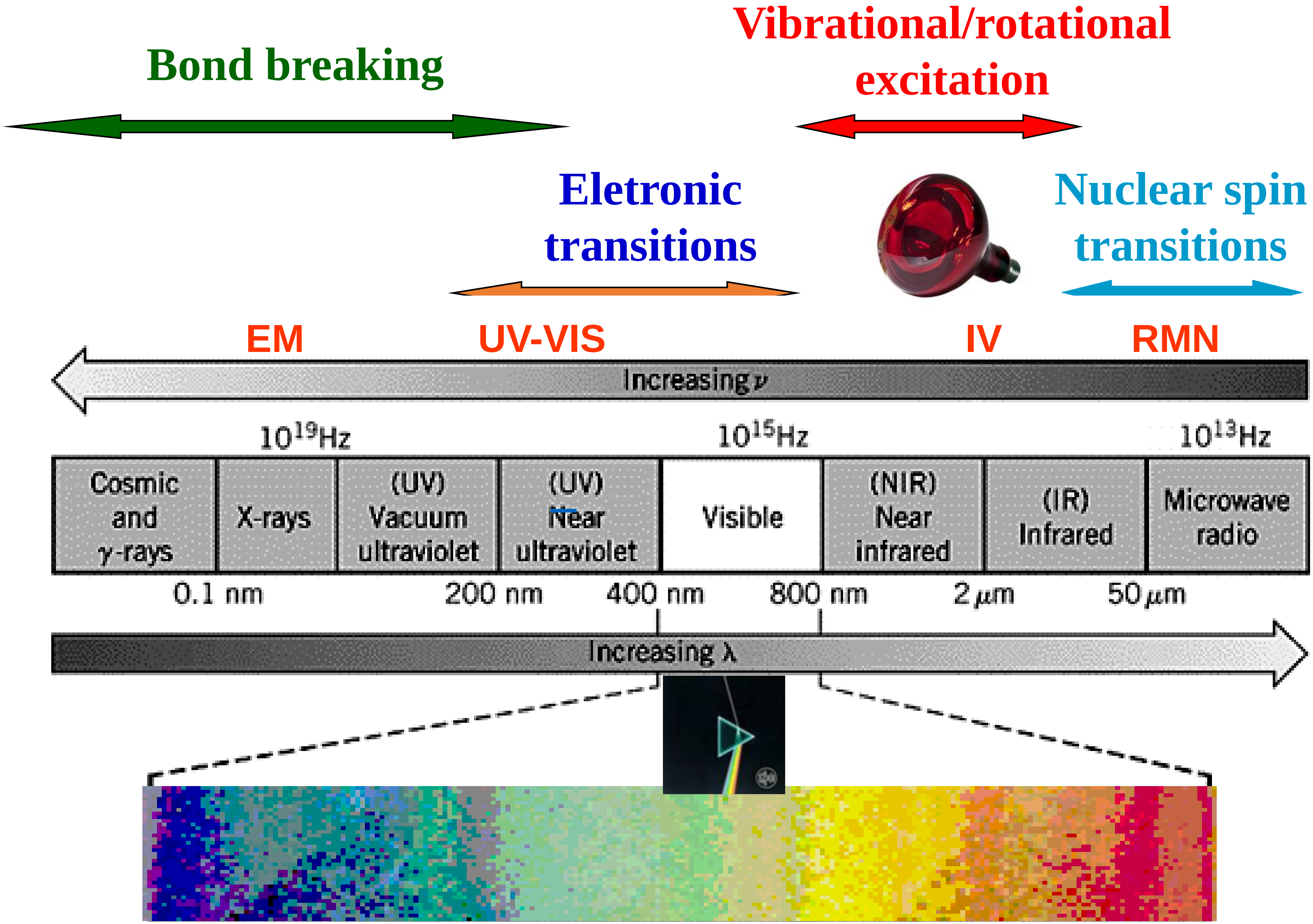
QFL0341 - Estrutura e Propriedades de Compostos Orgânicos - Noturno (2018)

23/08/2018

Introdução a métodos físico-químicos de caracterização de grupos funcionais

Espectroscopia vibracional (Infravermelho)



Bond breaking

Vibrational/rotational excitation

Eletronic transitions

Nuclear spin transitions

EM

UV-VIS

IV

RMN

As técnicas espectroscópicas permitem obter informações do universo estelar e também microscópico.

Consistem na perturbação do sistema (íons e moléculas) obtendo-se respostas emitidas (ou transmitidas) através das interações da luz com a matéria em diferentes comprimentos de ondas.

Determinação da fórmula molecular

Análise elementar

Espectrometria de massas

Determinação de grupos funcionais:

Análise funcional orgânica

Espectrofotometria no Ultravioleta e infravermelho

RMN de ${}^{1}H$ (indiretamente) e RMN de ${}^{13}C$ (diretamente)

Sites de referência para espectros

https://sdbs.db.aist.go.jp/sdbs/cgi-bin/cre_index.cgi

Infrared radiation

$\lambda = 2.5$ to 17 μm

$\nu \equiv 1/\lambda = 4000$ to 600 cm^{-1} (unities in wavenumber=
número de onda)

These frequencies match the frequencies of covalent bond stretching and bending vibrations.

Infrared spectroscopy can be used to find out about **covalent bonds** in molecules.

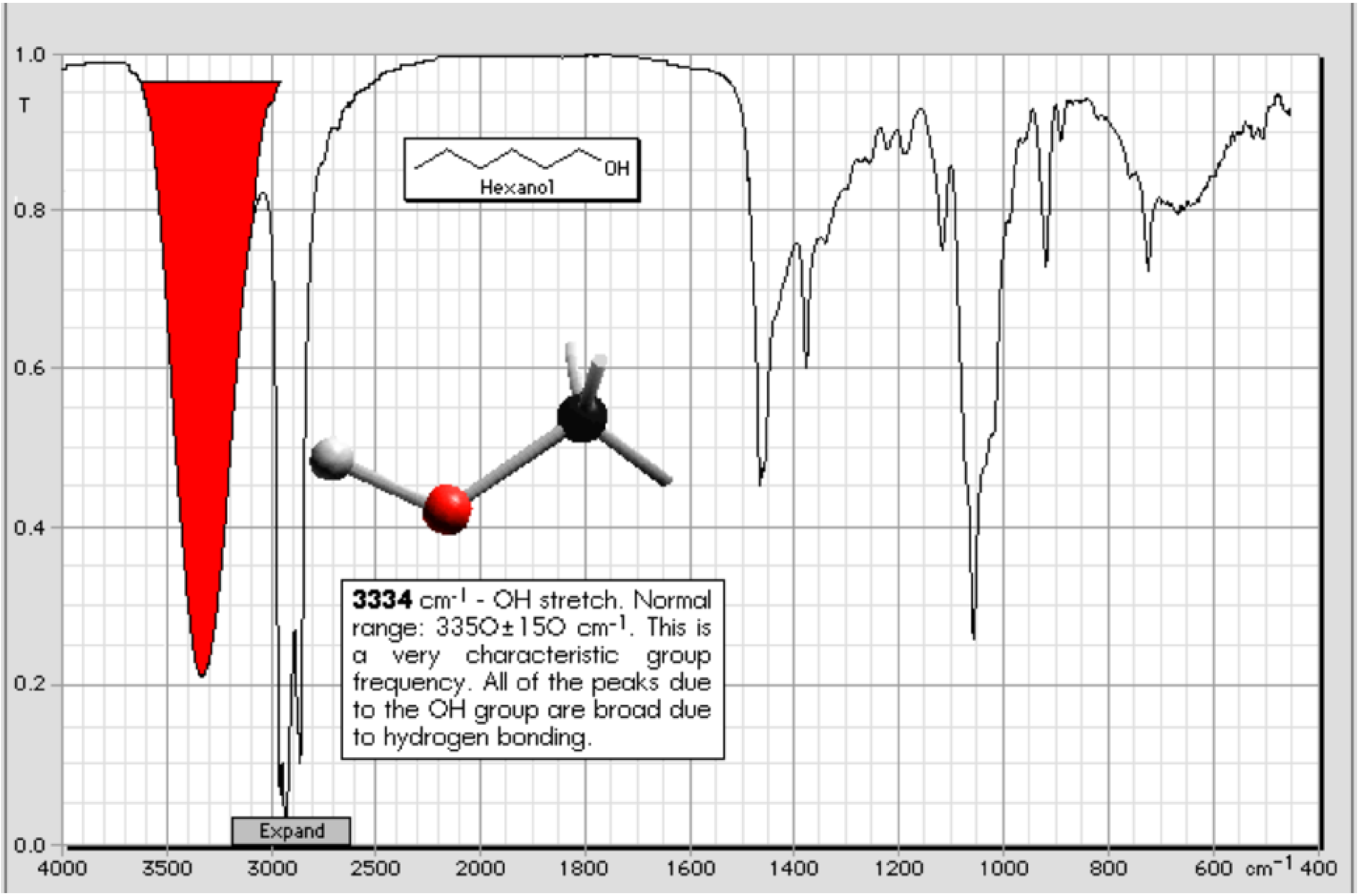
IR is used to tell:

1. what type of bonds are present

2. some structural information

Absorption bands for alcohols (streching of O-H)

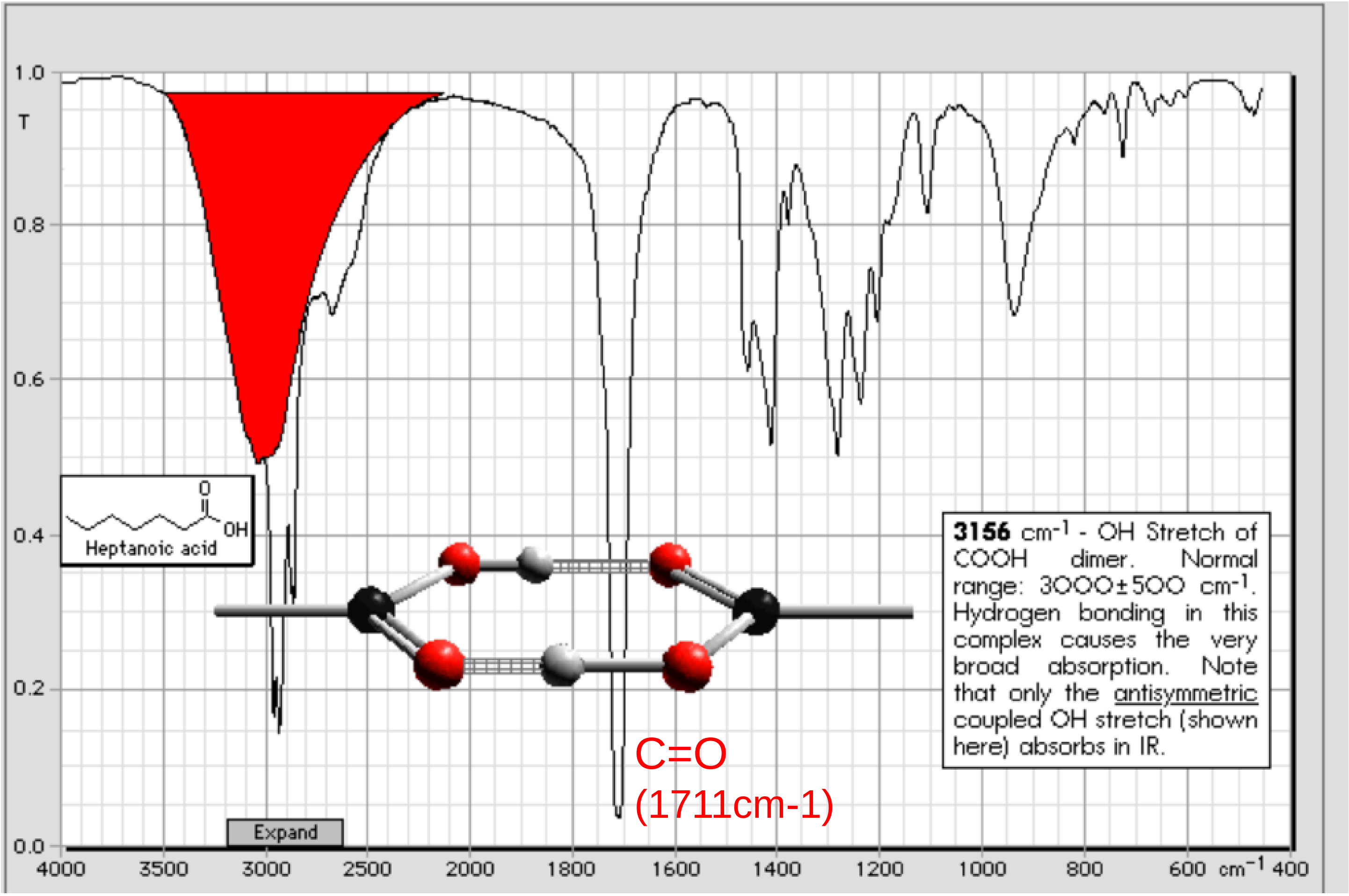
Broadening caused by different extension of hydrogen bonding)



3334 cm^{-1} - OH stretch. Normal range: 3350±150 cm^{-1}. This is a very characteristic group frequency. All of the peaks due to the OH group are broad due to hydrogen bonding.

