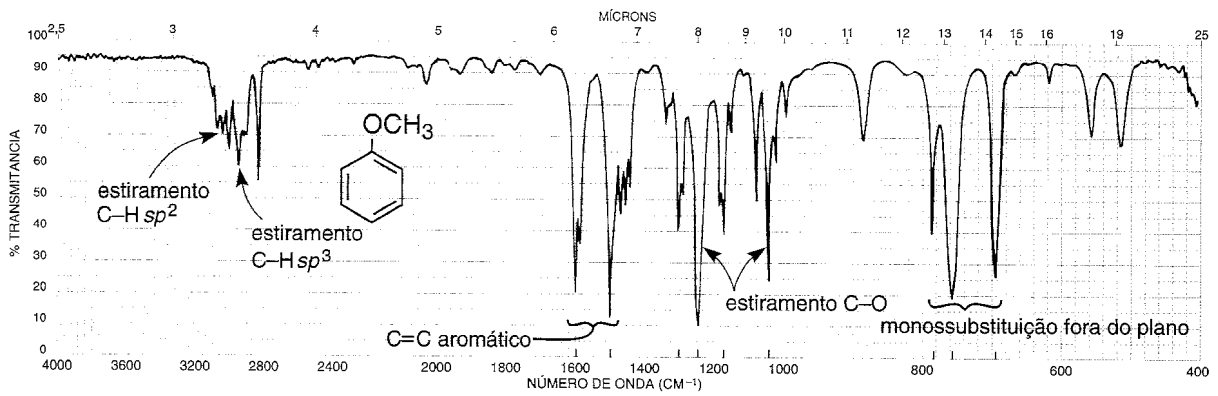
TABLE 6. ETHERS AND RELATED GROUPS  
 $\epsilon^a$  of  $\nu\text{C}-\text{O}$  bands are usually greater than 200.

Group	Band ( $\text{cm}^{-1}$ )	Remarks	Figs.	
1) Ethers, general	aliph. and ring $\text{C}-\text{O}-\text{C}$ [1]	1150~1070	$\text{C}-\text{O}-\text{C}$ antisym. stretching. Common with other $\text{C}-\text{O}$ bands. Effect of $\alpha$ -branching unclear.	(29)
	arom. and vinyl $=\text{C}-\text{O}-\text{C}$	1275~1200	Antisym. stretching. Common with other $=\text{C}-\text{O}$ . So-called "1250 $\text{cm}^{-1}$ band." $\nu\text{C}=\text{C}$ of vinyl ethers intensified.	(30), (41)-f
		1075~1020	Sym. stretching. Weaker than 1250 $\text{cm}^{-1}$ band.	
	Methoxyl group has following bands in addition.			
aliph. $-\text{OCH}_3$ [2]	2830~2815 ( $\epsilon^a$ 50)	$\text{CH}_3$ sym. stretching. Lacks in $-\text{OC}_2\text{H}_5$ . The asym. stretching is at 2990~2970 (present in $-\text{OC}_2\text{H}_5$ ) but position is non-characteristic.		
arom. $-\text{OCH}_3$ [3]	2850	$\text{CH}_3$ sym. stretching. Following bands also present, but position non-characteristic: 3000, 2950, 2915 (the 3 appear as triplets), 1460 and 1340 ( $\delta\text{CH}$ ), 1250 ( $=\text{C}-\text{O}-\text{C}$ antisym. stretching), 1180 and 1125 (methyl rocking and arom.?), 1040~1020 ( $=\text{C}-\text{O}-\text{C}$ sym. stretching).	(31)	
4) Spiroketal of steroidal sapogenins [1,6]	1350~ 650	Many characteristic sharp bands.		
5) Epoxy		[1,7,9,12]	3000 ( $\epsilon^a$ 40)	(34)
		3040 ( $\epsilon^a$ 20)	Epoxy methine group of strained rings.	
		3050 ( $\epsilon^a$ 30)	Methylene group of terminal epoxy rings.	
		1250	So-called "8 $\mu$ band"; sym. stretching of ring.	
		950~ 810	So-called "11 $\mu$ band"; asym. stretching of ring.	
840~ 750	So-called "12 $\mu$ band."			

