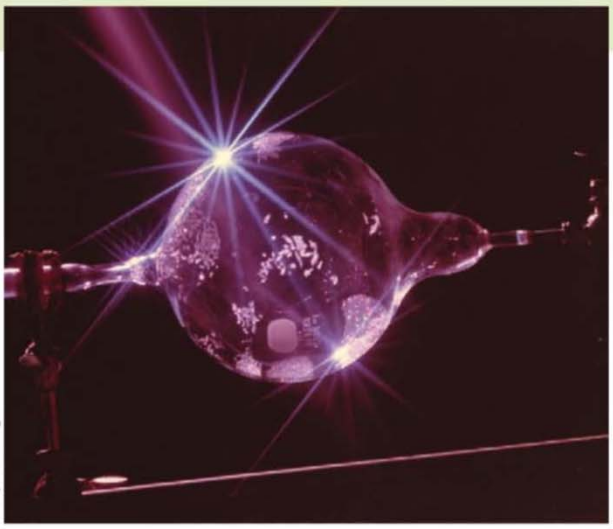
The Chemistry of the Noble Gases

It was a shock when, in 1962, we learned that the noble gases were not chemically inert as our chemistry professors had taught us. Xenon at the very least was found to form compounds! The first was an ionic compound, now known to be $XeF^+Pt_2F_{11}^-$. However, this was followed shortly thereafter with the discovery of a large number of covalently bonded compounds, including XeF_4, XeF_6, $XeOF_4$, and XeO_3.

Since 1962, the field of noble gas chemistry has expanded with the discovery of such interesting molecules as FXeOXeF and, at low temperatures, species such as HArF, HXeH, HXeCl, and even HKrF.

Initially, xenon compounds were thought to form only under the most severe conditions. Therefore, it was again a surprise when it was learned that irradiating a mixture of xenon and fluorine gases at room temperature gave crystals of XeF_2 (as seen in the photo).



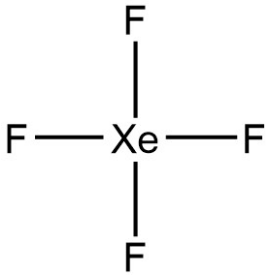
©Gary J. Schrobilgen

White crystals of xenon difluoride, XeF_2, form when a mixture of Xe and F_2 gases is irradiated with UV light.

F—Xe—F

70

Ex: XeF_4



D_{4h}

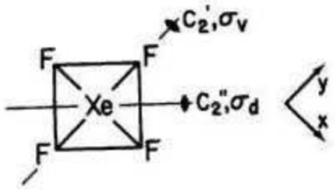


TABLE I: Determination of Γ_{vib} for XeF_4 [5]

	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v'$	$2\sigma_d''$
Γ_{tot}	15	1	-1	-3	-1	-3	-1	5	3	1

71

Ex: XeF_4

Decomposition into Irreducible representations

Motion	A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_g	A_{1u}	A_{2u}	B_{1u}	B_{2u}	E_u	Total
Cartesian 3N	1	1	1	1	1	0	2	0	1	3	**11**
Translation (x,y,z)	0	0	0	0	0	0	1	0	0	1	**2**
Rotation (R_x,R_y,R_z)	0	1	0	0	1	0	0	0	0	0	**2**
Vibration	1	0	1	1	0	0	1	0	1	2	**7**

$$\Gamma_{3N-6} = 1\,A_{1g} + 1\,B_{1g} + 1\,B_{2g} + 1\,A_{2u} + 1B_{2u} + 2\,E_u$$

72

Ex: XeF_4

Character table for point group D_{4h}

(x axis coincident with C'_2 axis)

D_{4h}	E	$2C_4$ (z)	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	linear functions, rotations	quadratic functions
A_{1g}	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	-	x^2+y^2, z^2
A_{2g}	+1	+1	+1	-1	-1	+1	+1	+1	-1	-1	R_z	-
B_{1g}	+1	-1	+1	+1	-1	+1	-1	+1	+1	-1	-	x^2-y^2
B_{2g}	+1	-1	+1	-1	+1	+1	-1	+1	-1	+1	-	xy
E_g	+2	0	-2	0	0	+2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1	-	-
A_{2u}	+1	+1	+1	-1	-1	-1	-1	-1	+1	+1	z	-
B_{1u}	+1	-1	+1	+1	-1	-1	+1	-1	-1	+1	-	-
B_{2u}	+1	-1	+1	-1	+1	-1	+1	-1	+1	-1	-	-
E_u	+2	0	-2	0	0	-2	0	+2	0	0	(x, y)	-

73

Símbolos de Mulliken

- **A**: simétrico em relação ao eixo principal;

  B: antissimétrico em relação ao eixo principal

- **1**: simétrico em relação a um eixo perpendicular (ou um plano vertical);

  2: antissimétrico em relação a um eixo perpendicular (ou um plano vertical)

- **g**: simétrico em relação ao centro de inversão (i)

  u: antissimétrico em relação ao centro de inversão (i)

- `: simétrico em relação ao plano horizontal (σ_h)

  ``: antissimétrico em relação ao plano horizontal (σ_h)

74

Ex: XeF_4

Decomposition into Irreducible representations

Motion	A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_g	A_{1u}	A_{2u}	B_{1u}	B_{2u}	E_u	Total
Cartesian 3N	1	1	1	1	1	0	2	0	1	3	11
Translation (x,y,z)	0	0	0	0	0	0	1	0	0	1	2
Rotation (R_x,R_y,R_z)	0	1	0	0	1	0	0	0	0	0	2
Vibration	1	0	1	1	0	0	1	0	1	2	7

$$\Gamma_{3N-6} = 1\,A_{1g} + 1\,B_{1g} + 1\,B_{2g} + 1\,A_{2u} + 1B_{2U} + 2\,E_u$$

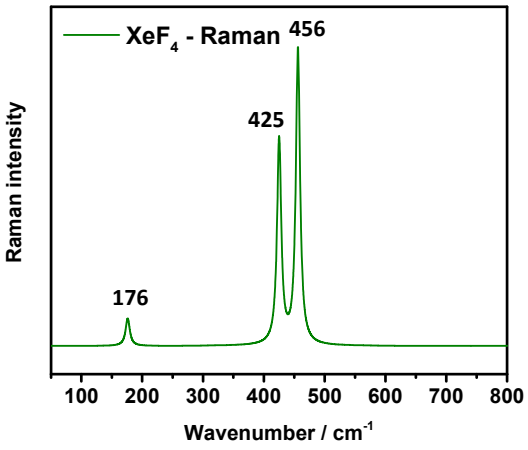
ativo Raman **ativo IR**

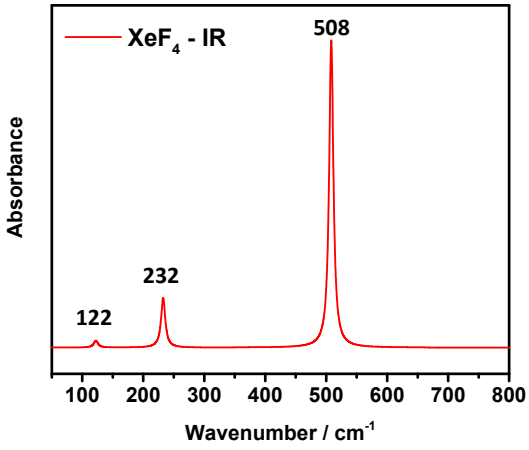
75

Ex: XeF_4

$\Gamma_{3N-6} = 1\ A_{1g} + 1\ B_{1g} + 1\ B_{2g} + 1\ A_{2u} + 1B_{2U} + 2\ E_u$