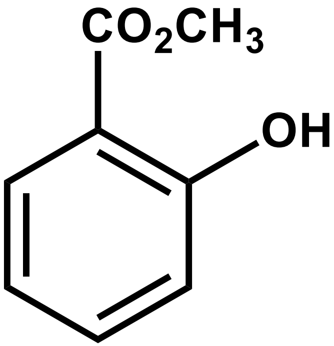
Absorption bands for carboxylic acids (streching of O-H)

The broadening of bands in carboxylic acids are very effective



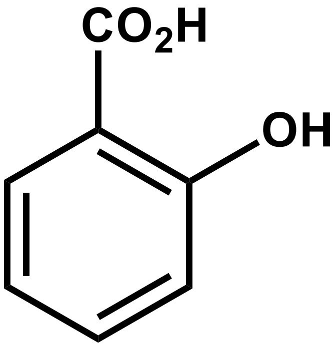
3156 cm^{-1} - OH Stretch of COOH dimer. Normal range: 3000±500 cm^{-1}. Hydrogen bonding in this complex causes the very broad absorption. Note that only the antisymmetric coupled OH stretch (shown here) absorbs in IR.

Como caracterizar os derivados do ácido salicílico com base nos íons moleculares nos espectros de massas?



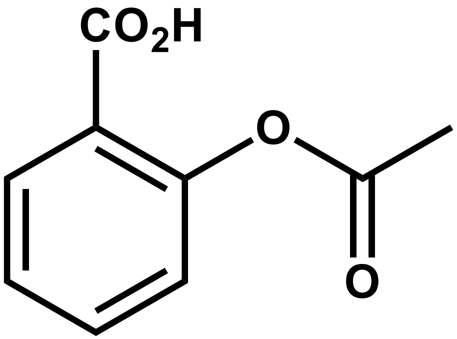
$C_8H_8O_3$

m/z 152



$C_7H_6O_3$

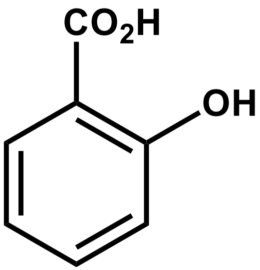
m/z 138



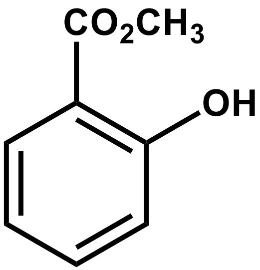
$C_9H_8O_4$

m/z 180

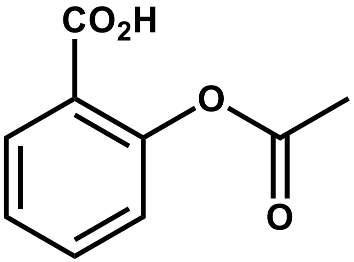
Como caracterizar os derivados do ácido salicílico com base nos espectros na região do Infravemelho?



Ácido salicílico

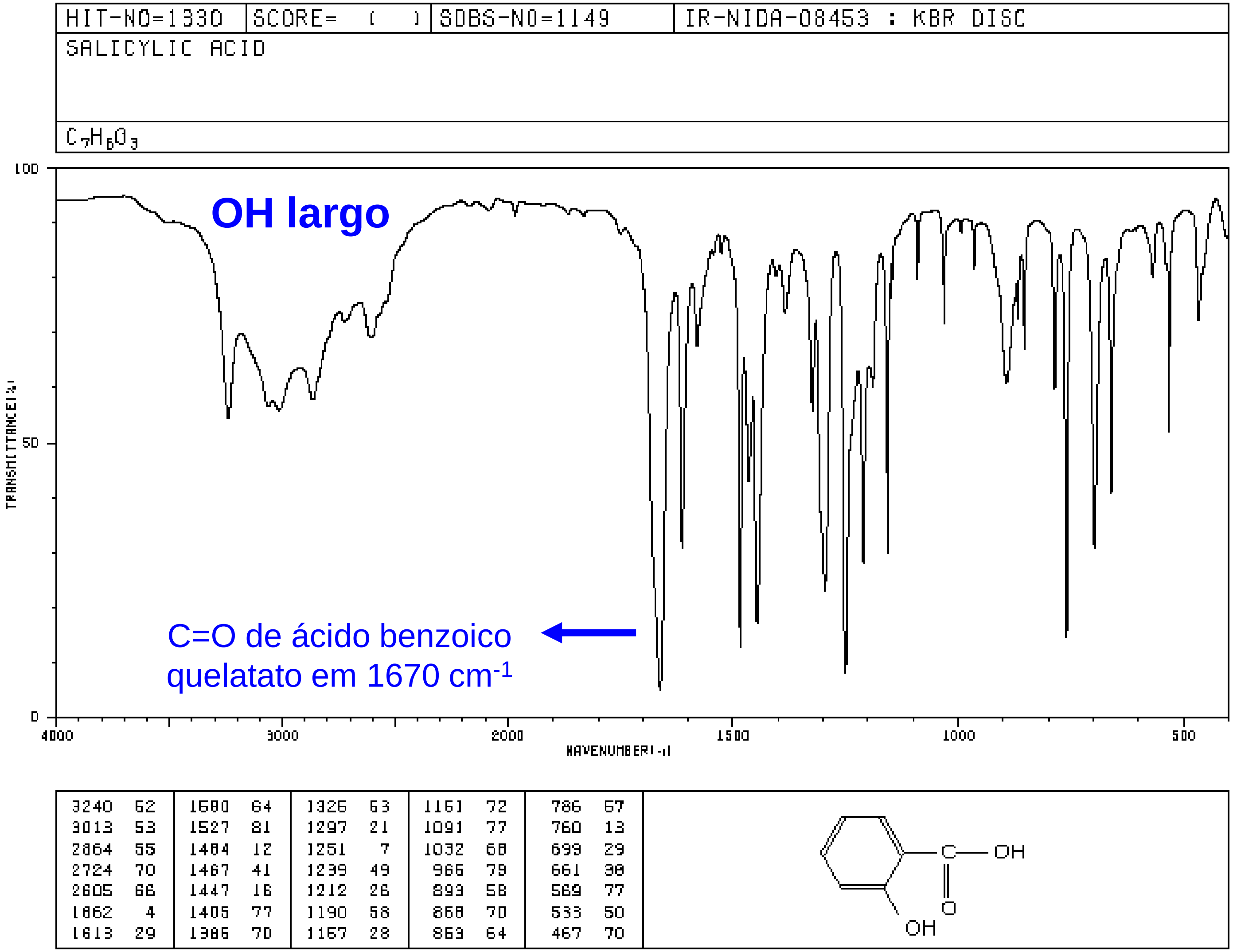


Salicílato de metila



Ácido acetil salicílico

Espectro no Infravermelho do ácido salicílico



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SALICYLIC ACID

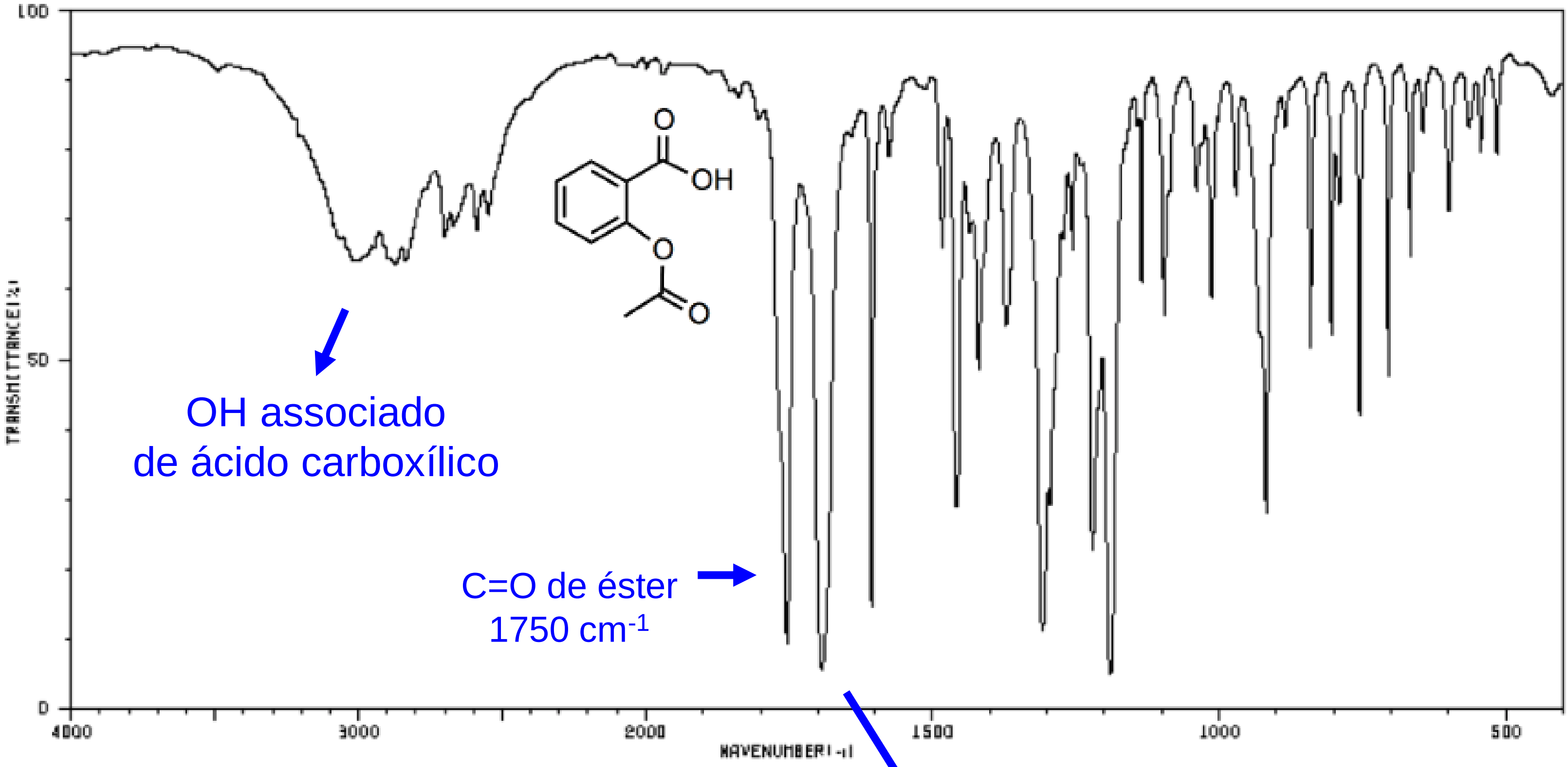
$C_7H_6O_3$

OH largo

C=O de ácido benzoico quelatato em 1670 cm^{-1}

3240	62	1680	64	1326	63	1161	72	786	67
3013	53	1527	81	1297	21	1091	77	760	13
2864	55	1484	12	1251	7	1032	68	699	29
2724	70	1467	41	1239	49	966	79	661	38
2605	66	1447	16	1212	26	893	58	569	77
1862	4	1405	77	1190	58	868	70	533	50
1613	29	1386	70	1167	28	863	64	467	70

Espectro no Infravermelho da aspirina?