## Espectro IV de ÉTERES



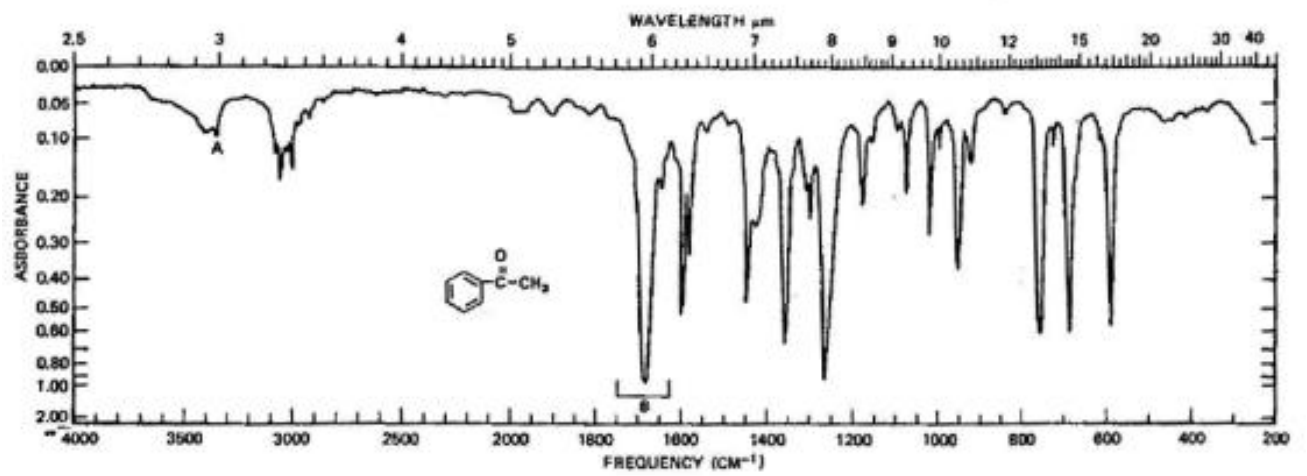
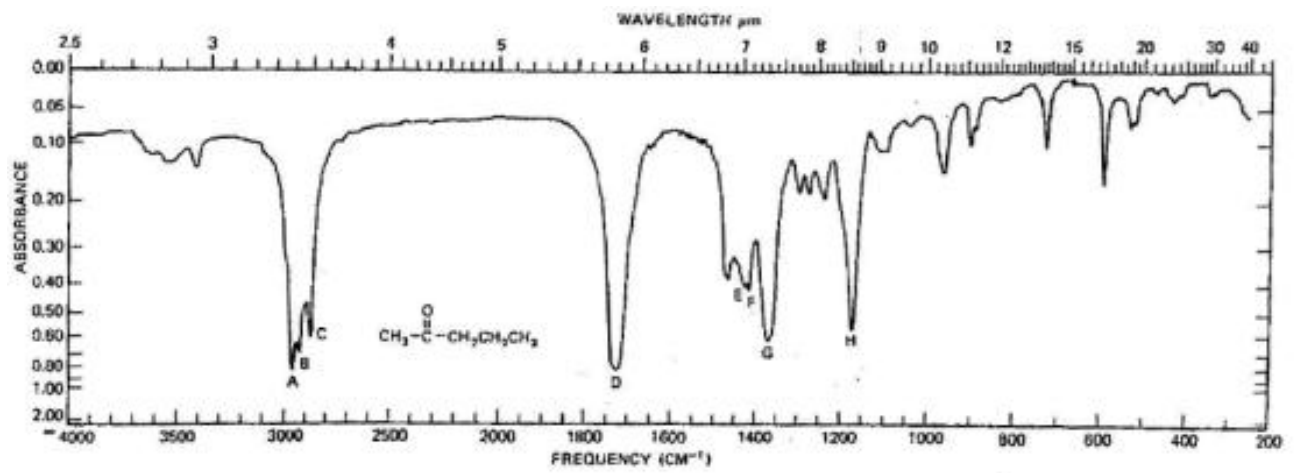
Espectro infravermelho de éter dibutílico (líquido puro, placas de KBr).



Espectro infravermelho de anisol (líquido puro, placas de KBr).

TABLE 8 CARBONYL GROUPS (Bold figures denote  $\nu_{\text{C=O}}$ )

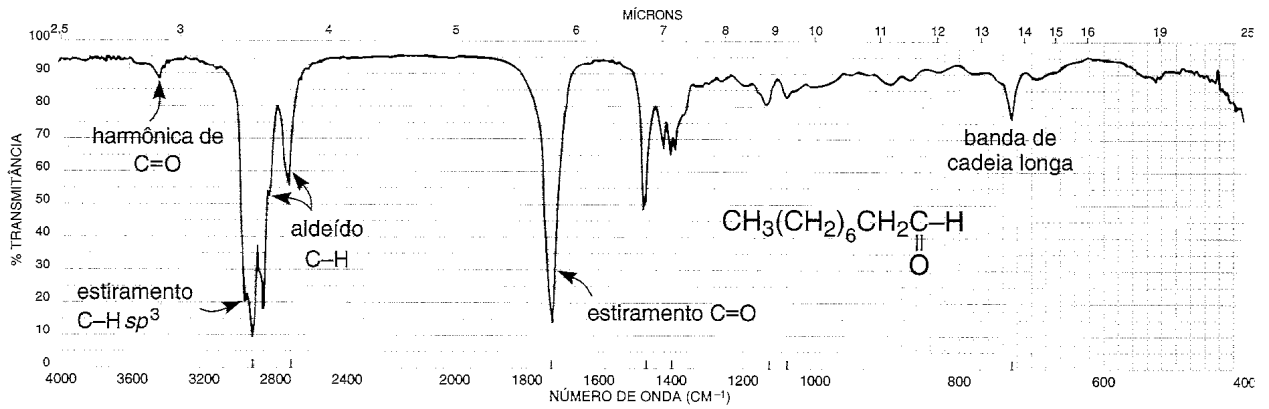
	Group	Band ( $\text{cm}^{-1}$ )	Remarks	Figs.
1	<b>Ketone</b> -CO-	<b>1715</b>	$\epsilon^{\text{a}}$ 300~600. Values of $\text{CHCl}_3$ solutions and solids, lower by 10~20 $\text{cm}^{-1}$ . Values of gases, +20 $\text{cm}^{-1}$ . Occasionally overtone at ca. 3400 $\text{cm}^{-1}$ .	(41)
		1100 (aliph.) } 1~ 1300 (arom.) } several	$\epsilon^{\text{a}}$ 50~150. Caused by C-C-C bending and C-C stretching of -C-(CO)-C-	
1	a) $\alpha, \beta$ -unsatd.	<b>1675</b>	$\nu_{\text{C=C}}$ shows clearly at 1650~1600 $\text{cm}^{-1}$ ; in <i>s-cis</i> forms, may be shifted below 1600 $\text{cm}^{-1}$ and intensity becomes comparable to that of $\nu_{\text{C=O}}$ .	(41), (43)
1	b) Ar-CO-	<b>1690</b>	Affected by <i>I</i> , <i>M</i> , and steric effects of substituents.	(44), (67)
1	c) $\alpha, \beta\text{-}\gamma, \delta$ -unsatd.	<b>1665</b>		
1	d) $\alpha, \beta\text{-}\alpha', \beta'$ -unsatd.			
1	e) Ar-CO-Ar			
1	f) $\triangleright$ -CO-R	<b>1695</b>	Conj. with cyclopropane lowers by ca. 20 $\text{cm}^{-1}$ .	(42)
1	g) 7 memb. and larger	<b>1705</b>		
1	h) 6-membered	<b>1715</b>	Same as standard value. Shift caused by conj. with unsatd. groups is same with aliph. ketones.	(41)
1	i) 5-membered	<b>1745</b>	Shift caused by conj. with unsatd. groups is same with aliph. ketones.	(40)
1	j) 4-membered	<b>1780</b>		
1	k) 3-membered	<b>1850</b>		
1	l) $\alpha$ -halo- $\begin{array}{c} \text{C}-\text{C}- \\   \quad    \\ \text{X} \quad \text{O} \\ (\text{X:halogen}) \end{array}$	shift of 0~+25	Shift to higher freq. is larger the smaller the angle between C=O and C-X. No shift when angle exceeds 90°. Following values apply to satd. aliph. and cyclic ketones: -Cl, 0~+25; -Br, 0~+20; -I, 0~+10 $\text{cm}^{-1}$	(75)
1	m) -CX <sub>2</sub> -CO- and -CX-CO-CX (X:halogen)	shift of 0~+45	Effect of single halogen substitution appears additively. Shift of +45 $\text{cm}^{-1}$ results when Cl on both sides of C=O are in same plane with C=O. Co-existence of several conformers give rise to each corresp. band, the relative intensities of which are dependent upon state of measurement.	