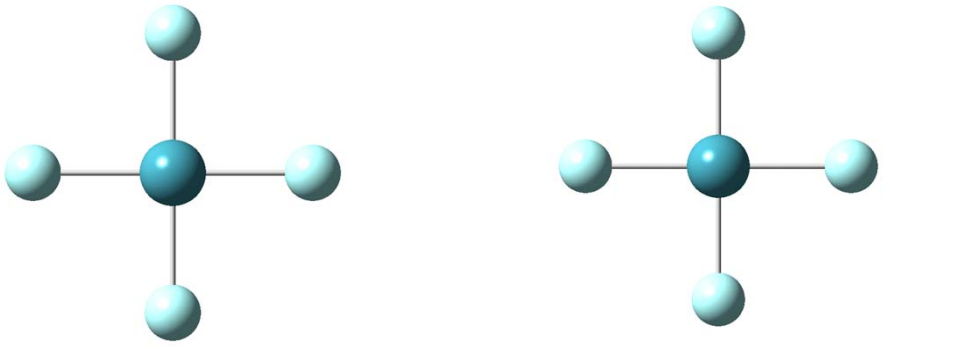
ativo Raman **ativo IR**





76

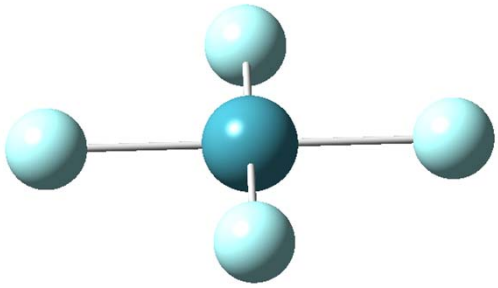
Ex: XeF_4



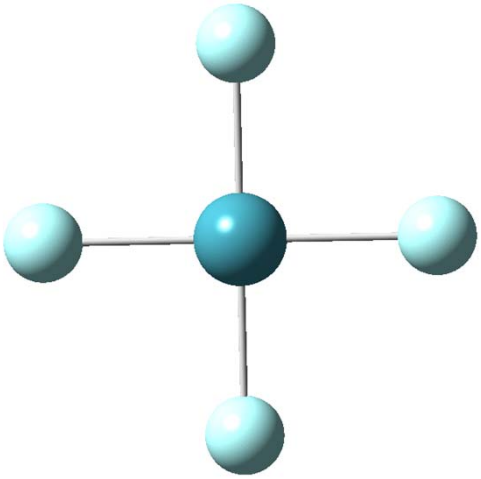
122 cm^{-1} (E_u)

77

Ex: XeF_4



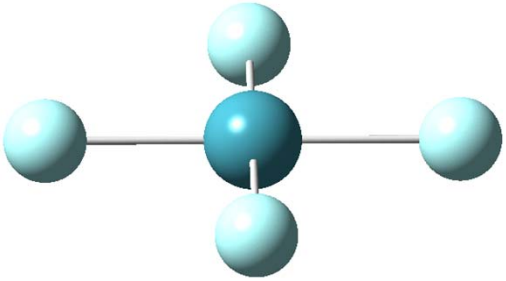
132 cm^{-1} (B_{2u})
(inativo R e IR)



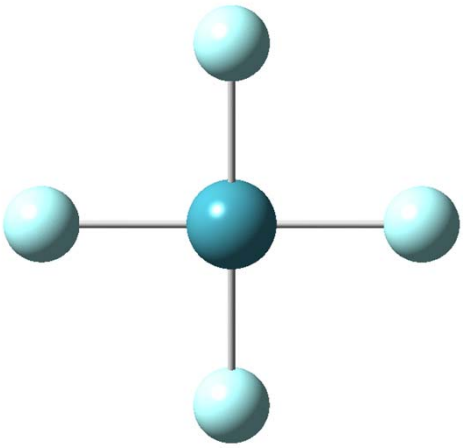
176 cm^{-1} (B_{2g})

78

Ex: XeF_4



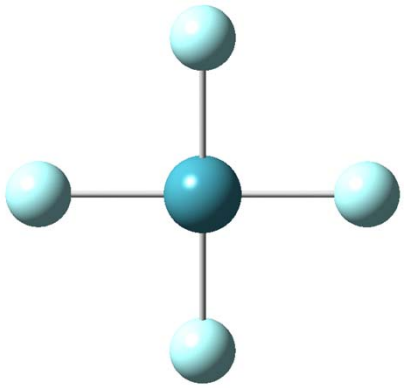
232 cm^{-1} (A_{2u})



425 cm^{-1} (B_{1g})

79

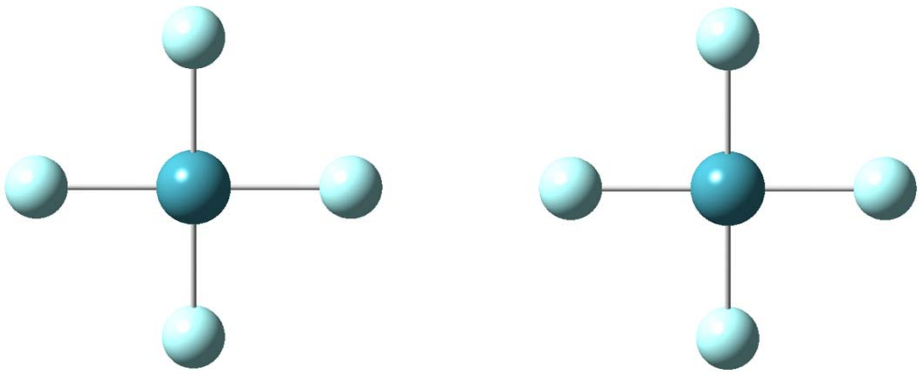
Ex: XeF_4



456 cm^{-1} (A_{1g})

80

Ex: XeF_4



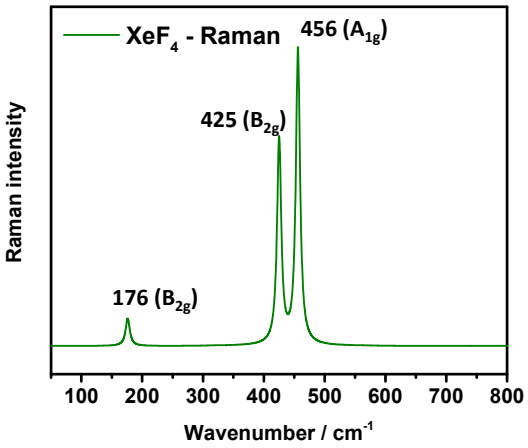
508 cm^{-1} (E_u)

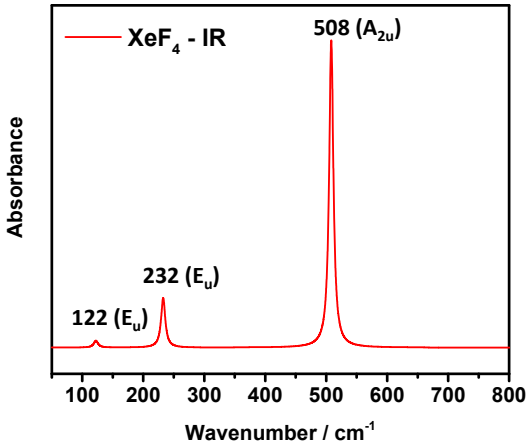
81

Ex: XeF_4

$$\Gamma_{3N-6} = 1\,A_{1g} + 1\,B_{1g} + 1\,B_{2g} + 1\,A_{2u} + 1B_{2U} + 2\,E_u$$

ativo Raman **ativo IR**





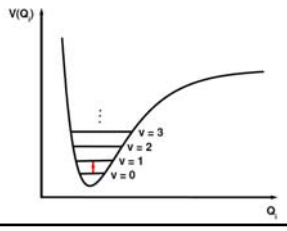
82

Espectroscopia Vibracional

Infravermelho

- Absorção (ressonância)
- Fonte (contínua)
- Esp. estritamente vibracional

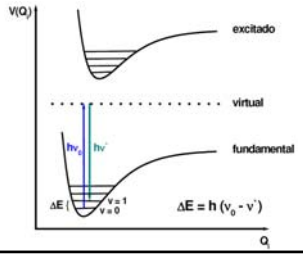
$$\left(\frac{\partial \mu}{\partial Q_i}\right)_0 \neq 0$$ (mom. de dipolo)