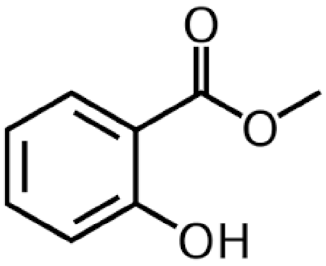


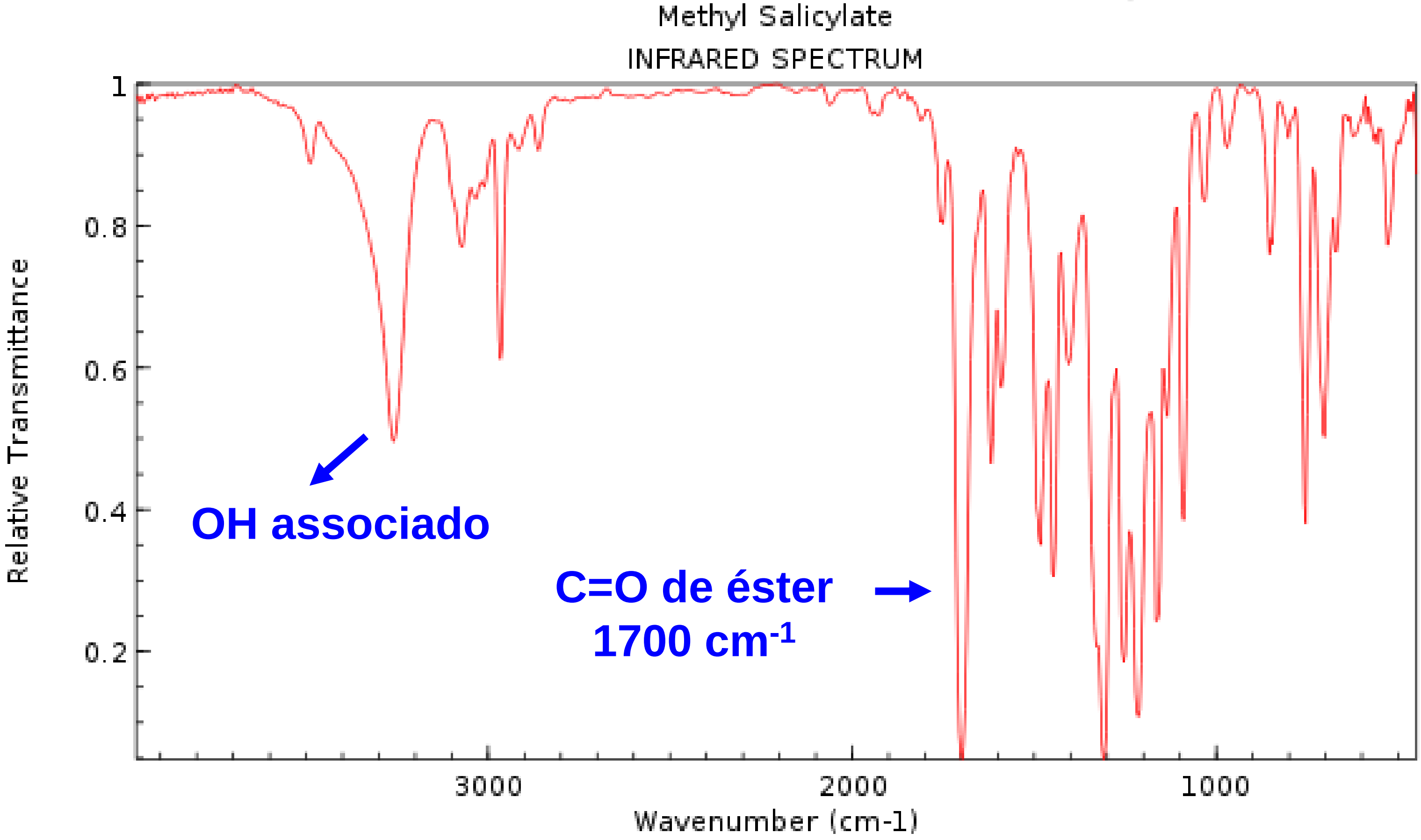
OH associado
de ácido carboxílico

C=O de éster
1750 cm^{-1}

C=O de ácido benzoico
1690 cm^{-1}

Espectro no Infravermelho do salicilato de metila



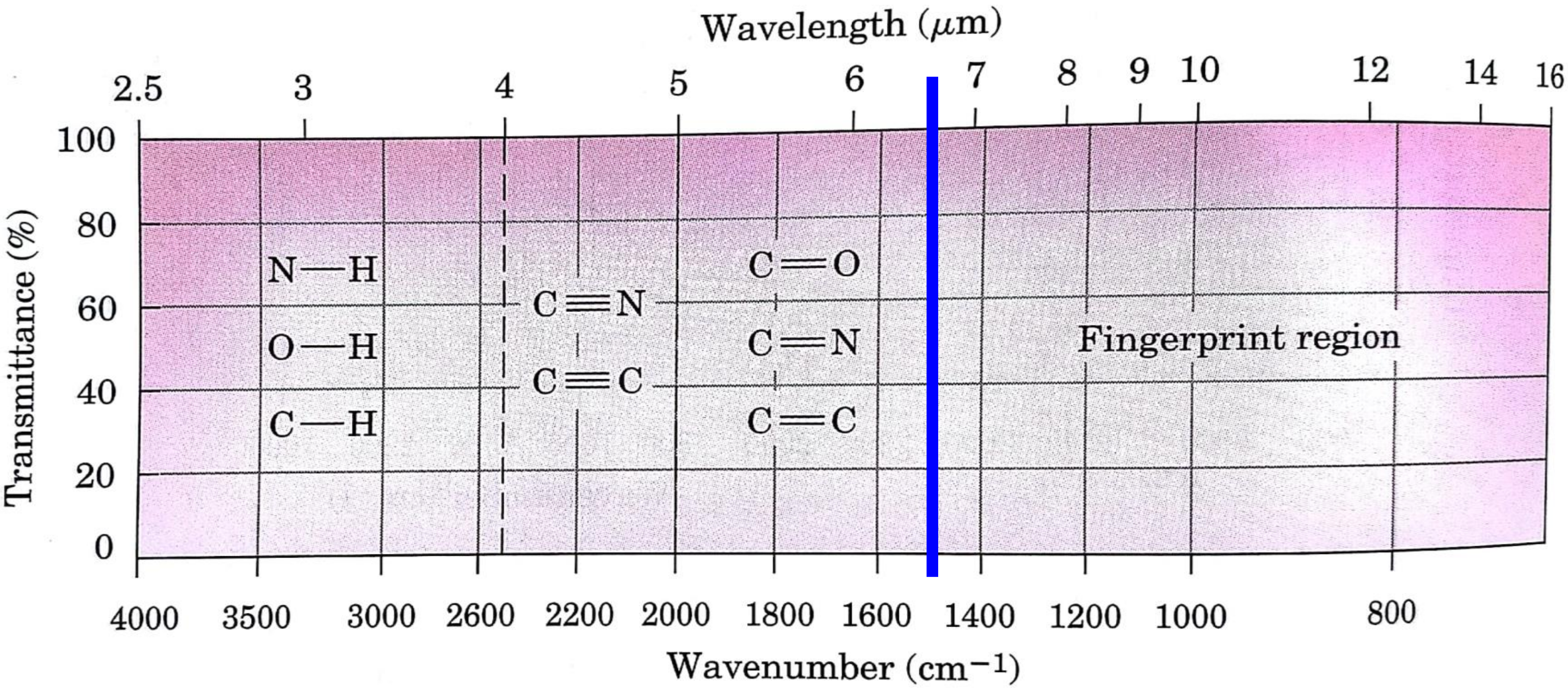


OH associado

C=O de éster
1700 cm^{-1}

NIST Chemistry WebBook (https://webbook.nist.gov/chemistry)

Principais bandas de absorção no Infravermelho de compostos orgânicos



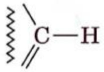
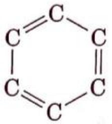
Região de grupos funcionais

Região de maior frequência
(Estiramentos ou deformações axiais)

Região de impressão digital

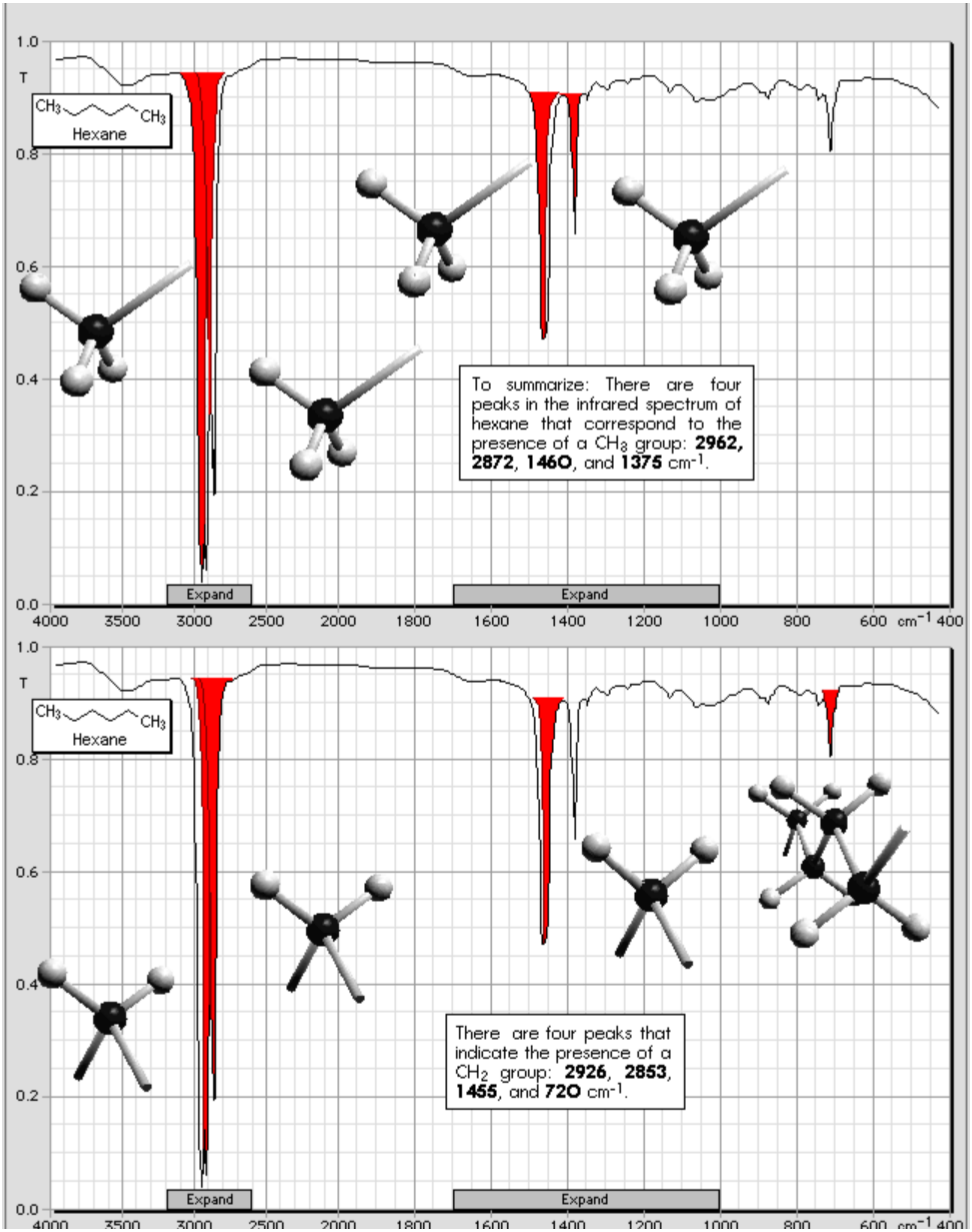
Região de menor frequência
(deformações angulares)

TABLE 12.1 Characteristic IR Absorptions of Some Functional Groups

Functional group class	Band position (cm^{-1})	Intensity of absorption
Alkanes, alkyl groups		
C—H	2850–2960	Medium to strong
Alkenes		
=C—H	3020–3100	Medium
C=C	1640–1680	Medium
Alkynes		
≡C—H	3300	Strong
—C≡C—	2100–2260	Medium
Alkyl halides		
C—Cl	600–800	Strong
C—Br	500–600	Strong
C—I	500	Strong
Alcohols		
O—H	3400–3650	Strong, broad
C—O	1050–1150	Strong
Aromatics		
	3030	Weak
	1660–2000 1450–1600	Weak Medium
Amines		
N—H	3300–3500	Medium
C—N	1030–1230	Medium
Carbonyl compounds[a]		
C=O	1670–1780	Strong
Carboxylic acids		
O—H	2500–3100	Strong, very broad
Nitriles		
C≡N	2210–2260	Medium
Nitro compounds		
NO_2	1540	Strong

[a] Carboxylic acids, esters, aldehydes, and ketones.

Infrared spectrum of hexane



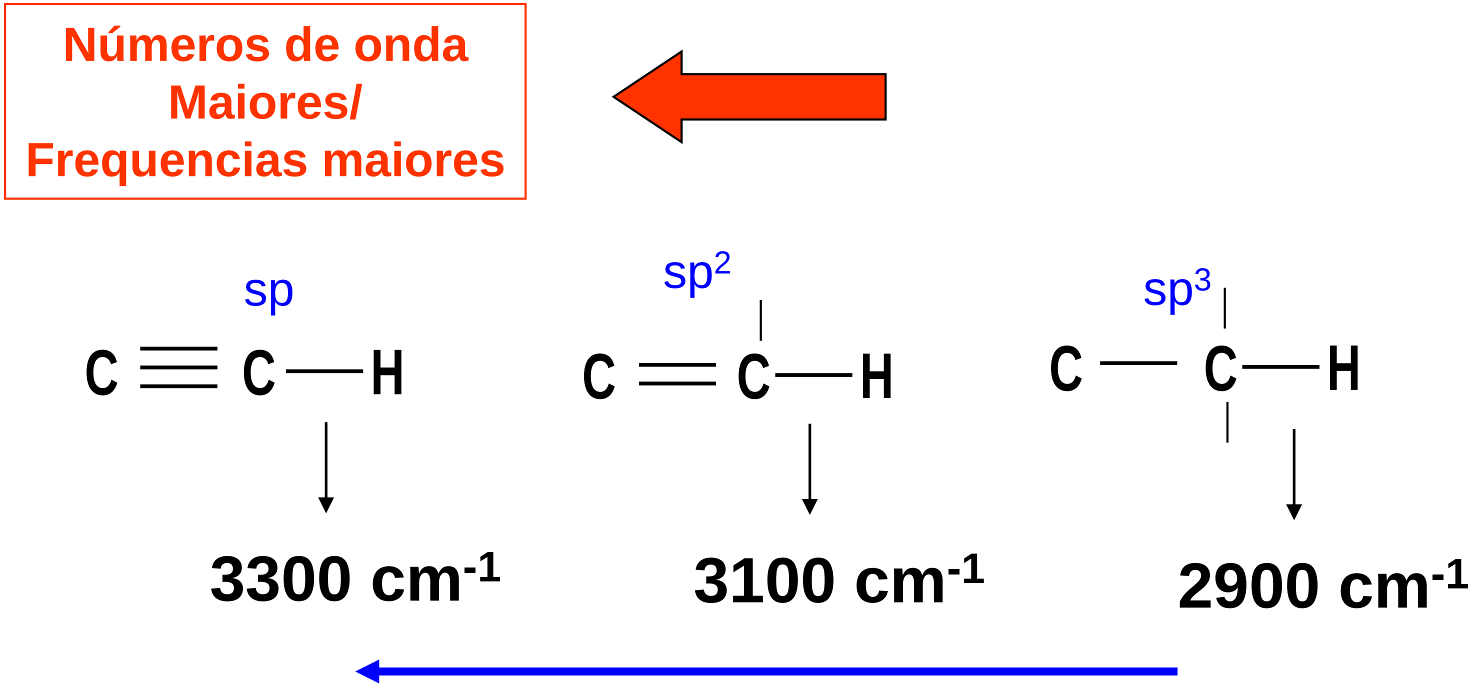
To summarize: There are four peaks in the infrared spectrum of hexane that correspond to the presence of a CH_3 group: **2962, 2872**, **1460**, and **1375** cm^{-1}.