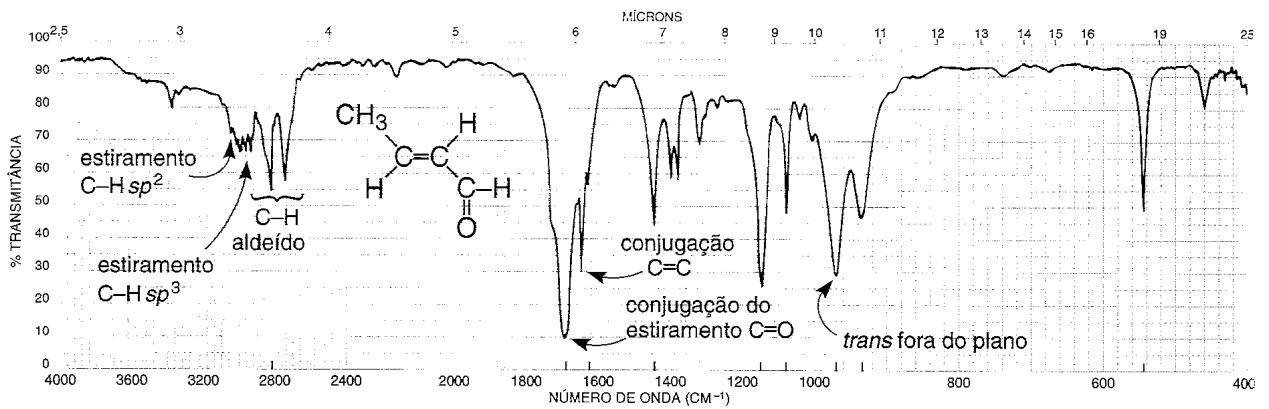
## ALDEIDOS

2	Aldehyde -CHO	2820, 2720  1725	Two bands due to Fermi resonance between $\nu$ C-H and overtone of $\delta$ C-H. Several bands also at $1400\sim 1000\text{ cm}^{-1}$ , but not practical.
	2 a) $\alpha, \beta$ -unsatd.	1685	
2	b) $\alpha, \beta\text{-}\gamma, \delta$ -unsatd.	1675	
2	c) Ar-CHO	1700	

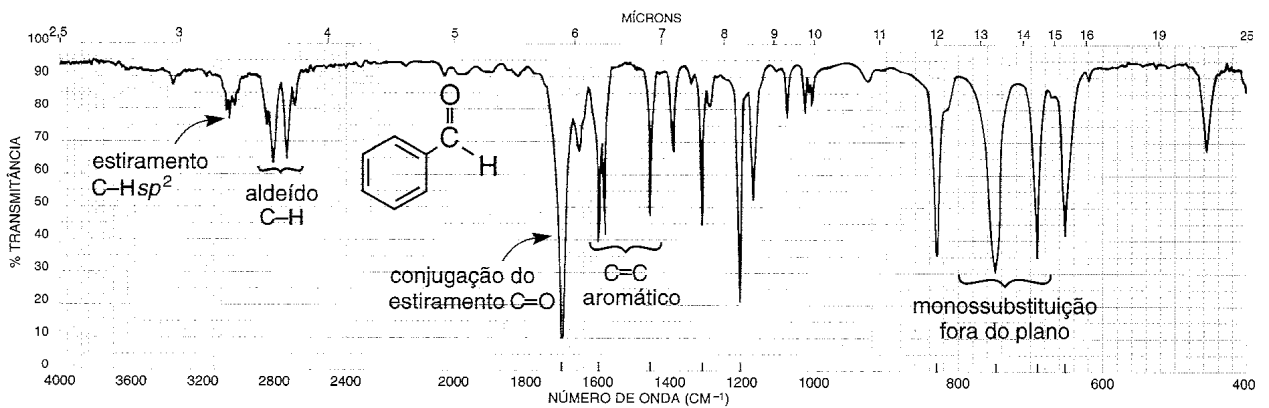
## Espectros IV de ALDEIDOS



Espectro infravermelho de nonanal (líquido puro, placas de KBr).