Raman

- Espalhamento (inelástico)
- Fonte (monocromática)
- Esp. vibracional/vibrônica

$$\left(\frac{\partial \alpha}{\partial Q_i}\right)_0 \neq 0$$ (polarizabilidade)



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Vantagens / Desvantagens

Infravermelho

Vantagens

- Alta seção de choque
- Custo baixo

Desvantagens

- Interferência de H_2O
- Limitação - tipo de amostra
- Esp. estritamente vibracional

Raman

Desvantagens

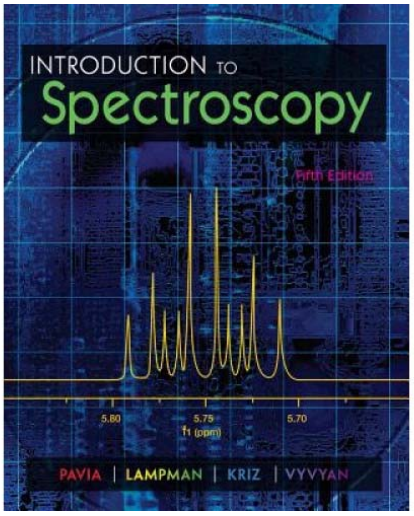
- Baixa seção de choque
- Custo alto

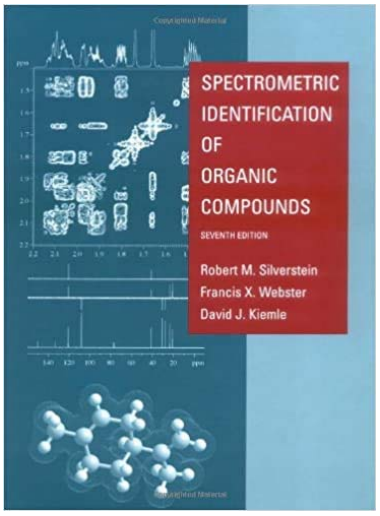
Vantagens

- Não há interferência de H_2O
- Tipo de amostra (lim. física)
- Efeitos de intensificação (ex: Raman ressonante e SERS)

84

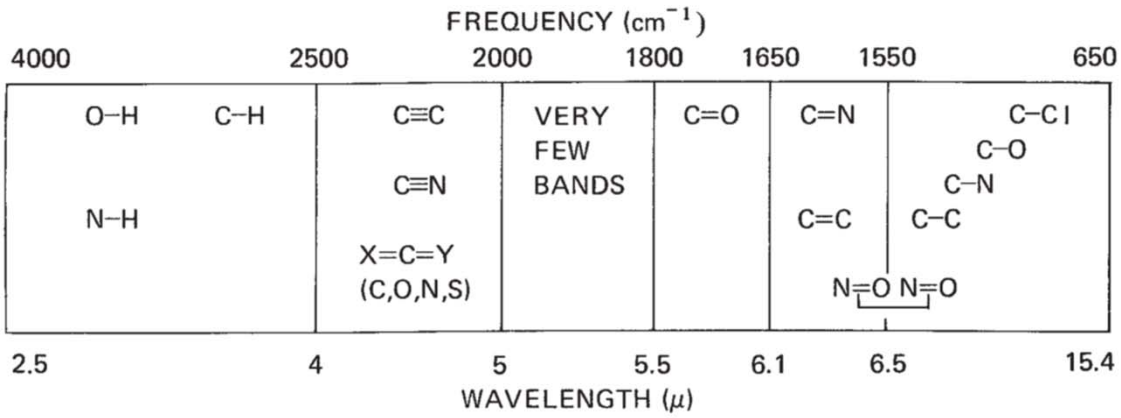
Análise de espectros - IR





85

Frequências características – Estiramentos



86

Frequências características

C–H stretching ~3000 cm^{-1}

C–H bending ~1340 cm^{-1}

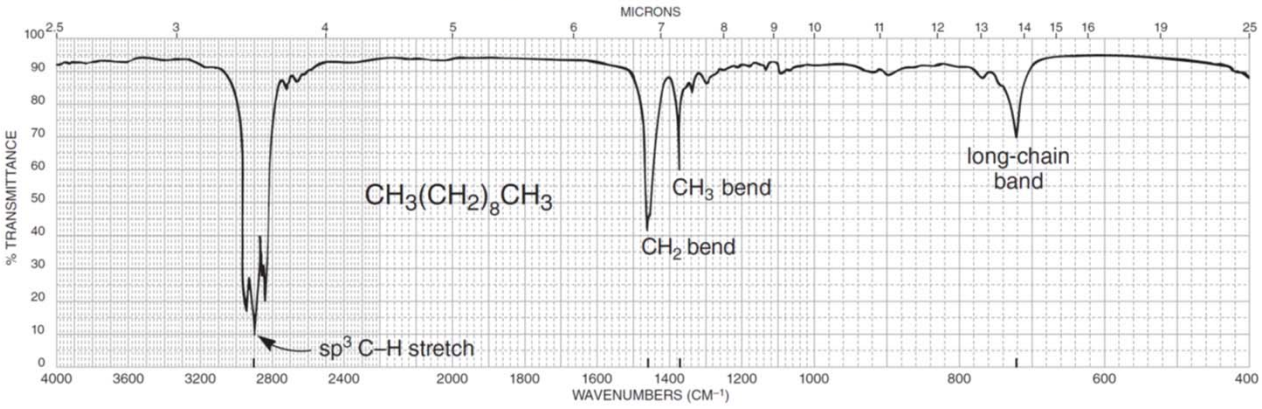


FIGURE 2.7 The infrared spectrum of decane (neat liquid, KBr plates).

87

Frequências características

Ex: Cicloexano

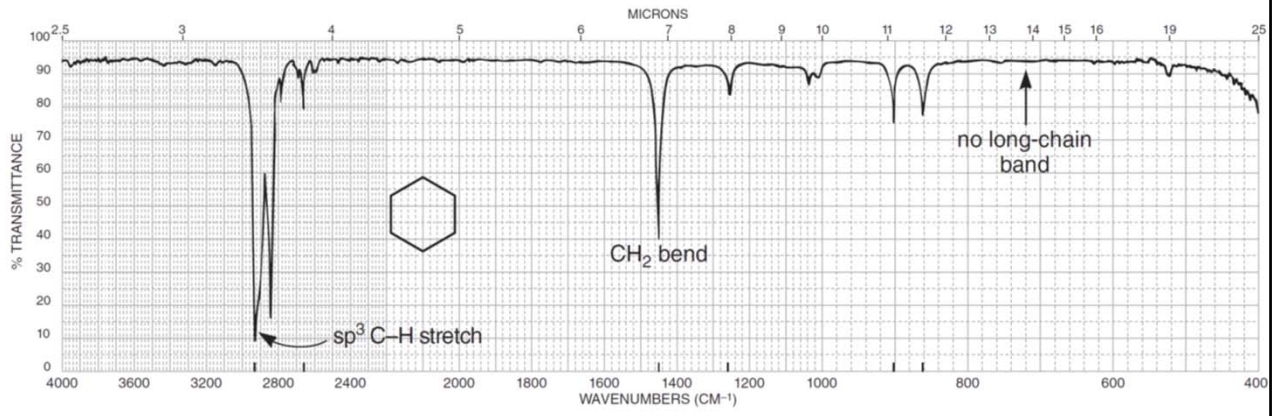


FIGURE 2.9 The infrared spectrum of cyclohexane (neat liquid, KBr plates).