There are four peaks that indicate the presence of a CH_2 group: **2926**, **2853**, **1455**, and **720** cm^{-1}.

Hidrocarbonetos

Como as bandas no IV são afetadas?

Efeito da eletronegatividade do carbono sobre a banda C-H



Números de onda Maiores/ Frequencias maiores

sp

$C \equiv C-H$

3300 cm^{-1}

sp^2

$C = C-H$

3100 cm^{-1}

sp^3

$C-C-H$

2900 cm^{-1}

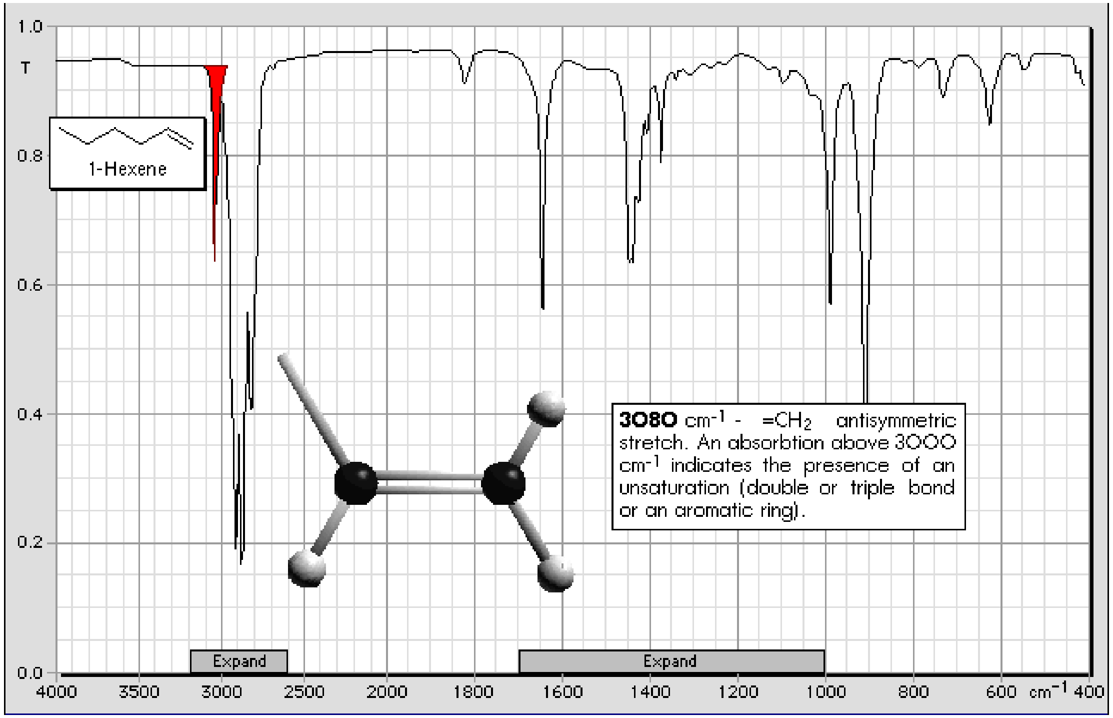
Maior força atrativa entre C-H

Stretching frequencies for **carbon-carbon** bonds and correlations with bond strengths (bond order)

	Bond strength*	Bond order	ν
$C-C$	350	1	1000 cm^{-1}
$C=C$	600	2	1600 cm^{-1}
$C\equiv C$	840	3	2200 cm^{-1}

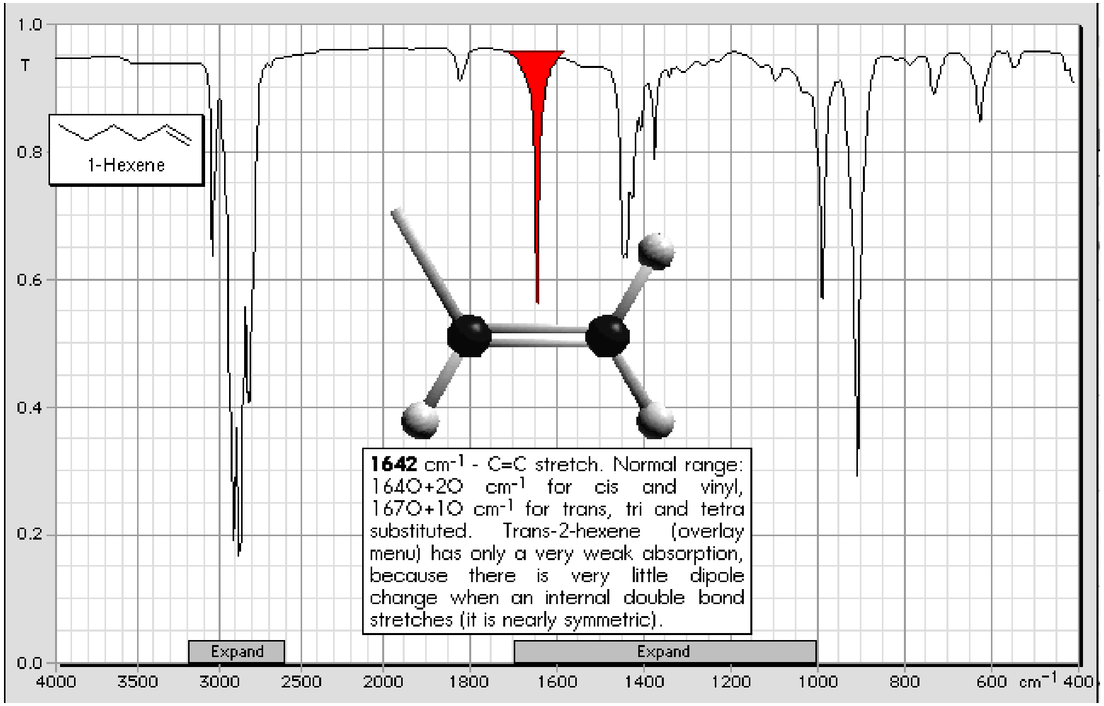
*In kJ/mol

Infrared spectrum for 1-hexene



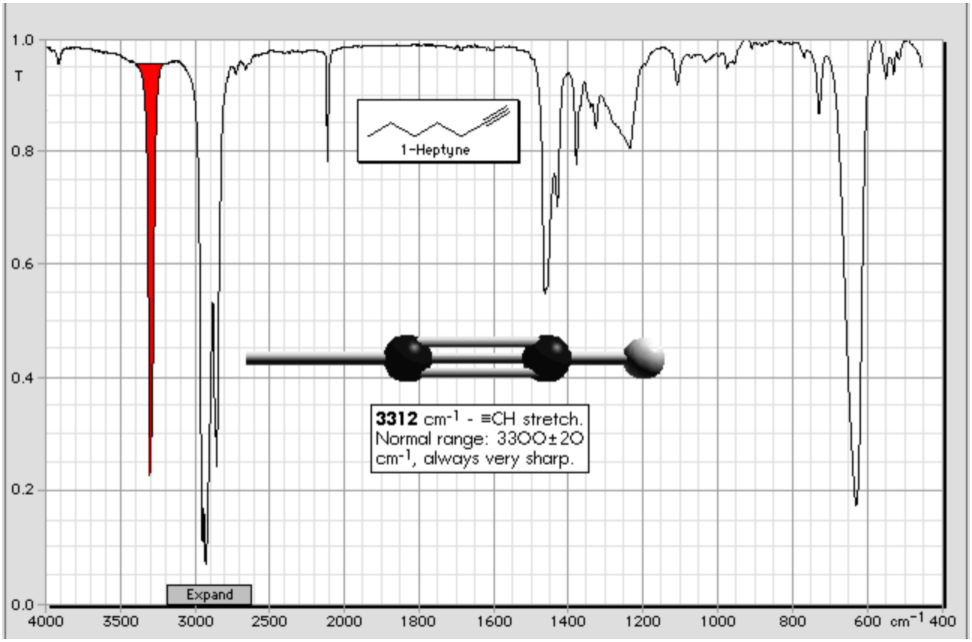
3080 cm^{-1} - $=CH_2$ antisymmetric stretch. An absorbtion above 3000 cm^{-1} indicates the presence of an unsaturation (double or triple bond or an aromatic ring).

1642 cm^{-1}

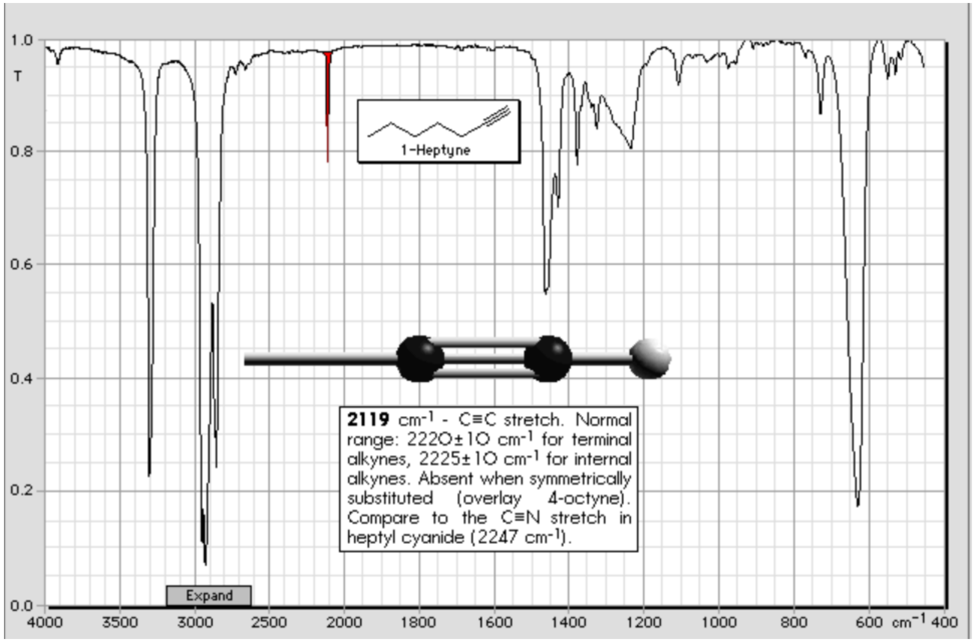


1642 cm^{-1} - C=C stretch. Normal range: 1640+20 cm^{-1} for cis and vinyl, 1670+10 cm^{-1} for trans, tri and tetra substituted. Trans-2-hexene (overlay menu) has only a very weak absorption, because there is very little dipole change when an internal double bond stretches (it is nearly symmetric).

Infrared spectra for 1-heptyne



3312 cm^{-1} - ≡CH stretch. Normal range: 3300±20 cm^{-1}, always very sharp.



2119 cm^{-1} - C≡C stretch. Normal range: 2220±10 cm^{-1} for terminal alkynes, 2225±10 cm^{-1} for internal alkynes. Absent when symmetrically substituted (overlay 4-octyne). Compare to the C≡N stretch in heptyl cyanide (2247 cm^{-1}).