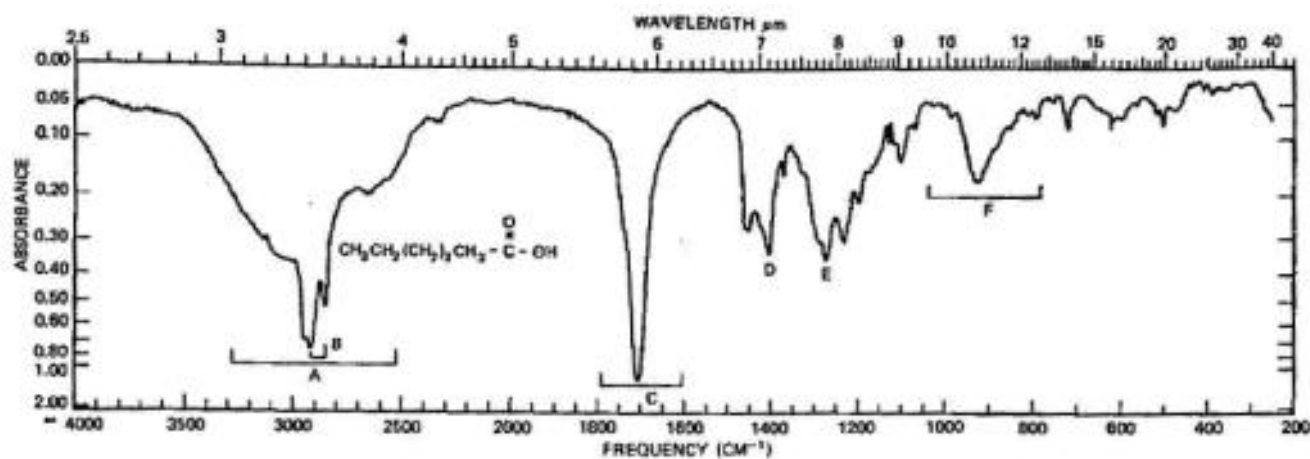
Espectro infravermelho de crotonaldeído (líquido puro, placas de KBr).



Espectro infravermelho de benzaldeído (líquido puro, placas de KBr).

## ÁCIDOS CARBOXÍLICOS

3	Acid -COOH	<p>3000~2500</p> <p>1760 (monomer) 1710 (dimer) 1420 1300~1200</p> <p>920</p>	<p>Data are mostly for dimers because H-bonding power is unusually strong, and they exist also in gas state.</p> <p>Very characteristic. Group of small bands. Band at highest freq. is due to <math>\nu\text{OH}</math>, and others are combinations. <math>3550\text{ cm}^{-1}</math> in monomers.</p> <p>Considerably stronger than ketonic <math>\nu\text{C=O}</math>. <math>\epsilon^a</math> up to 1500. Two bands may be observed with gases or solutions.</p> <p>Both due to coupling between in-plane O-H bending and C-O stretching of dimer.</p> <div style="text-align: center;"> </div> <p>Broad, medium intensity. O-H out-of-plane bending of dimer.</p>	(52), (53)
3 a)	C=C-COOH and Ar-COOH	<p>1720 (monomer) 1690 (dimer)</p>	<p>Values for <math>\alpha\text{-Br}</math> and <math>\alpha\text{-Cl}</math>. Larger for <math>\alpha\text{-F}</math>, ca. <math>+50\text{ cm}^{-1}</math>.</p>	(68)
3 b)	$\alpha$ -halo-	<p>Shift of <math>+10\sim 20\text{ cm}^{-1}</math></p>		(55), (70)
4	Carboxylate -COO-	<p>1610~1550 and 1400</p>	<p>C-O antisym. and sym. stretching, resp., of <math>-\text{C} \begin{matrix} \diagup \text{O} \\ \diagdown \text{O} \end{matrix} -</math></p> <p>When an acid is converted into its inorganic salt, the five characteristic freq. are replaced by these two. Instead of being converted to inorganic salts, they can be changed to ammonium salts by adding few drops of <math>\text{Et}_3\text{N}</math> to <math>\text{CHCl}_3</math> solution; carboxylate ions are not formed in <math>\text{CCl}_4</math>, while addition of <math>\text{NH}_3</math> or <i>p</i>-amines gives confusing <math>\text{N}^+\text{H}_4</math> and <math>\text{N}^+\text{H}_3</math> bands that overlap with <math>-\text{COO}^-</math> band.</p>	(64)