88

Frequências características

Ex: 1-Hexeno

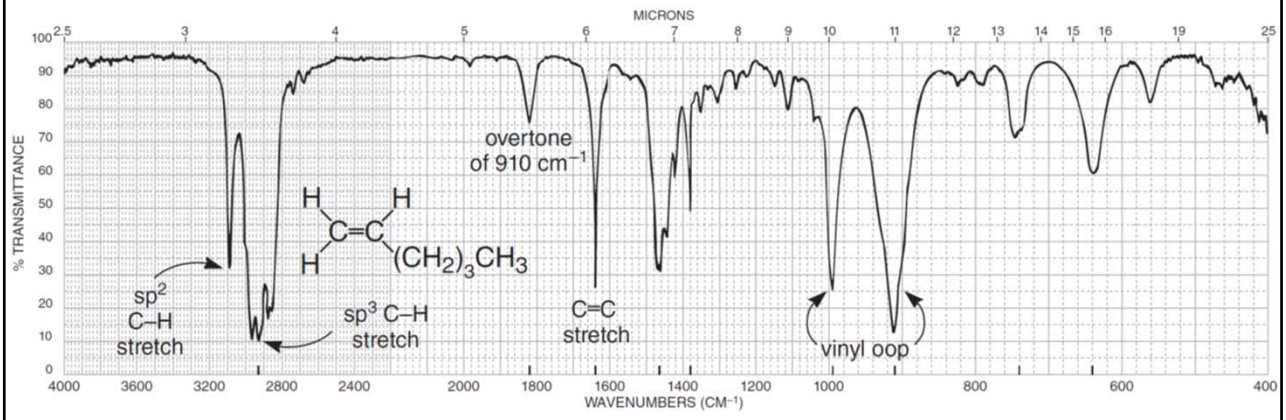


FIGURE 2.10 The infrared spectrum of 1-hexene (neat liquid, KBr plates).

89

Frequências características

Ex: 1-Octino

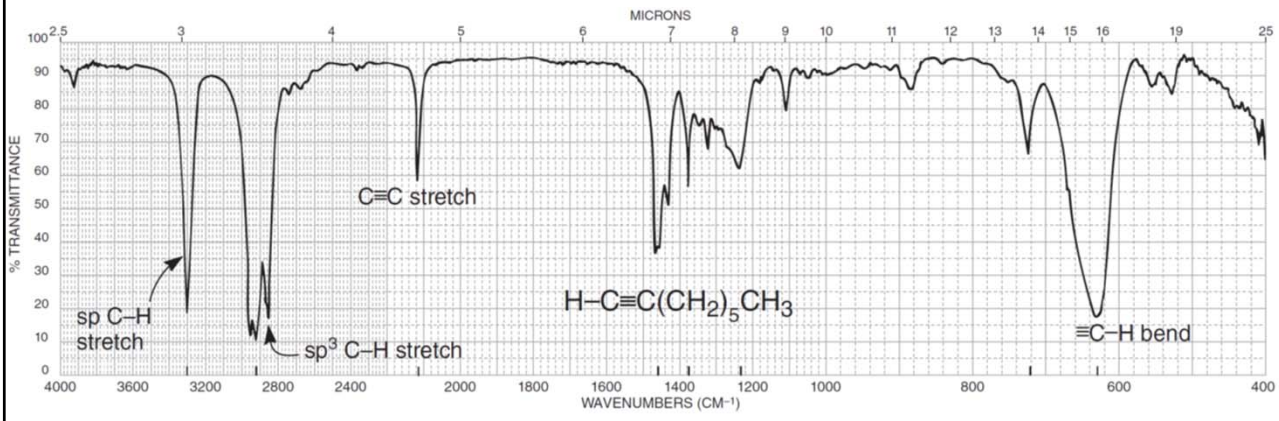


FIGURE 2.14 The infrared spectrum of 1-octyne (neat liquid, KBr plates).

90

Frequências características

Ex: 4-Octino

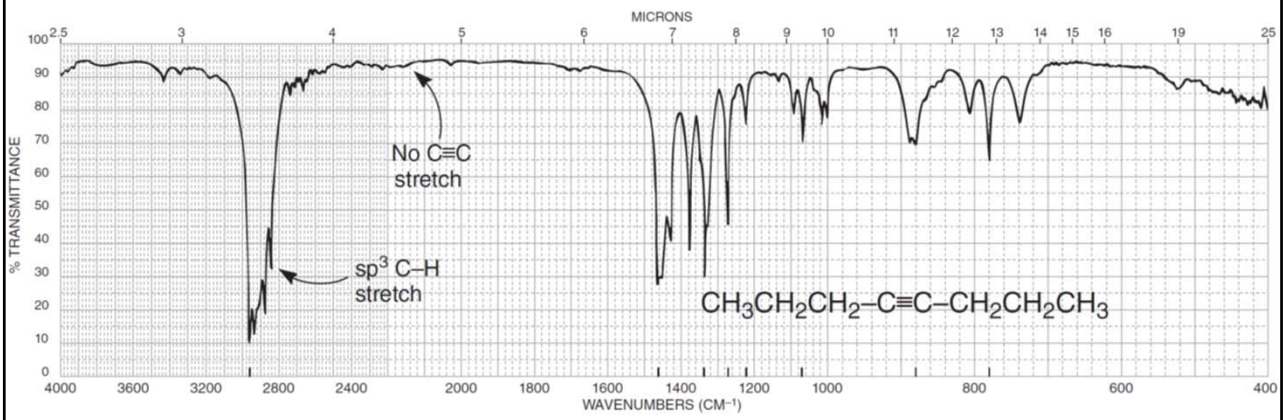
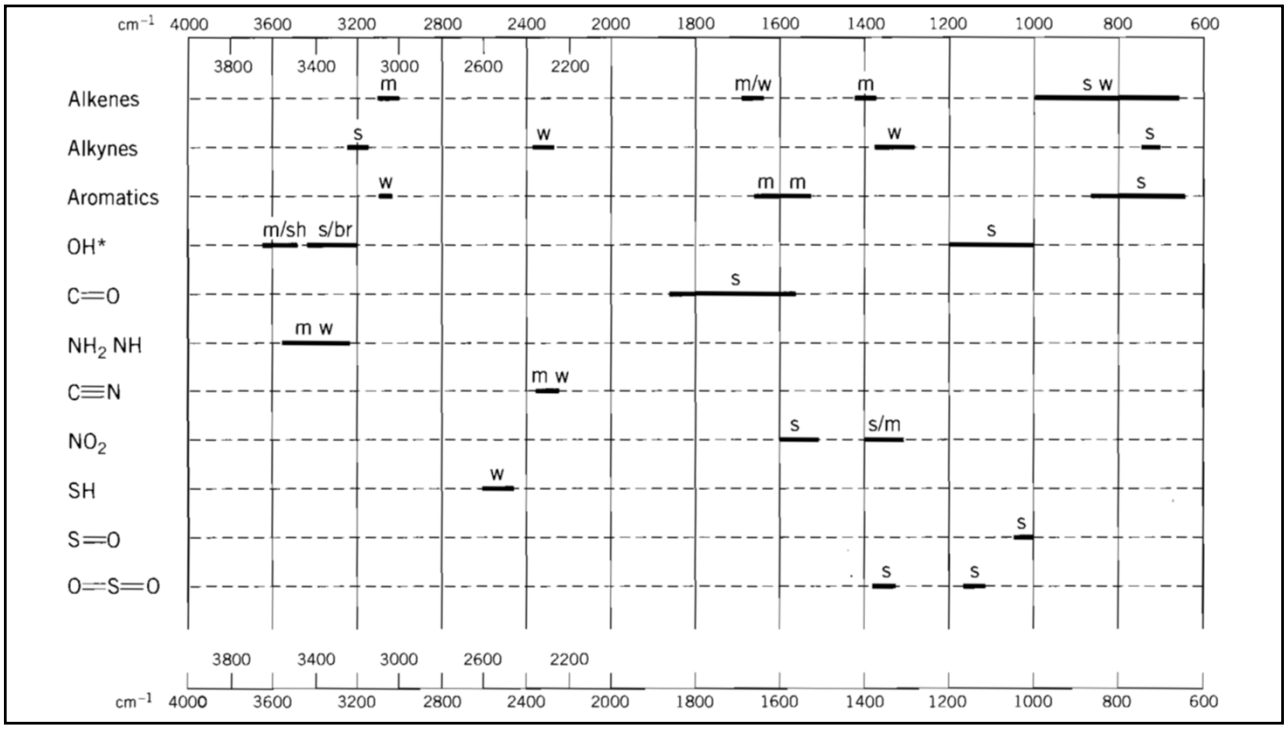
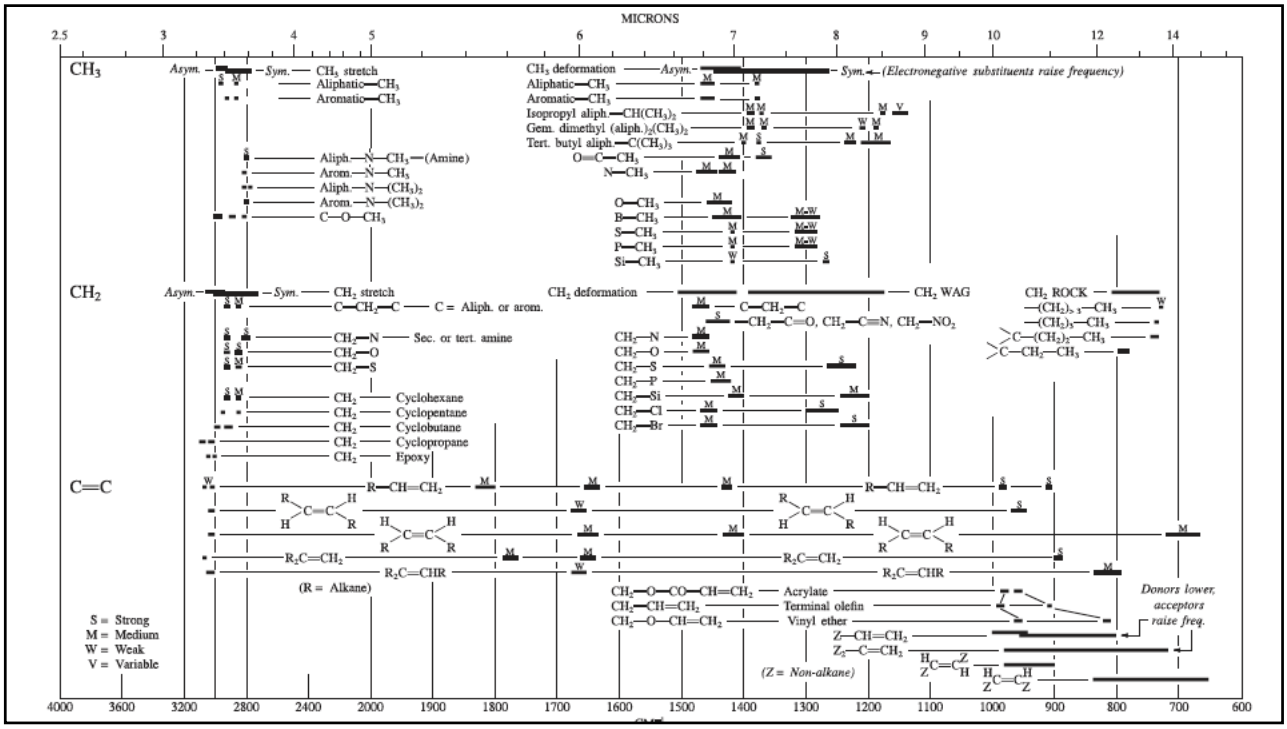