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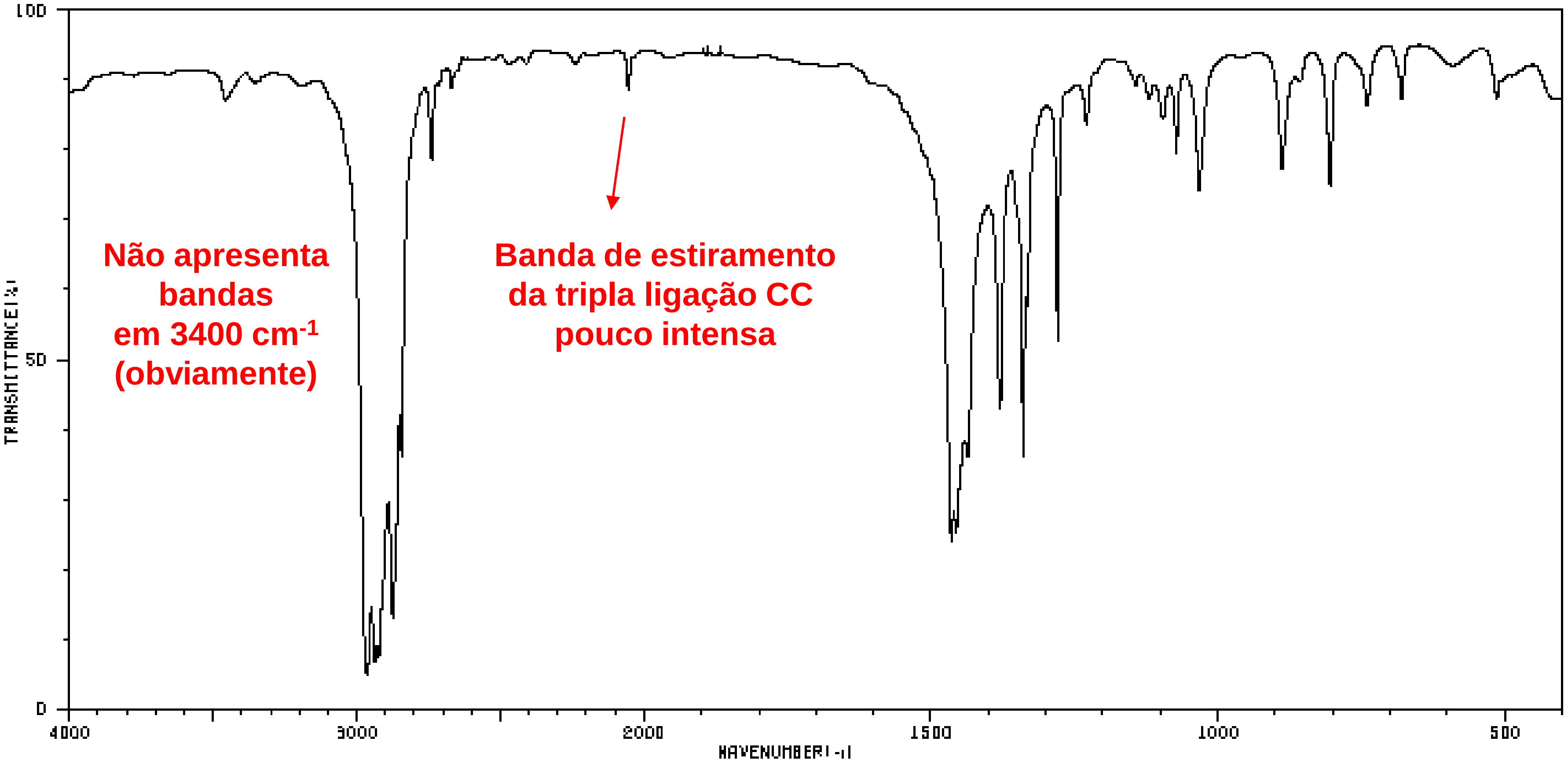
2-HEXYNE

C_6H_{10}



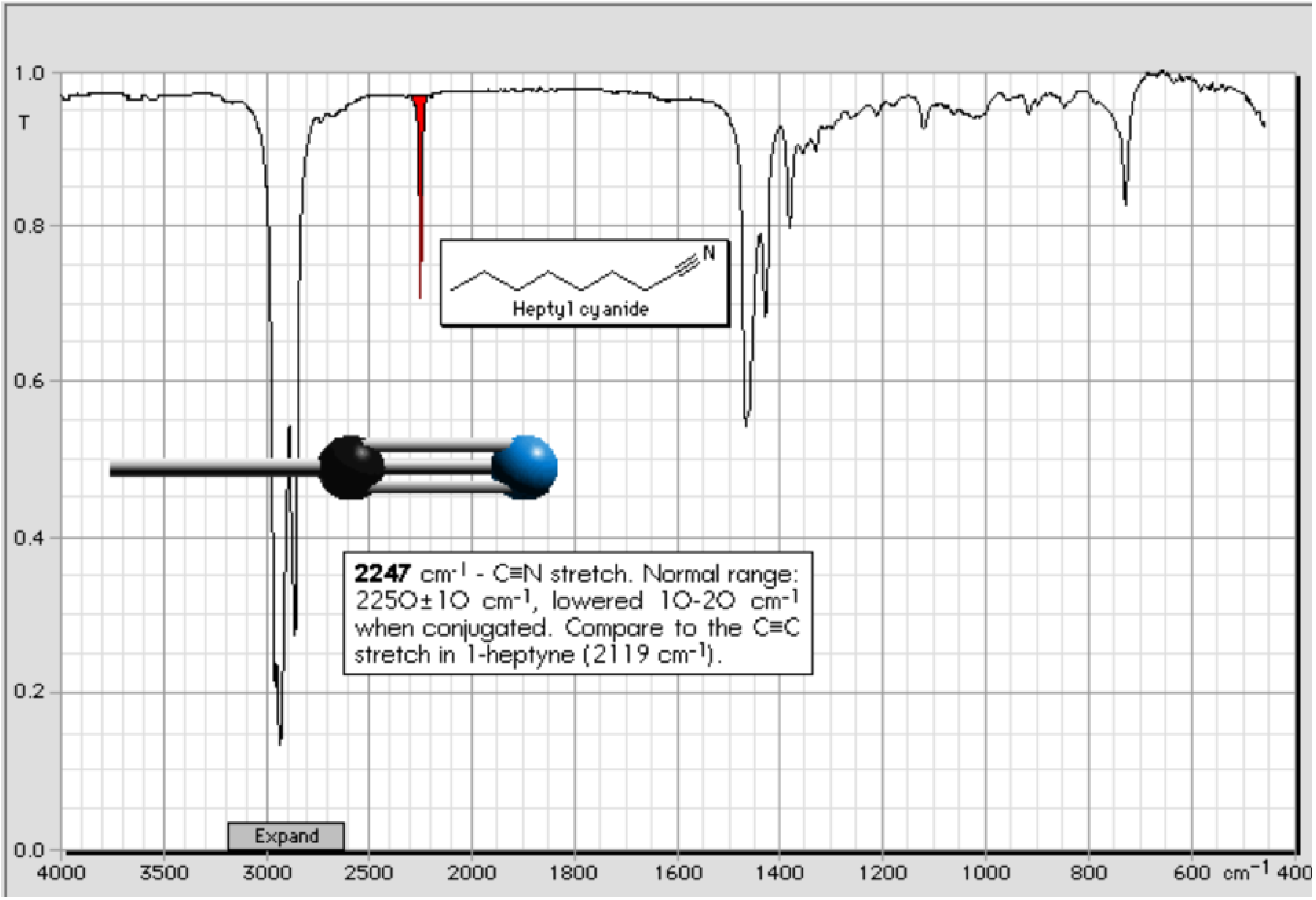
Não apresenta bandas em 3400 cm^{-1} (obviamente)

Banda de estiramento da tripla ligação CC pouco intensa

3468	84	2739	77	1340	36	1073	77	606	86
3354	86	2671	86	1333	55	1033	72		
2964	4	2054	84	1279	50	889	74		
2936	6	1466	29	1229	81	806	72		
2922	7	1456	24	1144	86	740	84		
2875	12	1438	34	1120	84	679	84		
2844	36	1380	41	1096	81	614	84		

$H_3C-C\equiv C-(CH_2)_2-CH_3$

Infrared spectra for heptyl cyanide



2247 cm⁻¹ - C≡N stretch. Normal range: 2250±10 cm⁻¹, lowered 10-20 cm⁻¹ when conjugated. Compare to the C≡C stretch in 1-heptyne (2119 cm⁻¹).

Higher frequency (2247 cm^{-1}) than triple bond C-C (2120 cm^{-1})

Efeito da massa atômica (C-X) dos grupos Ligados ao átomo de carbono

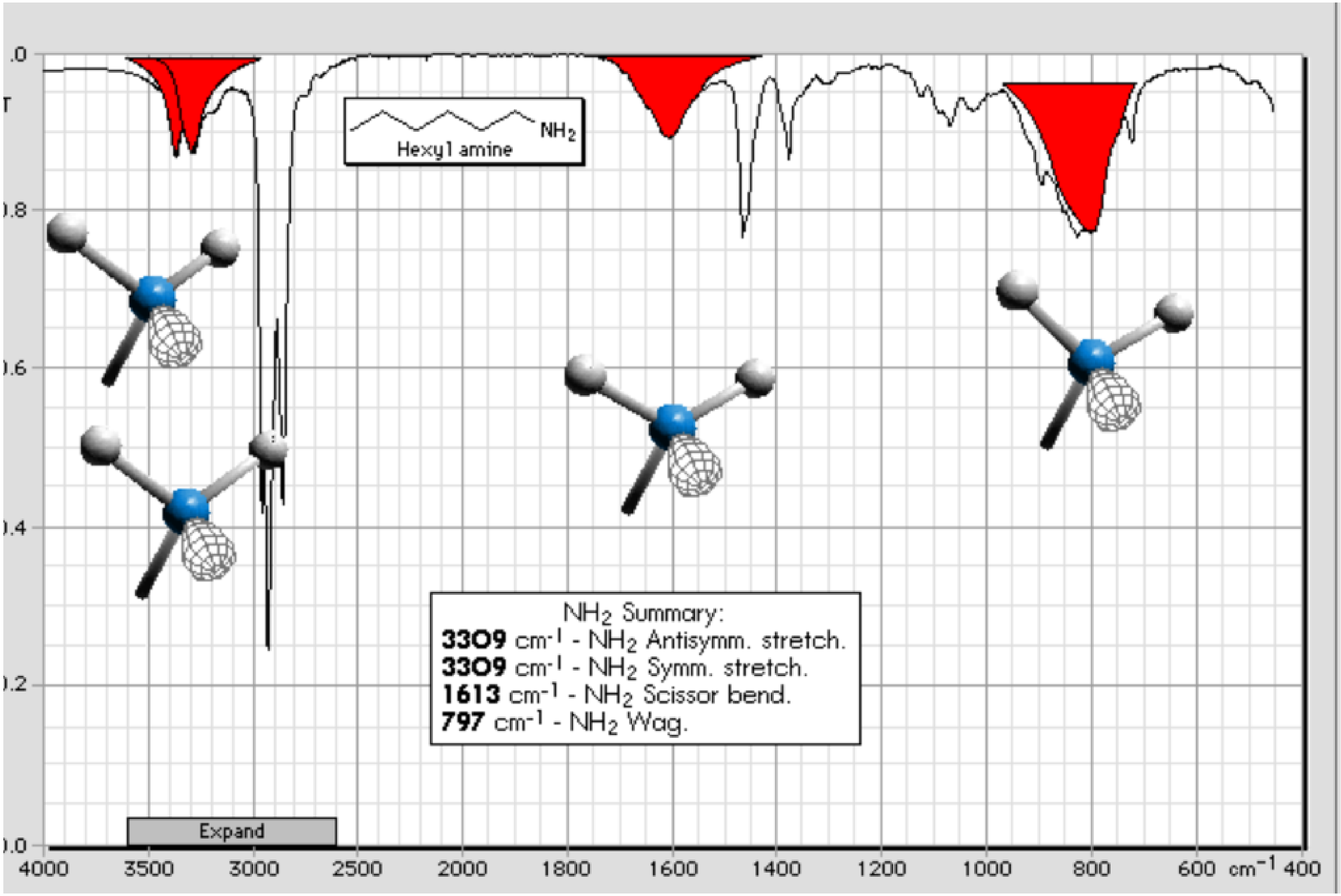
Números de onda menores

C-H	C-C	C-O	C-Cl	C-Br	C-I
3000	1200	1100	750	600	500

frequencias menores

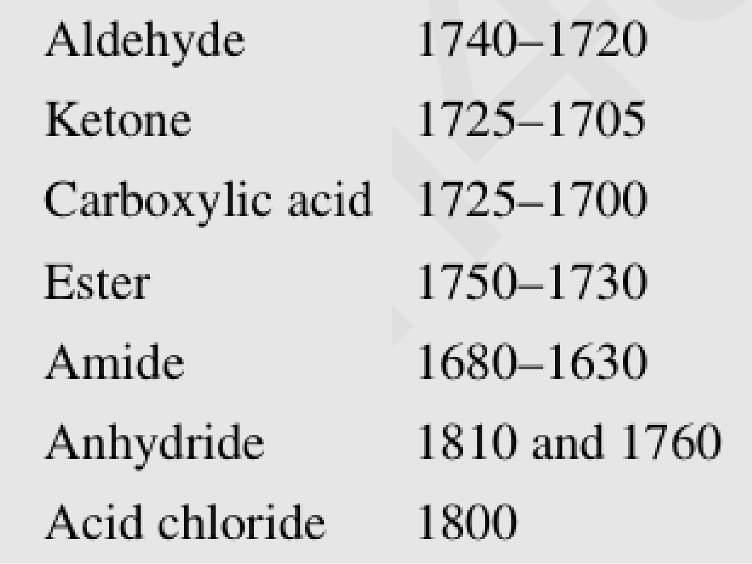
Quanto maior a massa dos átomos, menor será a frequencia