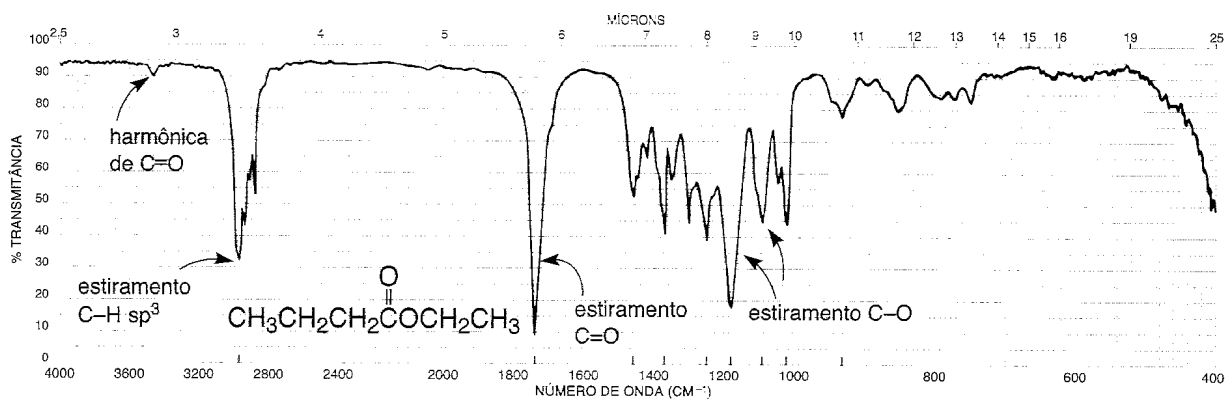




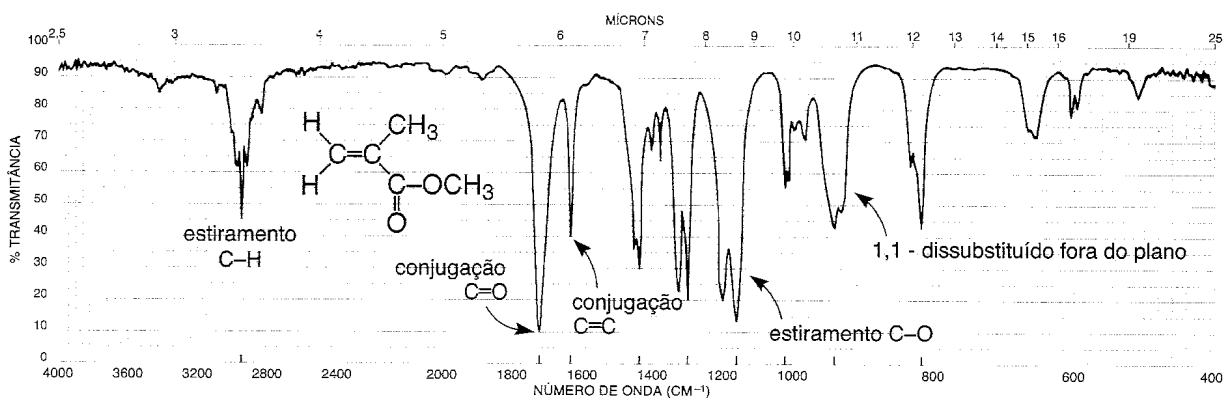
## ÉSTERES

5	Ester -CO-O-	1735  two at 1300~1050	Intensity intermediary between ketone and carboxyl, ( $\epsilon^a$ 500~1000).  Asym. and sym. stretching, resp., of ester C-O-C. The asym. stretching ("ester band") is usually stronger than $\nu\text{C}=\text{O}$ and broad; also occasionally split. This higher $\nu\text{C}-\text{O}$ band is fairly constant according to type of ester: [7] H-CO-OR, 1180 $\text{cm}^{-1}$ ; CH <sub>3</sub> -CO-OR, 1240 $\text{cm}^{-1}$ ; R-CO-OR, 1190 $\text{cm}^{-1}$ ; R-CO-OCH <sub>3</sub> , 1165 $\text{cm}^{-1}$	(23), (72)      (58), (86)  (38)
5 a)	-C=C-CO-O-	1720	Shift caused by conjugated unsaturation relatively small. $\nu\text{C}-\text{O}$ at 1300~1250 (vs) and 1200~1050 $\text{cm}^{-1}$ (s).	(59)
5 b)	Ar-CO-O-	1720	$\nu\text{C}-\text{O}$ at 1300~1250 (vs) and 1180~1100 $\text{cm}^{-1}$ (s).	(59)
5 c)	-CO-O-C=C-	1760	$\nu\text{C}=\text{C}$ at 1690~1650 (s) (may shift up to 1715 $\text{cm}^{-1}$ )[1] In CH <sub>3</sub> -CO-O-C=C (enol and phenol acetates), one of the $\nu\text{C}-\text{O}$ appears at 1210 $\text{cm}^{-1}$ (vs).	(58)
5 d)	$\alpha$ -halo-	shift of +10~+40 $\text{cm}^{-1}$	Shift dependent on electronegativity and number of $\alpha$ -halo atoms; dependent also on angle between C-X and C=O as with ketones.	
5 c)	Ar-CO-O-Ar	1735		
5 f)	$\alpha$ -keto ester	1745		
5 g)	$\beta$ -keto ester	keto: 1735  enol: 1650	The $\beta$ -keto group ( $\nu\text{C}=\text{O}$ , 1720 $\text{cm}^{-1}$ ) does not affect ester $\nu\text{C}=\text{O}$ .  Broad C=C at ca. 1630 $\text{cm}^{-1}$ (vs).	(51)

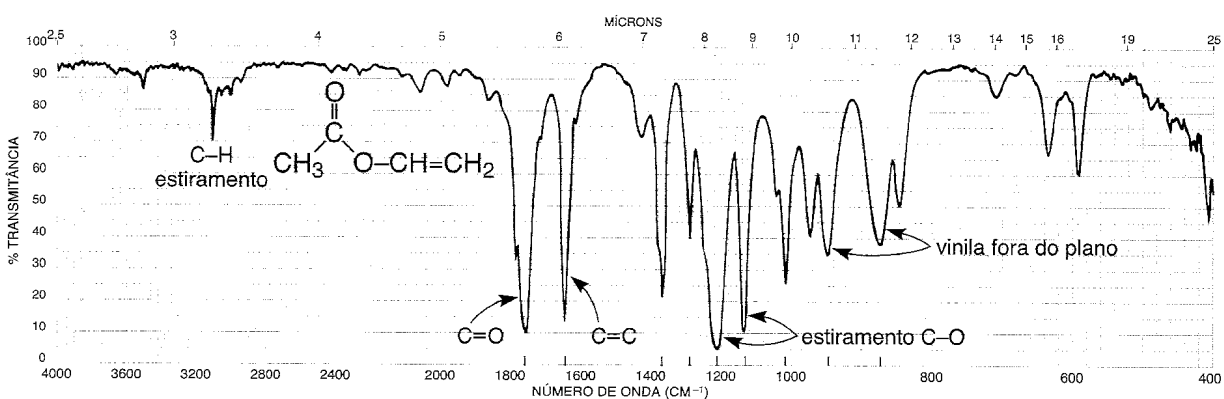
## Espectros IV de ÉSTERES



Espectro infravermelho de butirato de etila (líquido puro, placas de KBr).

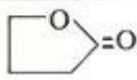

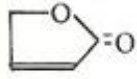
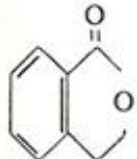
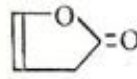
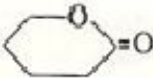
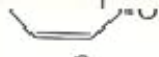

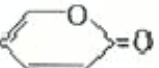


Espectro infravermelho de metacrilato de metila (líquido puro, placas de KBr).