FIGURE 2.15 The infrared spectrum of 4-octyne (neat liquid, KBr plates).

91


cm⁻¹ 4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600
3800 3400 3000 2600 2200
Alkenes
Alkynes
Aromatics
OH*
C=O
NH2 NH
C≡N
NO2
SH
S=O
O=S=O
m
m/w
m
s w
s
w
w
s
w
m m
s
m/sh s/br
s
s
m w
m w
s
s/m
w
s
s
s

92


MICRONS
2.5 3 4 5 6 7 8 9 10 12 14
CH3
CH2
C=C
Asym.
Sym.
CH3 stretch
Aliphatic—CH3
Aromatic—CH3
CH3 deformation
(Electronegative substituents raise frequency)
Isopropyl aliph.—CH(CH3)2
Gem. dimethyl (aliph.)2C(CH3)2
Tert. butyl aliph.—C(CH3)3
Aliph.—N—CH3—(Amine)
Arom.—N—CH3
Aliph.—N—(CH3)2
Arom.—N—(CH3)2
C—O—CH3
O—CH3
B—CH3
S—CH3
P—CH3
Si—CH3
CH2 stretch
C—CH2—C
C = Aliph. or arom.
CH2 deformation
CH2 WAG
CH2 ROCK
CH2—N
CH2—O
CH2—S
CH2—P
CH2—Si
CH2—Cl
CH2—Br
Sec. or tert. amine
Cyclohexane
Cyclopentane
Cyclobutane
Cyclopropane
Epoxy
R—CH=CH2
R2C=CH2
R2C=CHR
(R = Alkane)
CH2—O—CO—CH=CH2 Acrylate
CH2—CH=CH2 Terminal olefin
CH2—O—CH=CH2 Vinyl ether
(Z = Non-alkane)
Donors lower, acceptors raise freq.
S = Strong
M = Medium
W = Weak
V = Variable
4000 3600 3200 2800 2400 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600

93

Frequências características

Ex: 2-Metil-2-butanona

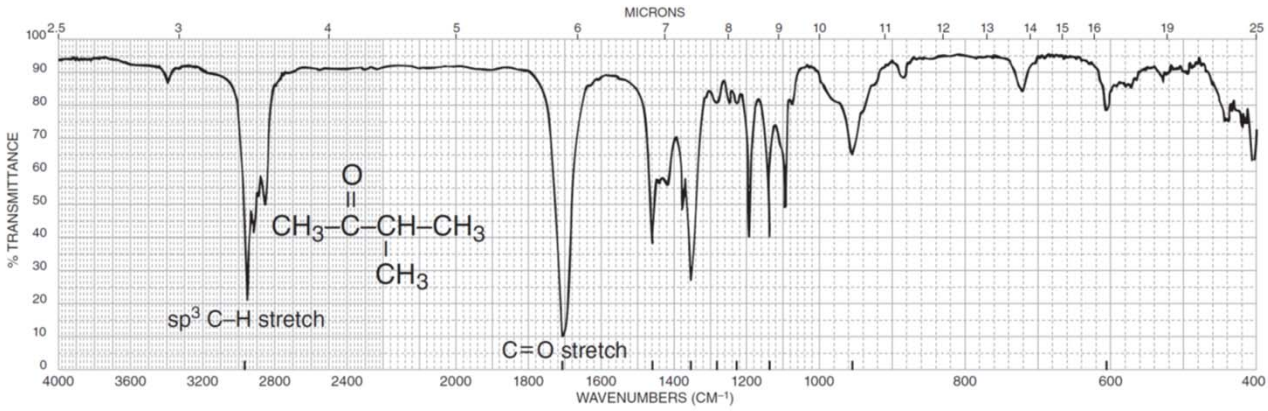


FIGURE 2.4 The infrared spectrum of 3-methyl-2-butanone (neat liquid, KBr plates).

94

Frequências características

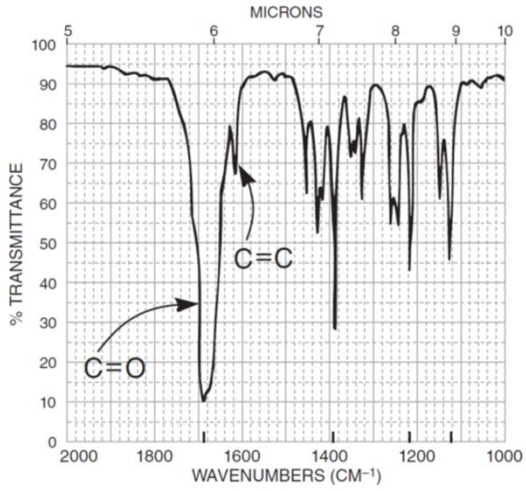


FIGURE 2.5 A comparison of the intensities of the C=O and C=C absorption bands.