Absorption spectrum of hexylamine



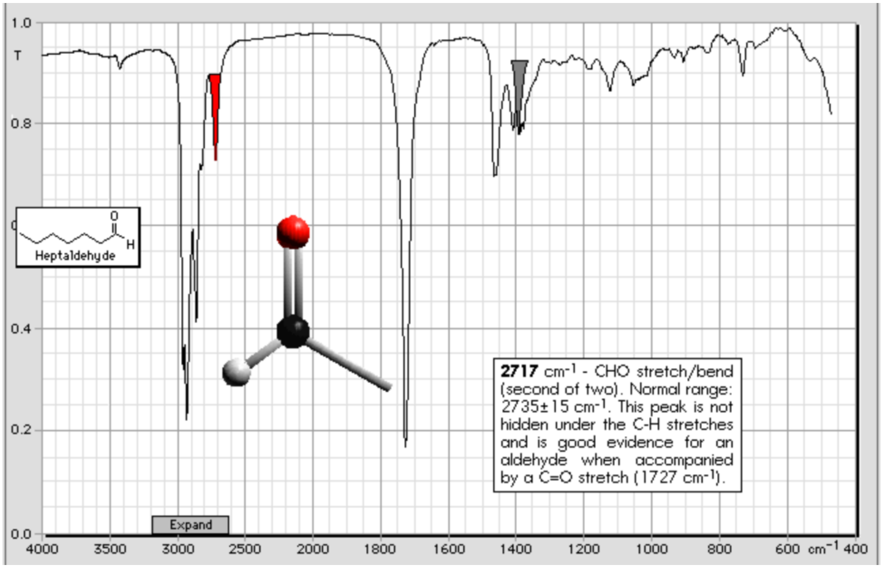
NH$_2$ Summary:
3309 cm^{-1} - NH$_2$ Antisymm. stretch.
3309 cm^{-1} - NH$_2$ Symm. stretch.
1613 cm^{-1} - NH$_2$ Scissor bend.
797 cm^{-1} - NH$_2$ Wag.

Wavenumber of carbonyl compounds in infrared spectrum

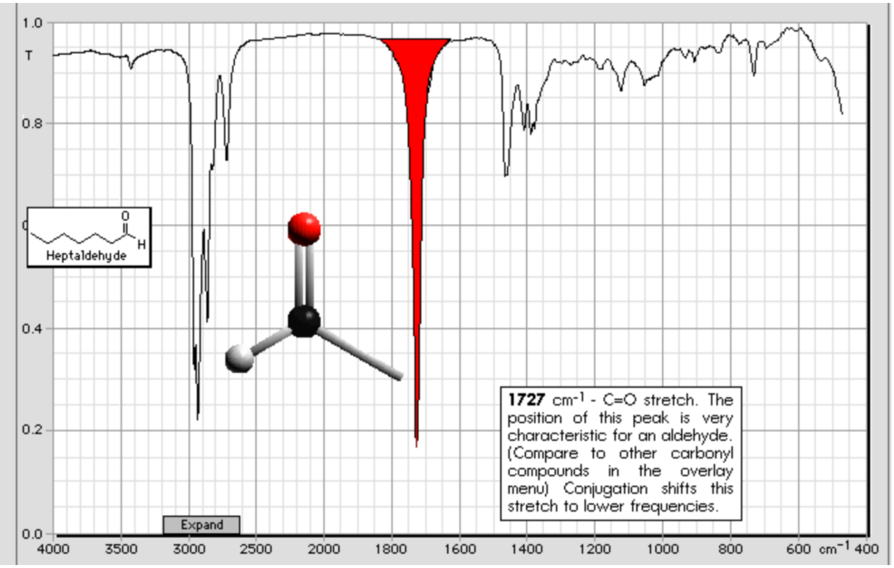


Aldehyde	1740–1720
Ketone	1725–1705
Carboxylic acid	1725–1700
Ester	1750–1730
Amide	1680–1630
Anhydride	1810 and 1760
Acid chloride	1800

Absorptions bands for heptaldehyde

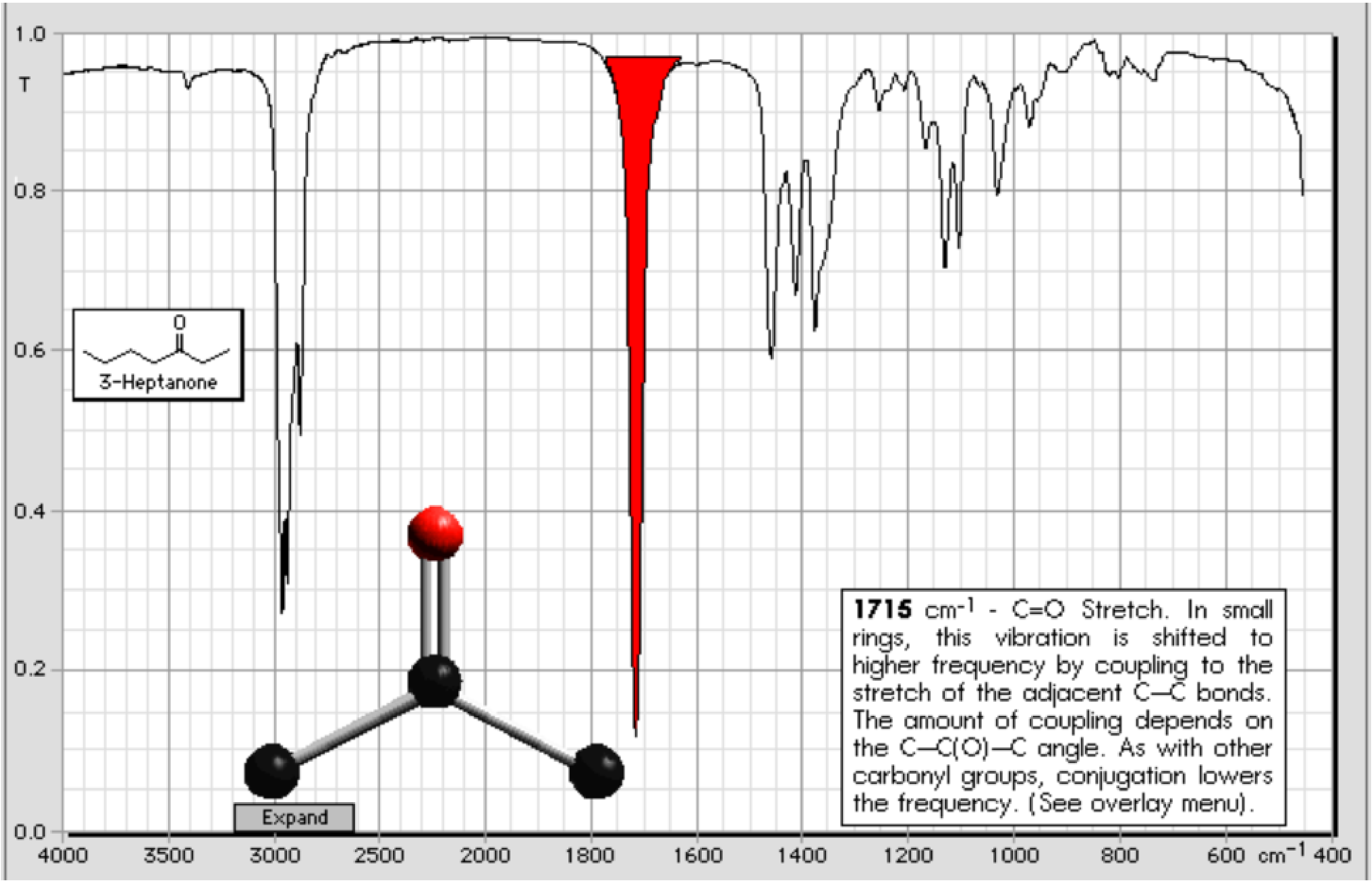


2717 cm^{-1} - CHO stretch/bend (second of two). Normal range: 2735±15 cm^{-1}. This peak is not hidden under the C-H stretches and is good evidence for an aldehyde when accompanied by a C=O stretch (1727 cm^{-1}).

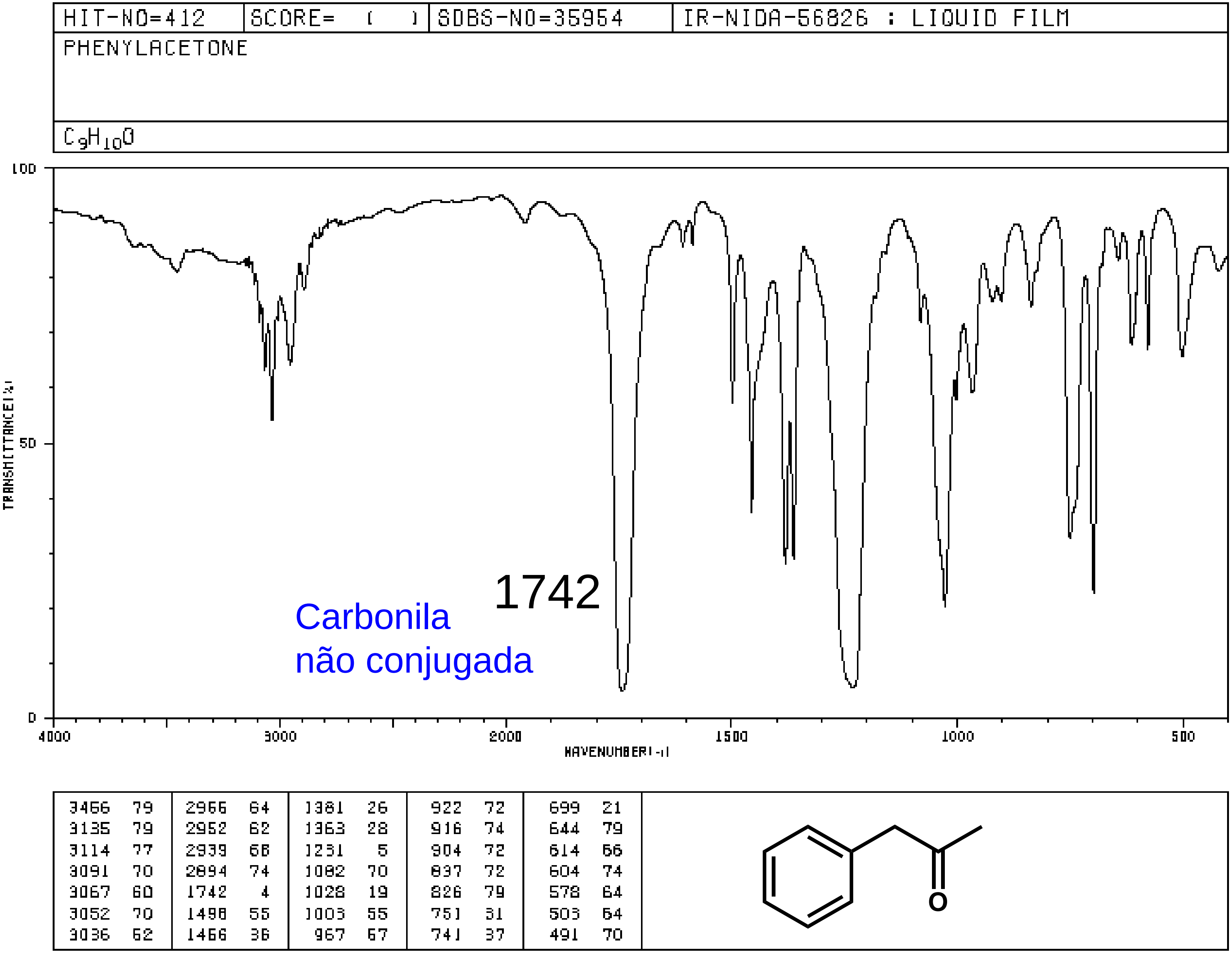


1727 cm^{-1} - C=O stretch. The position of this peak is very characteristic for an aldehyde. (Compare to other carbonyl compounds in the overlay menu) Conjugation shifts this stretch to lower frequencies.

Absorptions bands for 3-heptanone



1715 cm^{-1} - C=O Stretch. In small rings, this vibration is shifted to higher frequency by coupling to the stretch of the adjacent C—C bonds. The amount of coupling depends on the C—C(O)—C angle. As with other carbonyl groups, conjugation lowers the frequency. (See overlay menu).