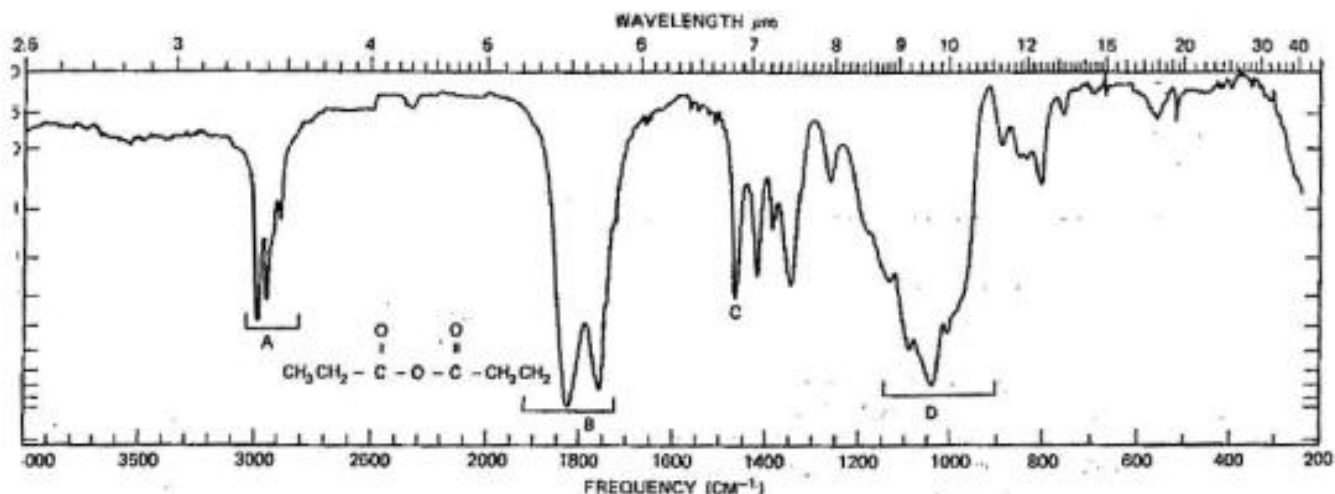
Espectro infravermelho de acetato de vinila (líquido puro, placas de KBr).

# LACTONAS

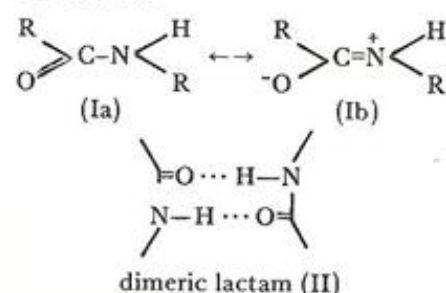
Group	Band (cm <sup>-1</sup> )	Remarks	Figs.
5 l) 	1770		(63)
5 m) 	1840		
5 n) 	1750 when $\alpha$ -H is present: 1785 and 1755 (doublet)	In non-polar solvents (CCl <sub>4</sub> , CS <sub>2</sub> ), the higher band is stronger, while in polar solvents (CHCl <sub>3</sub> , CH <sub>3</sub> CN, CH <sub>3</sub> OH) or liquids and solids, the lower band is stronger[2]. $\nu$ C=C is weak.	
5 o) 	1770	Around 1780 in non-polar solvents, and ca. 1760 in polar solvents; affected by polarity of solvents. Influenced by <i>M</i> and other effects of substituents on arom. ring.	(60)
5 p) 	1790	The band is not split, contrary to $\alpha$ , $\beta$ -unsatd.- $\gamma$ -lactones. $\nu$ C=C at 1660 cm <sup>-1</sup> (s).	
5 h) 	1735	Same as with aliph. est <sup>88</sup>	Same as with aliph
esters.		1720	
a. esters. $\nu$ C=C at 1685	5 j) 	1760	Same as with ali cm <sup>-1</sup> (s).
le 10-a for $\gamma$ -pyrones.	5 k) 	Table 10-4	$\alpha$ -Pyrones. See T:

## ANIDRIDOS

Acid anhydride -CO-O-CO	1820 and 1760	Relative intensity of two bands variable. Band separation usually ca. $60\text{ cm}^{-1}$ , but this may differ from $35$ to $90\text{ cm}^{-1}$ according to type[3]; lower band absorbs near $\nu\text{C=O}$ of corresp. ester or lactone. Higher and lower band, resp., is stronger in acyclic and cyclic anhydrides[4].	(62)
	1300~1050	1~2 strong bands arising from C-O-C portion.	
acrylic- or benzoic- 6-membered	1785 and 1725	$\Delta\text{C=O}$ , $50\sim70\text{ cm}^{-1}$ [3].	
$\alpha, \beta$ -unsatd. 6-membered	1800 and 1750	$\Delta\text{C=O}$ , $45\text{ cm}^{-1}$ when double bond is endo ( $75\text{ cm}^{-1}$ when exo)[3].	(51)
5-membered	1865 and 1785	$\Delta\text{C=O}$ , $80\text{ cm}^{-1}$ [3].	(61)
maleic	1850 and 1790	$\Delta\text{C=O}$ , $60\text{ cm}^{-1}$ . $1790\text{ cm}^{-1}$ band is split and behaves similarly to 5 m[3].	
phthalic	1850 and 1770	$1770\text{ cm}^{-1}$ band is split and behaves similarly to 5 m[2].	(61)