95

Frequências características

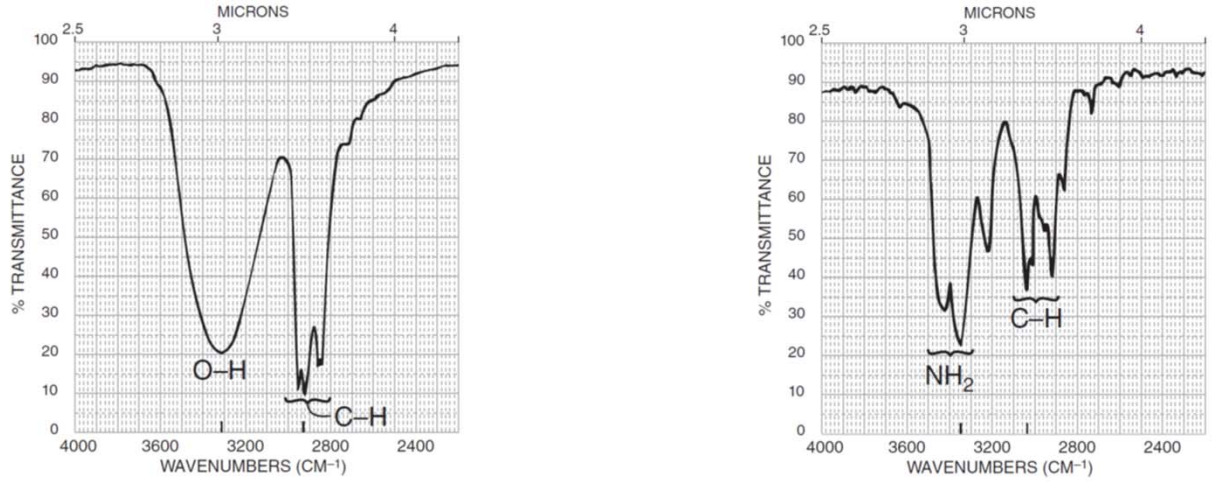


FIGURE 2.6 A comparison of the shapes of the absorption bands for the O—H and N—H groups.

96

Frequências características

Ex: Tolueno

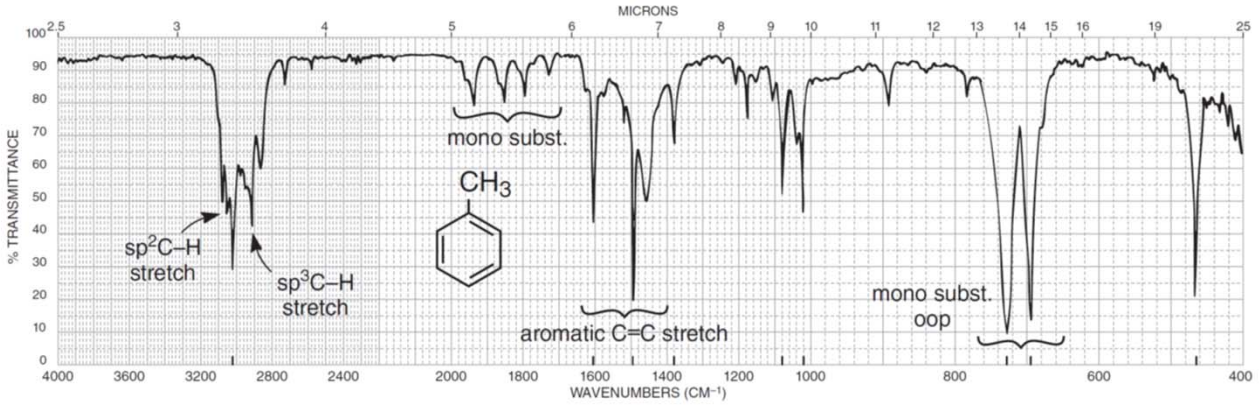


FIGURE 2.23 The infrared spectrum of toluene (neat liquid, KBr plates).

97

Frequências características

Ex: orto-dietilbenzeno

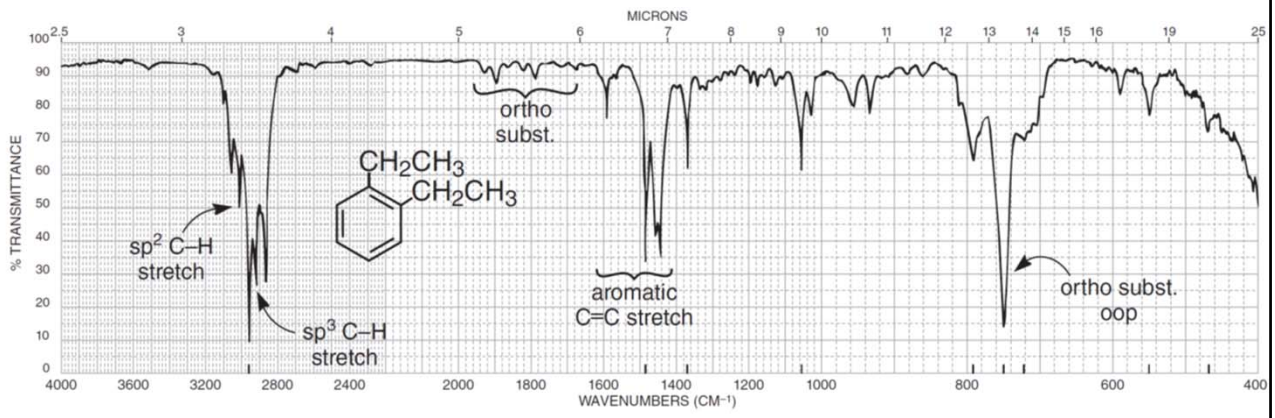


FIGURE 2.24 The infrared spectrum of *ortho*-diethylbenzene (neat liquid, KBr plates).

98

Frequências características

Ex: meta-dietilbenzeno

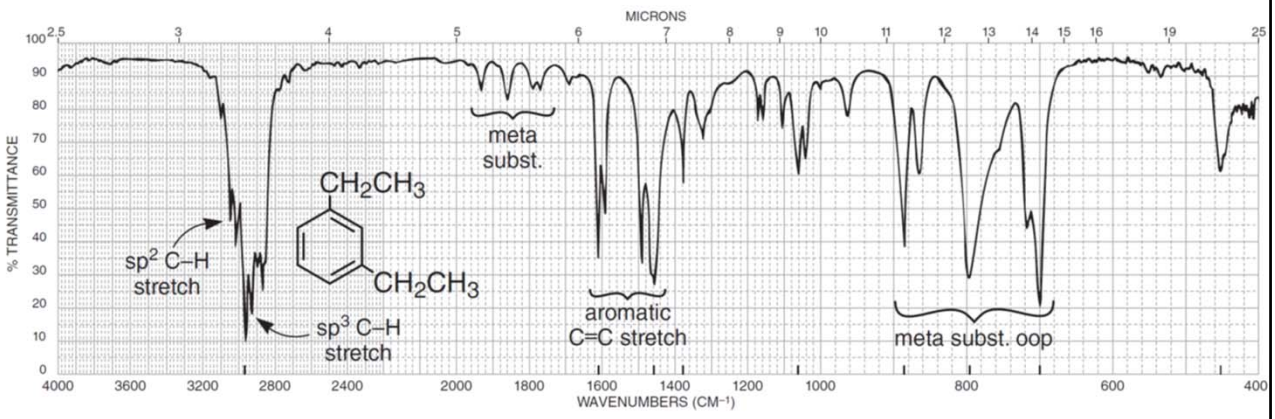


FIGURE 2.25 The infrared spectrum of *meta*-diethylbenzene (neat liquid, KBr plates).