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SDBS-NO=35954
IR-NIDA-56826 : LIQUID FILM

PHENYLACETONE

$C_9H_{10}O$

1742

Carbonila
não conjugada

3466	79	2966	64	1381	26	922	72	699	21
3135	79	2952	62	1363	28	916	74	644	79
3114	77	2939	68	1231	5	904	72	614	66
3091	70	2894	74	1082	70	837	72	604	74
3067	60	1742	4	1028	19	826	79	578	64
3052	70	1498	55	1003	55	751	31	503	64
3036	62	1466	36	967	67	741	37	491	70

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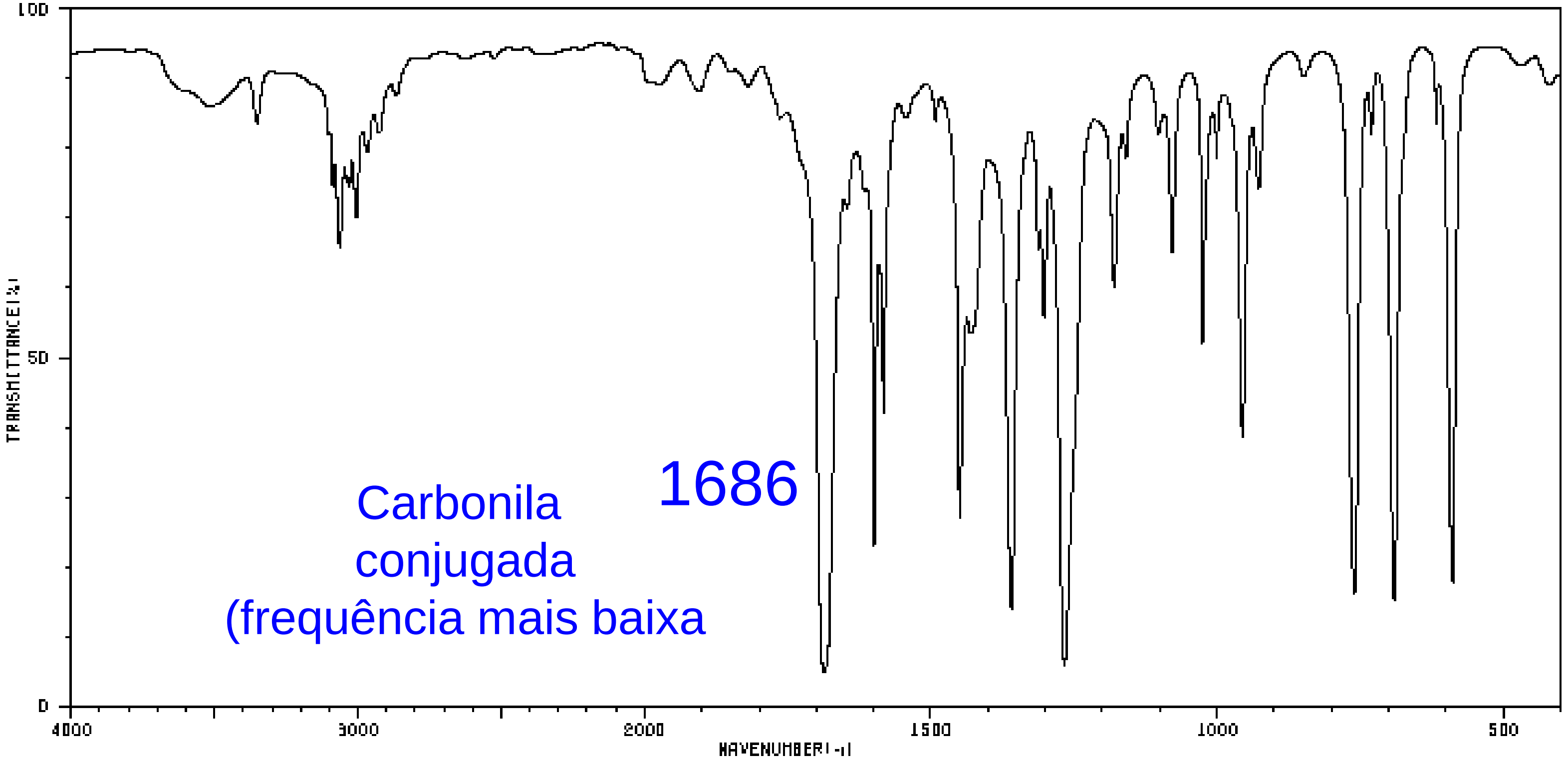
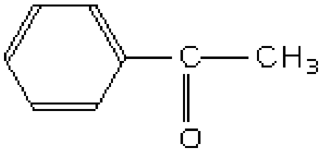
ACETOPHENONE			
C_8H_8O			



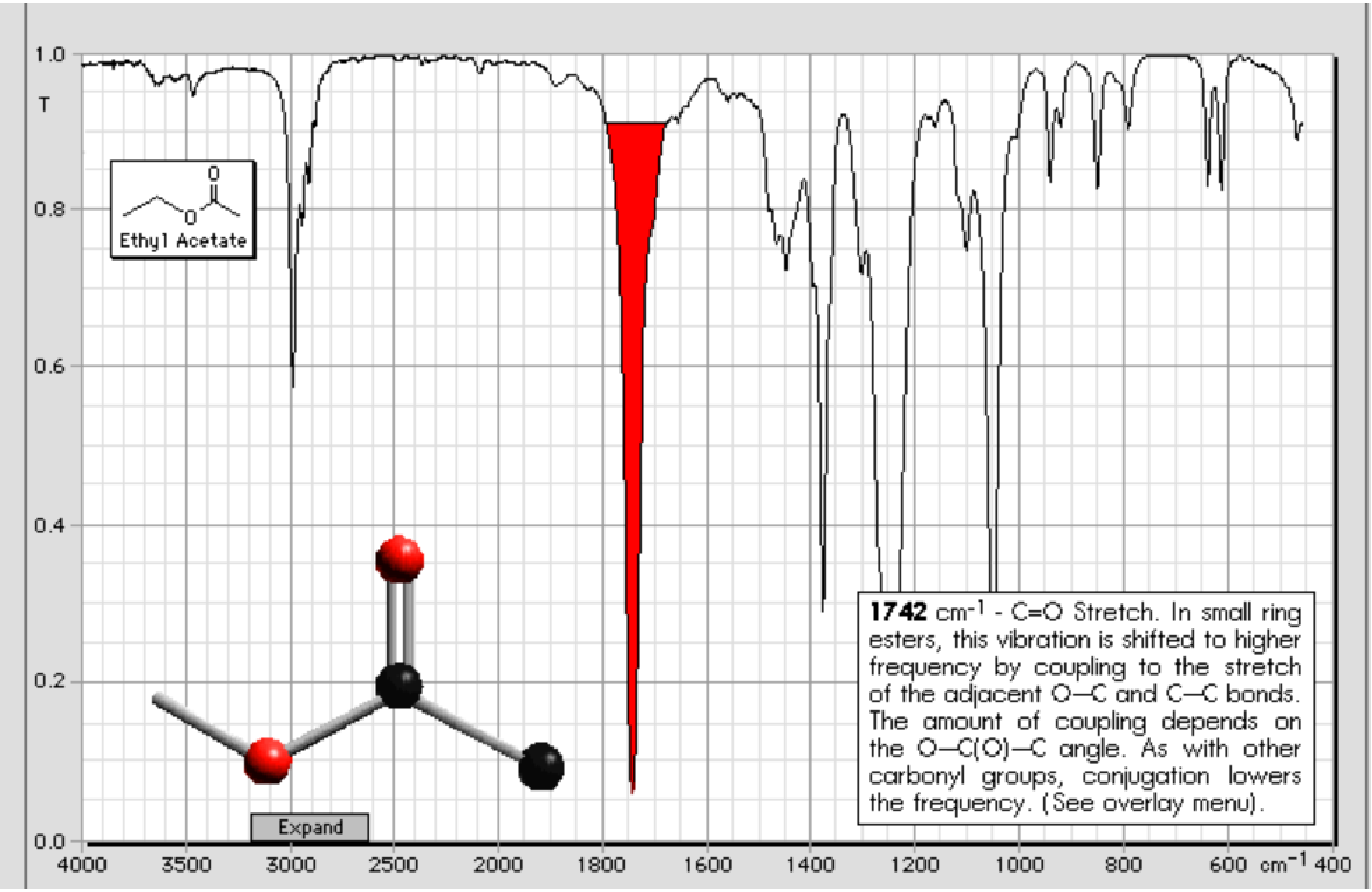
1686

Carbonila conjugada (frequência mais baixa

3604	84	2967	77	1646	81	1267	6	966	37
3352	81	2925	79	1492	81	1181	58	928	72
3087	72	2867	84	1450	26	1160	74	761	15
3063	64	1686	4	1430	62	1103	79	731	79
3040	72	1646	68	1360	13	1079	62	691	14
3029	72	1599	21	1313	82	1025	50	618	61
3006	68	1683	41	1303	63	1001	74	688	17



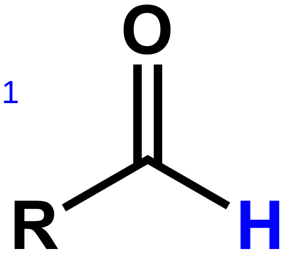
Absorptions bands for ethyl acetate (ester)



1742 cm^{-1} - C=O Stretch. In small ring esters, this vibration is shifted to higher frequency by coupling to the stretch of the adjacent O—C and C—C bonds. The amount of coupling depends on the O—C(O)—C angle. As with other carbonyl groups, conjugation lowers the frequency. (See overlay menu).

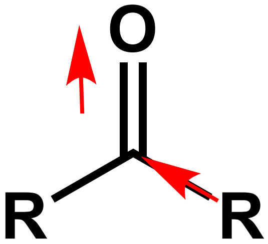
The oxygen (more electronegative than carbon) shift the carbonyl bands to a higher wavenumber (higher frequency)

1727 cm^{-1}



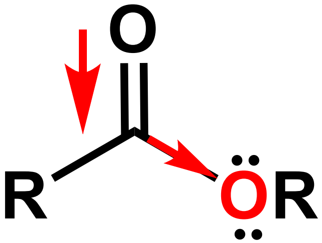
The **inductive effect of alkyl group** lowers the frequency for ketone carbonyl as compared to aldehydes

1715 cm^{-1}



The **inductive effect of alkyl group** lowers the frequency for ketone carbonyl as compared to aldehydes

1742 cm^{-1}



The **electron withdrawing** effect of the oxygen (efeito retirador de elétrons) increases the frequency for carbonyl esters (*a ligação torna-se mais curta aumentando a constante de força*)

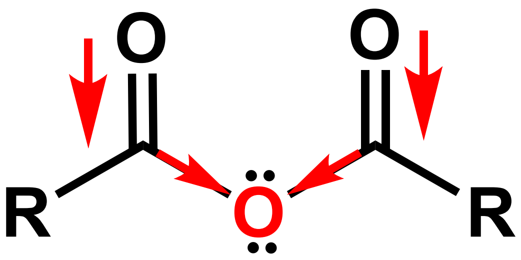
Absorptions bands for butyl anhydride

2 bands:

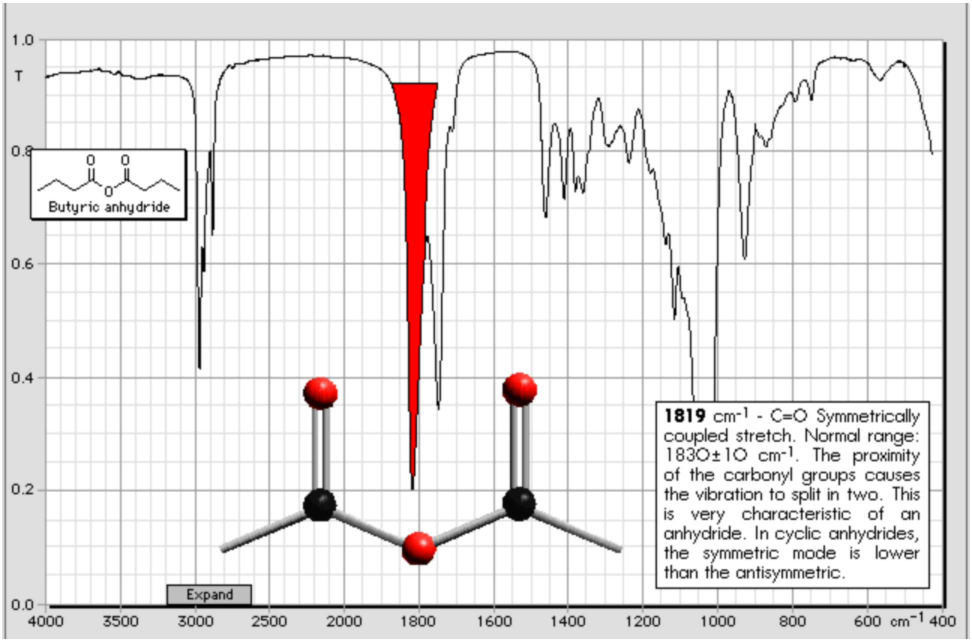
Symmetric at 1810 cm^{-1}

and

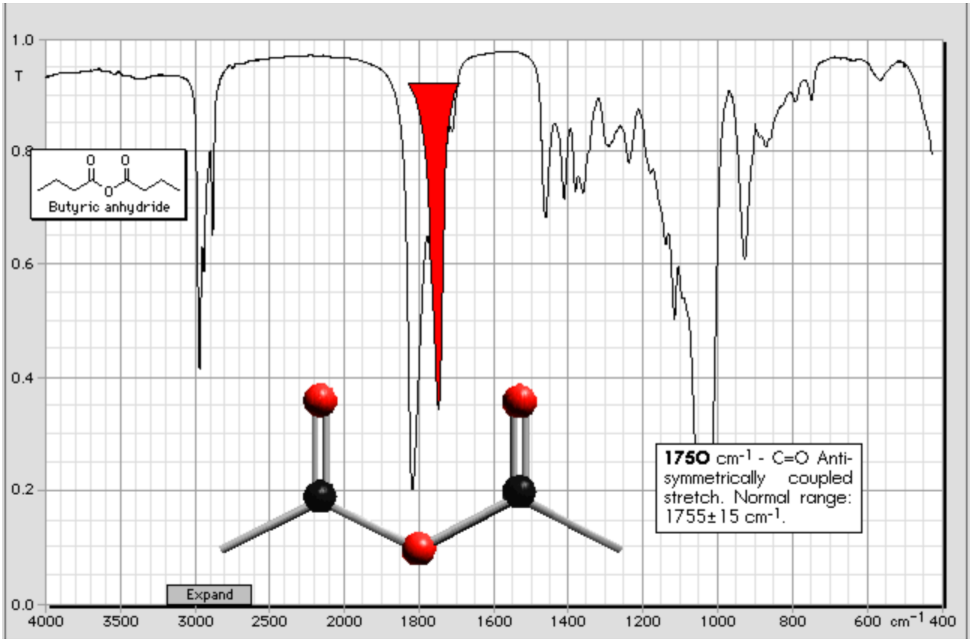
antisymmetric at 1740 cm^{-1})



The **electron withdrawing** effect of the oxygen between the two carbonyls increases their strenght,

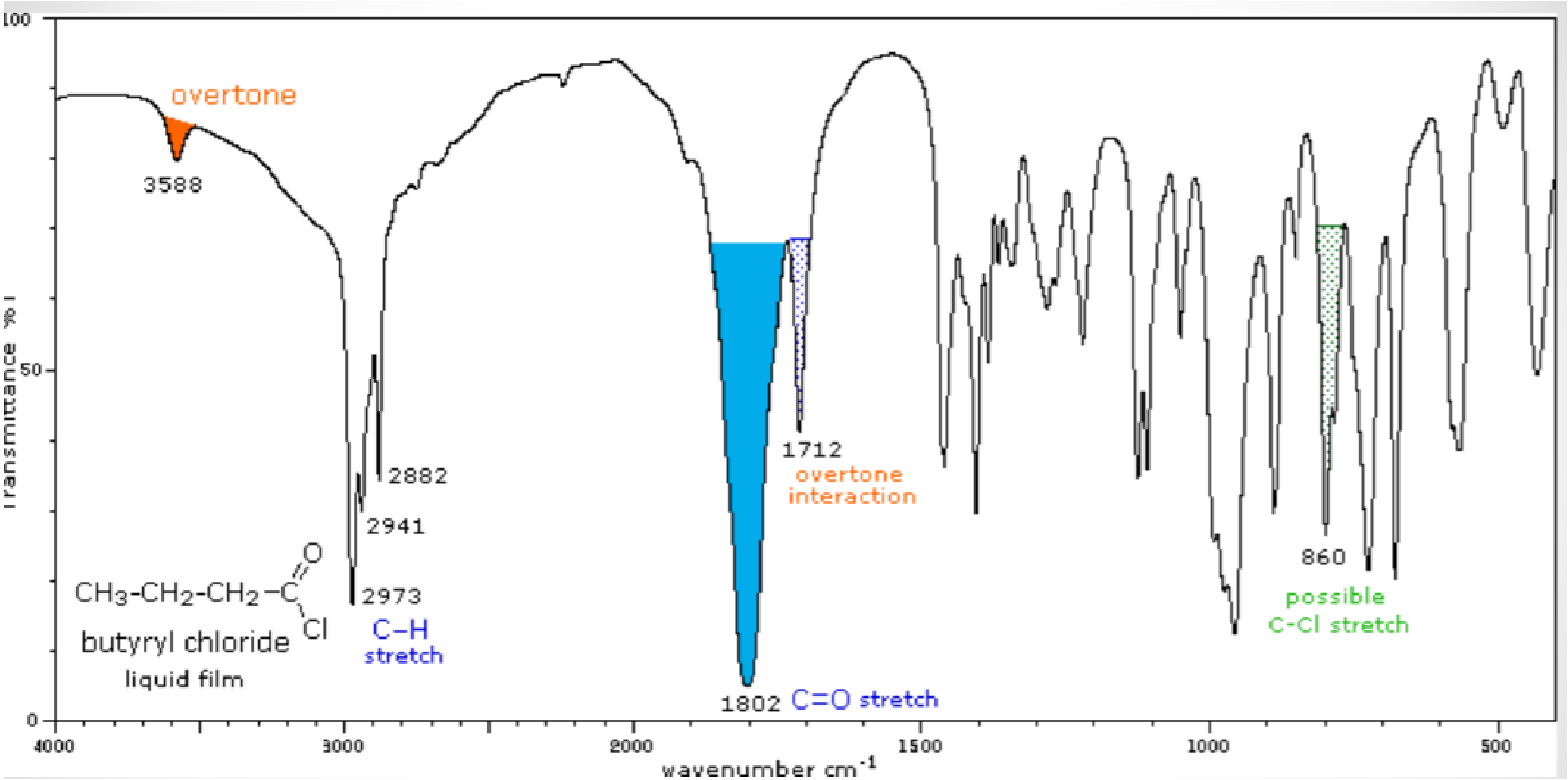


1819 cm^{-1} - C=O Symmetrically coupled stretch. Normal range: 1830±10 cm^{-1}. The proximity of the carbonyl groups causes the vibration to split in two. This is very characteristic of an anhydride. In cyclic anhydrides, the symmetric mode is lower than the antisymmetric.



1750 cm^{-1} - C=O Anti-symmetrically coupled stretch. Normal range: 1755±15 cm^{-1}.

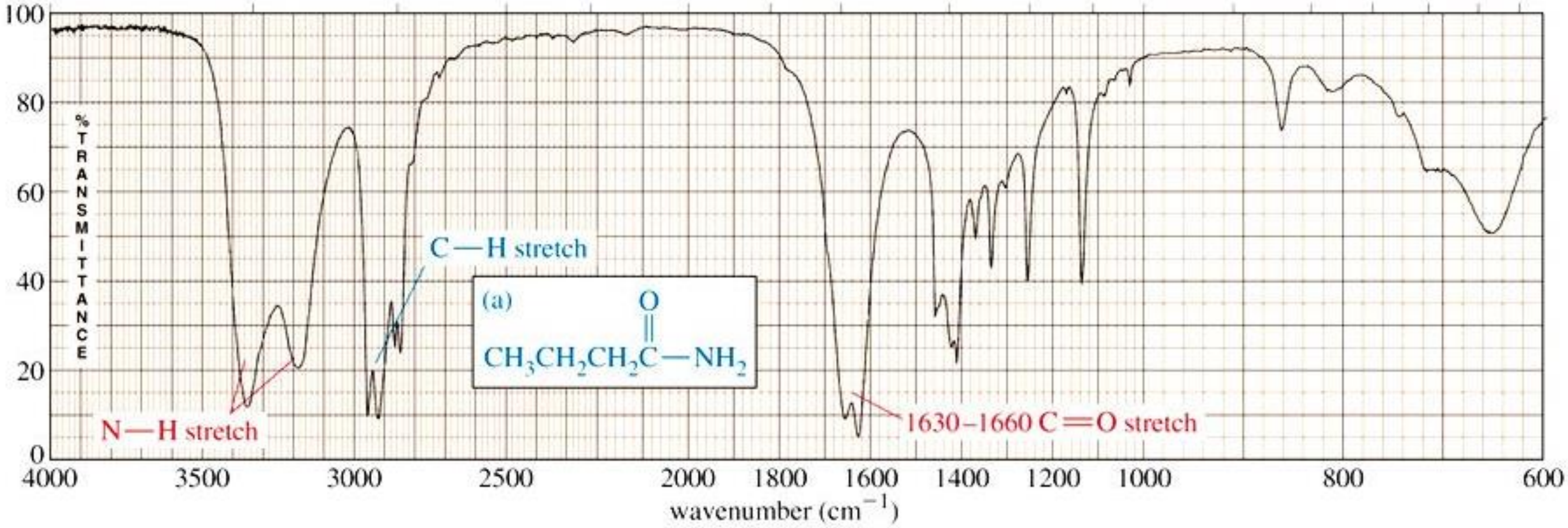
Absorptions bands for butyryl chloride



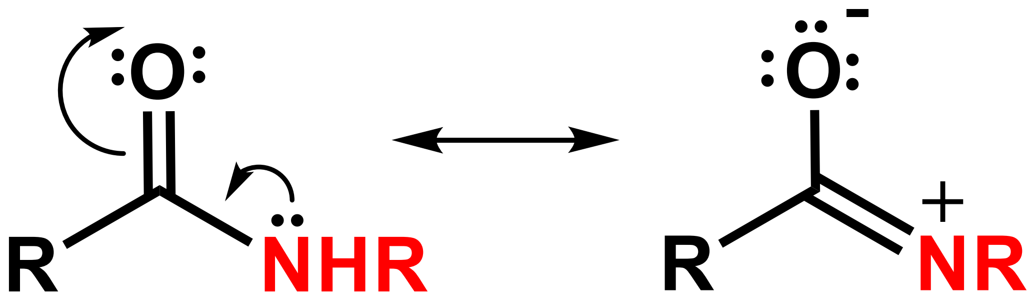
Effect of electronegativity of chlorine on carbonyl group

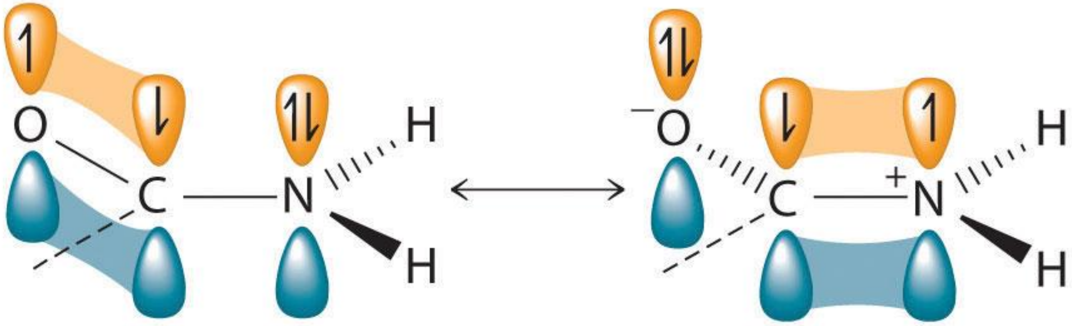
IR spectrum of amides

The amide functional group combines the features of amines and ketones because it has both the **N-H bond** and the **C=O bond**. Therefore amides show a very strong, somewhat broad band at the left end of the spectrum, in the range between **3100** and **3500 cm^{-1}** for the N-H stretch. At the same time they also show the stake-shaped band in the middle of the spectrum around **1710 cm^{-1}** for the C=O stretch. As with amines, primary amides show two spikes, whereas secondary amides show only one spike.



Absorptions bands for amides





Two bands at
1660 (I)-1630(II) cm^{-1}

Amide I band:
v **C=O** stretching
(*estiramento*)

Amide II band δ **N-H**
bending in plane
(*deformação angular no plano*)

The conjugation of the lone pair of electron weakens the force constant of carbonyl group!
(*a conjugação do par de elétrons do N enfraquece a constante de força da carbonila*)

IR SPECTRA: WHAT YOU CAN TELL AT A GLANCE

1) Is carbonyl group present (1820-1650 cm^{-1})?

	check also:
Acid (1710)	OH: 3400-2400 cm^{-1}
Amides (1690)	N-H: 3400 cm^{-1}
Ester (1735)	C-O: 1300-1000 cm^{-1}
Anhydrides	two bands: 1810 and 1760 cm^{-1}
Aldehydes (1725)	C-H: 2850 and 2750 cm^{-1}
Ketones (1715)	preceding 5 choices eliminated

2) If C=O is absent:

ROH	OH: 3400-3300 cm^{-1};
or ArOH	C-O near 1300-1000 cm-1
Amines	N-H: 3400 cm^{-1})
Ether	C-O: 1300-1000 cm^{-1}; absence of OH

Double bond/aromatic ring:

C=C: weak band near 1650 cm^{-1};

1600-1450cm^{-1})