## AMIDAS

10	Group	Band (cm <sup>-1</sup> )		Remarks	Figs.
		Free	Assoc.		(74)
	Amide -CO-N			Complicated but extensively studied.[11] Influenced by state of measurement as with -COOH. Data for both free and assoc. states are given.	
	primary -CONH <sub>2</sub>	two at: 3500,3400  1690  1600	several: 3350~3200  1650  1640	<p><math>\nu</math>NH</p> <p><math>\nu</math>C=O, "Amide I band."</p> <p>Mainly <math>\delta</math>NH, "Amide II band." Shifted higher upon association. Solid spectra of -CONH<sub>2</sub> show two strong bands at 1650~1640, but "I band" is stronger. In concentrated solutions, all four bands arising from free and assoc. states may appear.</p>	
	secondary -CO-NHR-	3440	3300 3070	<p><math>\nu</math>NH, 3300 cm<sup>-1</sup> band considered to be due to <i>trans</i> assoc. form (structure I in figure shown). Band at 3070 is due to first overtone of N-H in plane bend.</p> <p>In cyclic lactams, 3440 when free, and 3175 (dimeric, structure II) and 3070 cm<sup>-1</sup> when assoc. (3300 lacking).</p>	
		1680 1530	1655 1550	<p>"Amide I band"</p> <p>Mainly <math>\delta</math>NH, mixed with <math>\nu</math>C-N, "Amide II band." Present only in <i>trans</i> amides; in <i>cis</i> amides (e.g., small ring lactams) it is weak and shifted to 1440 cm<sup>-1</sup>.</p>	
		1260	1300	<p>Mainly <math>\nu</math>C-N, mixed with <math>\delta</math>NH, "Amide III band."</p> <p>Shift in positions of free and assoc. <math>\nu</math>NH and "Amide I~III bands" is consistent with assignment. Thus contribution of limiting structure Ib is enhanced upon association.</p>	
				 <p style="text-align: center;">(Ia) <math>\leftrightarrow</math> (Ib)</p> <p style="text-align: center;">dimeric lactam (II)</p>	
	tertiary -CO-N<	1650	1650	<p>Solid IR of amides are, however, especially sensitive to crystal orientation. Effect of substituents may thus not be exerted correctly, and a slight complication in structure may prevent the shift of "I" and "II" bands to lower frequencies in the solid state.</p> <p>In concentrated solutions the assoc. and free absorptions both appear.</p> <p>Since H-bonding with NH is absent, position is only slightly higher in the free state (similar to other C=O groups).</p>	

# AMINAS

**TABLE 7 AMINES AND AMMONIUM SALTS**  
(Non-diagnostic bands appear in italics)

**Table 7a Stretching vibrations**

Amino group	cm <sup>-1</sup>	Intensity	Remarks	Figs.
Free				
1) <i>p</i> -Amine R-NH <sub>2</sub> and Ar-NH <sub>2</sub>	$\left. \begin{array}{l} \sim 3500 \\ \sim 3400 \end{array} \right\}$	w in R-NH <sub>2</sub> <i>e<sup>a</sup></i> $\sim 30$ in Ar-NH <sub>2</sub>	The two correspond to $\nu_{as}$ and $\nu_s$ , resp. Wave-number relation: $\nu_s = 345.53 + 0.876 \nu_{as}$ [1]	(35), (36)
2) <i>s</i> -Amine R-NH-R	3350~3310	w	Especially weak in N-heterocyclic compounds, e.g., piperidine.	
Ar-NH-R	3450	<i>e<sup>a</sup></i> 30~40		
Pyrroles, indoles, etc. [2]	3490	<i>e<sup>a</sup></i> 150~300	Position and intensity both characteristic. See Table 10-2.	(38), (87)
C=NH	3400~3300		$\nu_{C=N}$ band at 1690~1640 cm <sup>-1</sup> .	

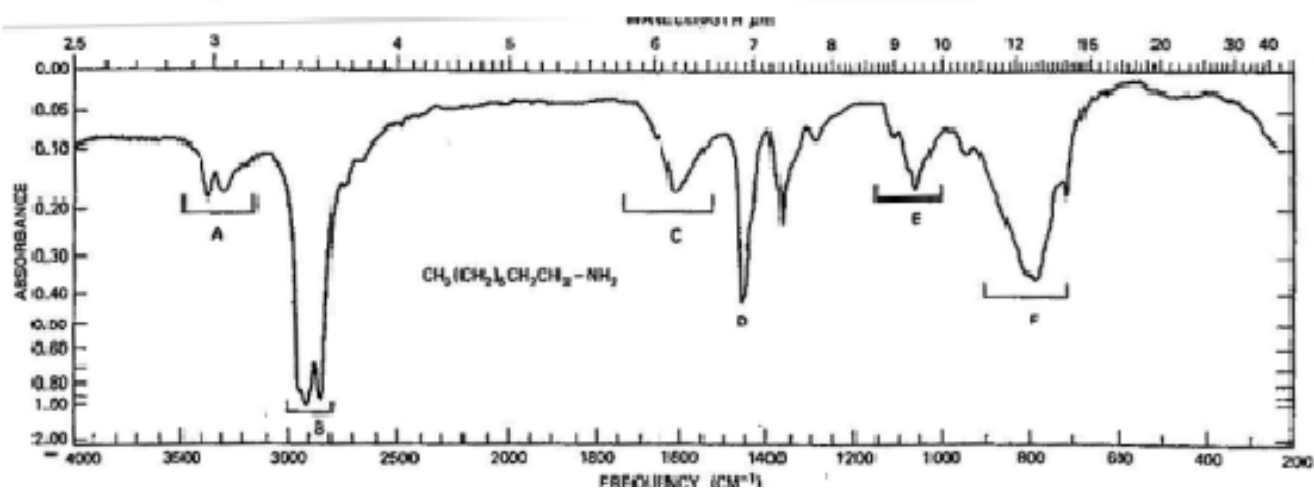
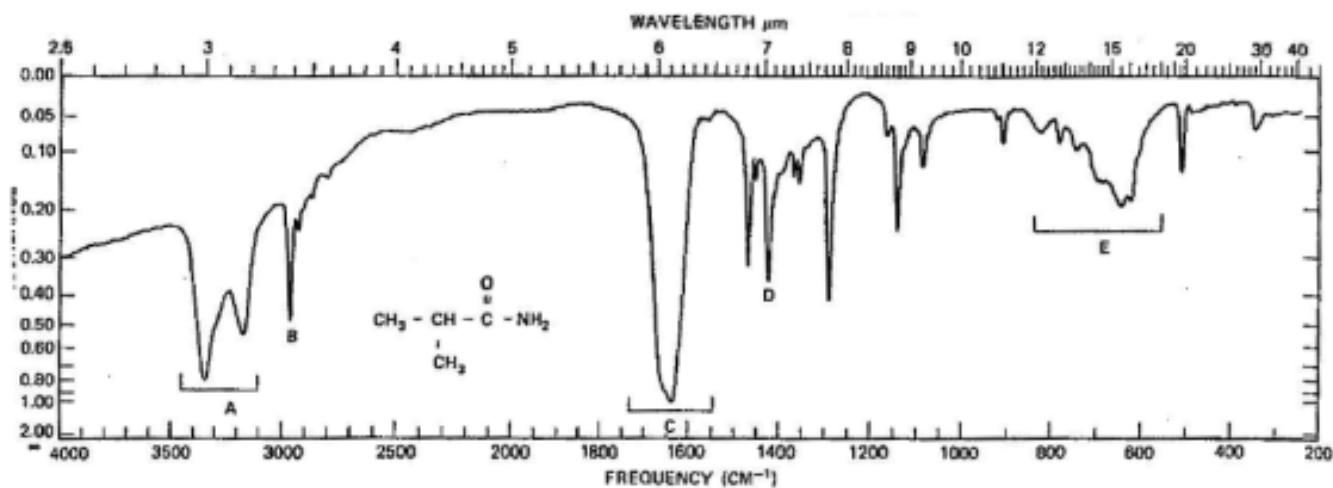
**Table 7b N-H Bending vibrations (lacking in *t*-amines)**