99

Frequências características

Ex: para-dietilbenzeno

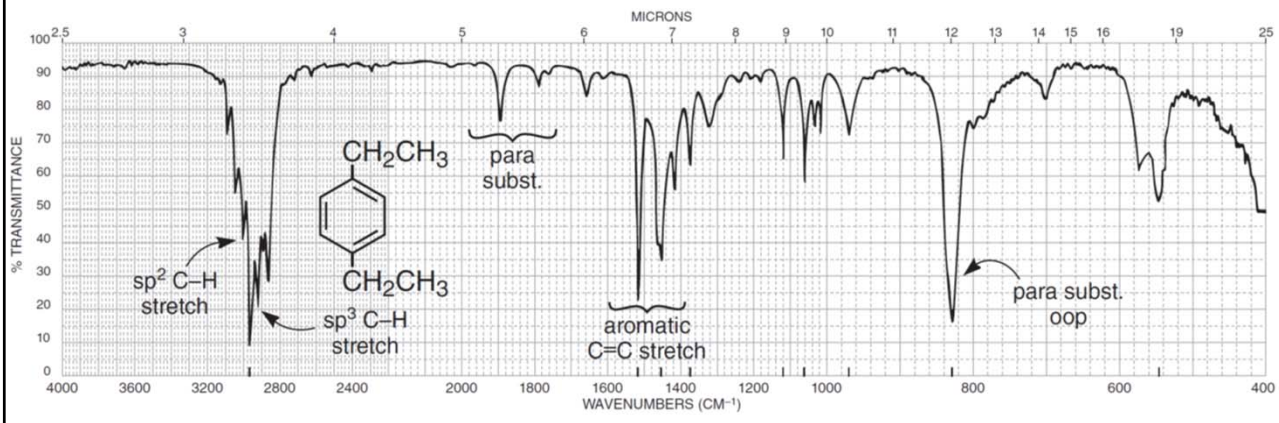


FIGURE 2.26 The infrared spectrum of *para*-diethylbenzene (neat liquid, KBr plates).

100

Frequências características

Ex: 1-hexanol

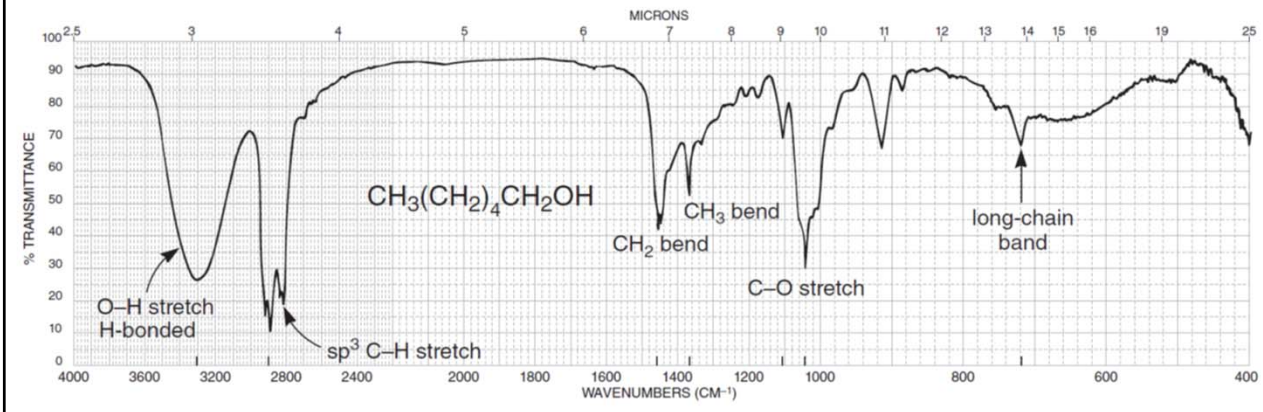


FIGURE 2.29 The infrared spectrum of 1-hexanol (neat liquid, KBr plates).

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Frequências características

Compostos carbonílicos

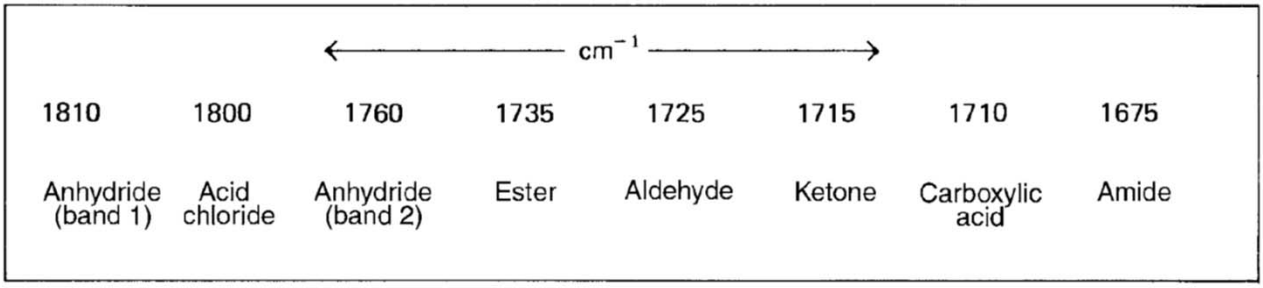

FIGURE 2.35 Normal base values for the C=O stretching vibrations for carbonyl groups.

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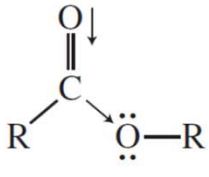
Frequências características

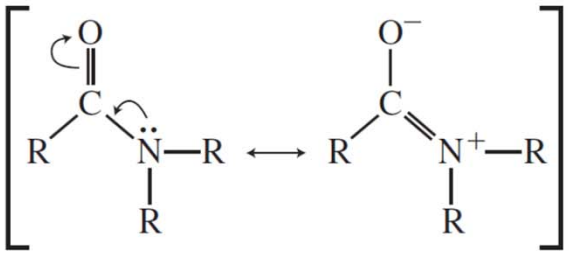
Compostos carbonílicos

Ester



Electron-withdrawing effect raises C═O frequency

Amide



Resonance effect lowers C═O frequency

103

Frequências características

Ex: butilamina

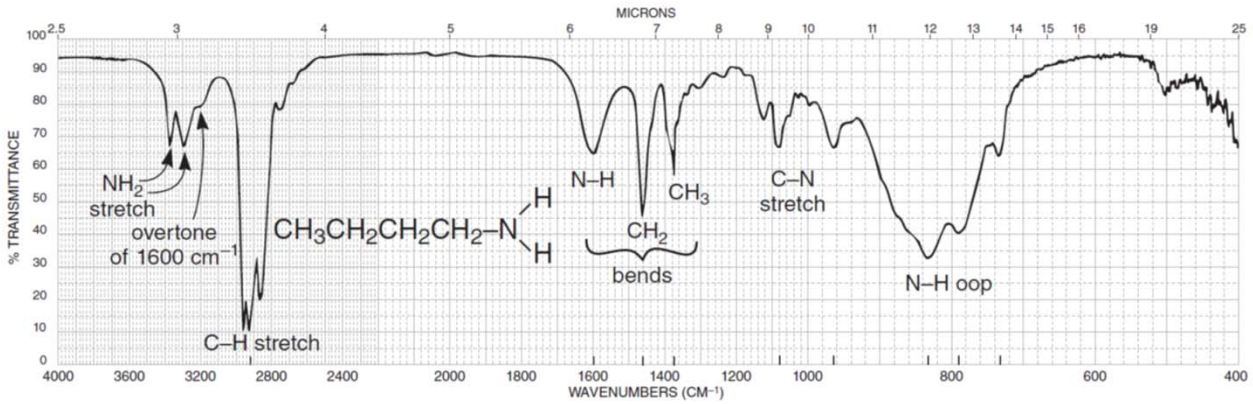


FIGURE 2.58 The infrared spectrum of butylamine (neat liquid, KBr plates).