Group	cm <sup>-1</sup>	Intensity	Remarks	Figs.
3) -NH <sub>2</sub>	1640~1560	s~m	In-plane bending, corresponds to CH <sub>2</sub> scissoring, same in R-NH <sub>2</sub> and Ar-NH <sub>2</sub> .	(35), (36)
	900~650	m (broad)	Out-of-plane bending, corresponds to CH <sub>2</sub> twisting, rather characteristic.	
4) -NH-	1580~1490	w	Difficult to detect, especially in Ar-NH- where it is blurred by arom. 1580 cm <sup>-1</sup> band.	

**Table 7c C-N Stretching vibrations**

The position does not differ much from C-C stretching vibrations, but the intensity is relatively large because of C-N polarity.

Group	cm <sup>-1</sup> (intensity)	Remarks	Figs.
5) R-N $\begin{array}{l} \text{H (R)} \\ \text{H (R)} \end{array}$	1230~1030 (m)	Two in <i>t</i> -amines. In cyclic amines, lower range of indicated region.	(35)
6) Ar-N $\begin{array}{l} \text{R} \\ \text{H (R)} \end{array}$	$\left\{ \begin{array}{l} 1360\sim 1250 \text{ (s)} \\ 1280\sim 1180 \text{ (m)} \end{array} \right.$	C <sub>arom.</sub> -N stretching. High position due to increase in double bond character. C <sub>aliph.</sub> -N stretching.	(36)



## SAIS DE AMINAS

Table 7d Amine salts

Group	cm <sup>-1</sup>	Shape (intensity)	Assignment and remarks	Figs.
7) -NH <sub>4</sub> <sup>+</sup>	3300~3030 1430~1390	broad (s) s		
Satd. amine[3]*				
8) -NH <sub>3</sub> <sup>+</sup>	~3000	broad (s)	$\nu_{as}NH_3^+$ and $\nu_s NH_3^+$ (corresponds to the two CH <sub>3</sub> bands), overlaps broadly over $\nu CH$ band, commonly named "ammonium band."	(35), (72)
	~2500	1~several (m)	Overtones, combination tones. Sometimes lacking.	
	~2000	m	Overtones, combination tones. Sometimes lacking.	(71)
	1600~1575 } 1500 }	s	$\delta_{as}NH_3^+$ and $\delta_s NH_3^+$ (corresponds to the two $\delta CH_3$ vibrations).	
9) -NH <sub>2</sub> <sup>+</sup>	2700~2250	broad(s), or group of relatively sharp bands.	$\nu_{as}NH_2^+$ and $\nu_s NH_2^+$ . Differentiation from $\nu CH$ band not so clear-cut as with <i>t</i> -amines. "Ammonium band."	
	2000	m	Mostly lacking. Overtones, combination tones.	
	1600~1575	m	$\delta NH_2^+$ .	(64)
10) -NH <sup>+</sup>	2700~2250	broad(s), or group of relatively sharp bands.	One is due to $\nu NH^+$ , others are overtones and combinations. Clearly separated from $\nu CH$ band. "Ammonium band." $\delta NH^+$ band is weak and of no practical value.	(37), (39)
11) )N <sup>+</sup> (			Quaternary ammonium salts lack characteristic bands.	
Unsatd. amine[4] (arom. amine)				
12) C= $\overset{+}{N}$ -H	2500~2300	broad(s), or group of relatively sharp bands.	"Ammonium band." Clearly separated from $\nu CH$ as with <i>t</i> -amine salts.	
	2200~1800	1~several (m)	"Immonium band." This is the difference between <i>t</i> -amine salts.	
	~1680	m	$\nu C=N^+$ . Higher by 20~50 cm <sup>-1</sup> than free $\nu C=N$ (1690~1640 cm <sup>-1</sup> , $\epsilon^a$ variable from 5~880)[4,5].	(98)