104

Frequências características

Ex: dibutilamina

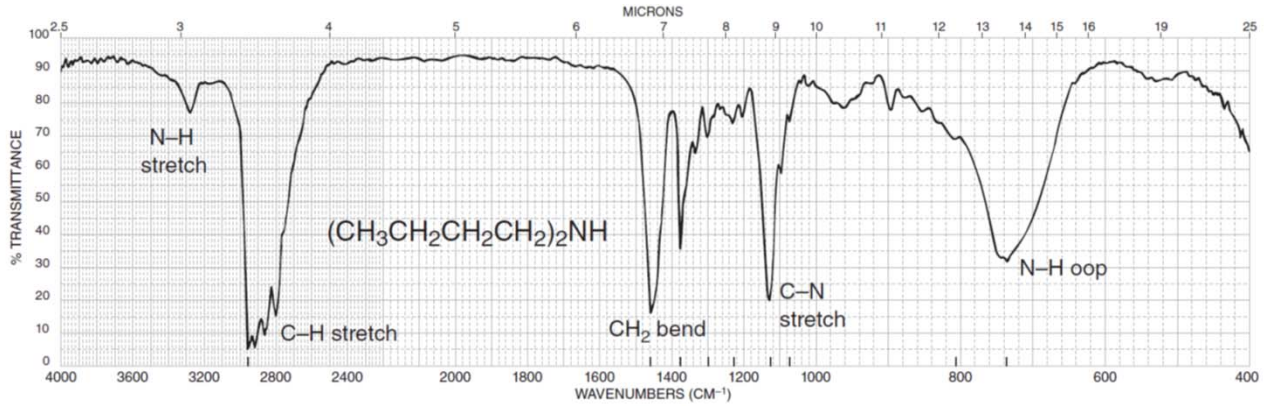


FIGURE 2.59 The infrared spectrum of dibutylamine (neat liquid, KBr plates).

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Frequências características

Ex: tributilamina

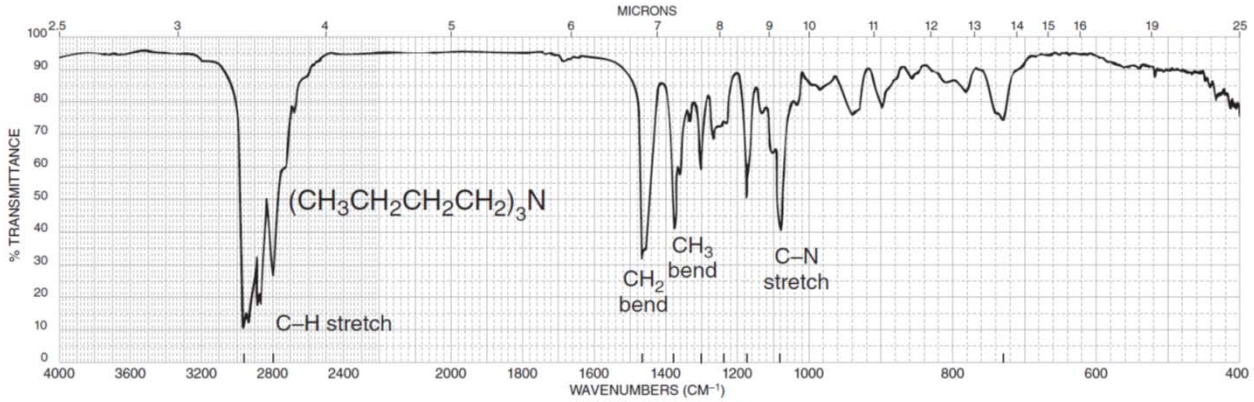

FIGURE 2.60 The infrared spectrum of tributylamine (neat liquid, KBr plates).

106

Frequências características

Ex: benzonitrila

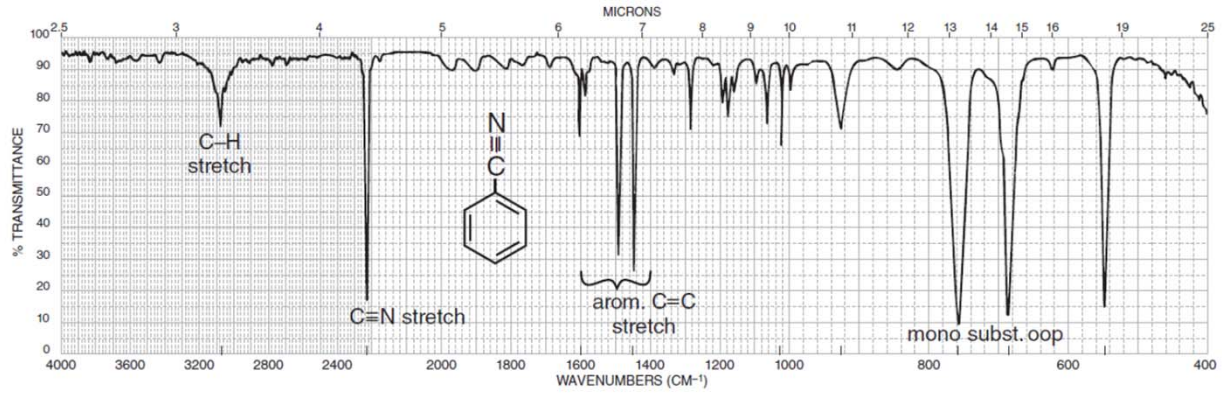

FIGURE 2.63 The infrared spectrum of benzonitrile (neat liquid, KBr plates).

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Frequências características

Ex: benzonitrila

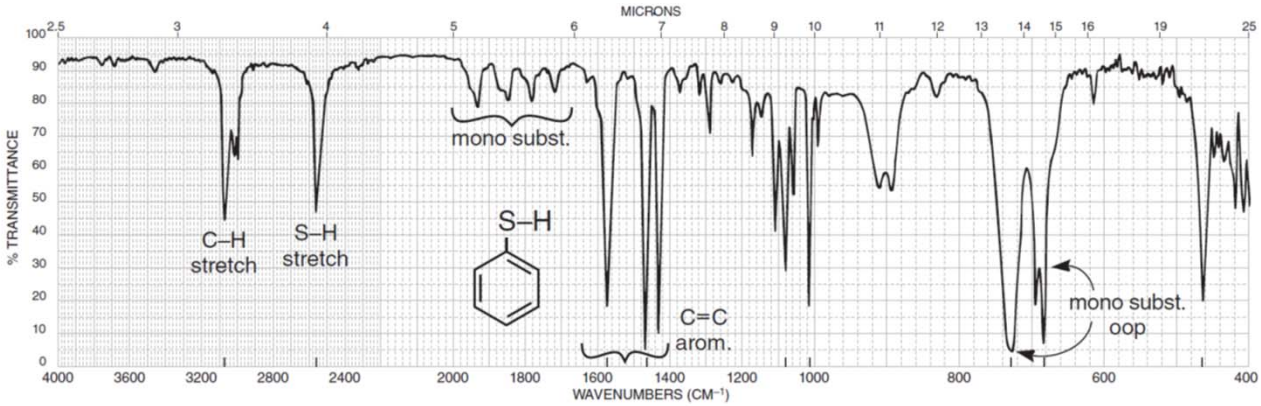

FIGURE 2.68 The infrared spectrum of benzenethiol (neat liquid, KBr plates).

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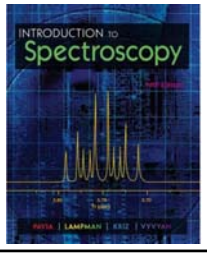
Frequências características



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Site - Exercícios

http://www.cheminfo.org/Spectra/IR/Exercises/Browse_Spectra/index.html

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Grau de insaturação

Alcanos: C_nH_{2n+2}

Álcoois: $C_nH_{2n+2}O_x$

Aminas: $C_nH_{2n+2+x}N_x$

...

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