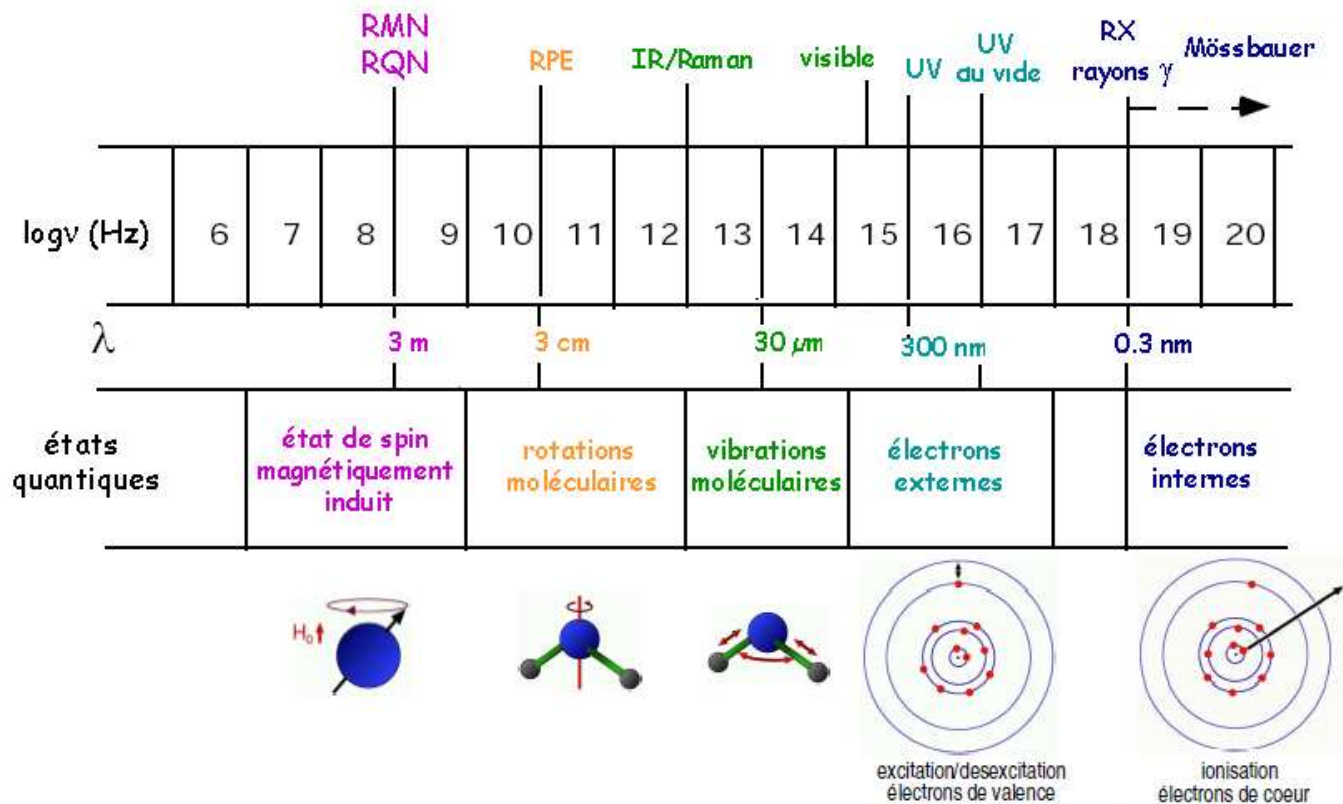
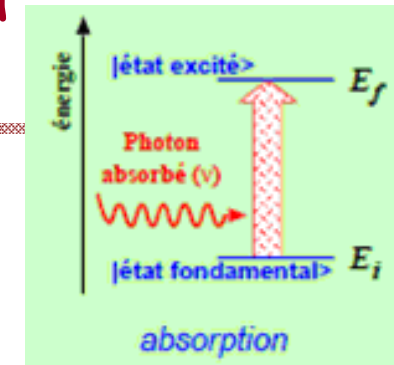


Spectroscopie infrarouge

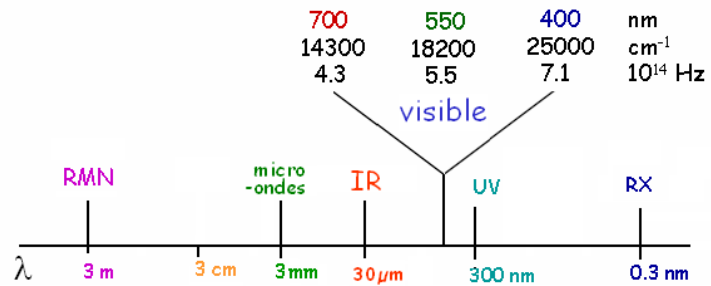
I - Spectroscopies d'absorption

1. Généralités

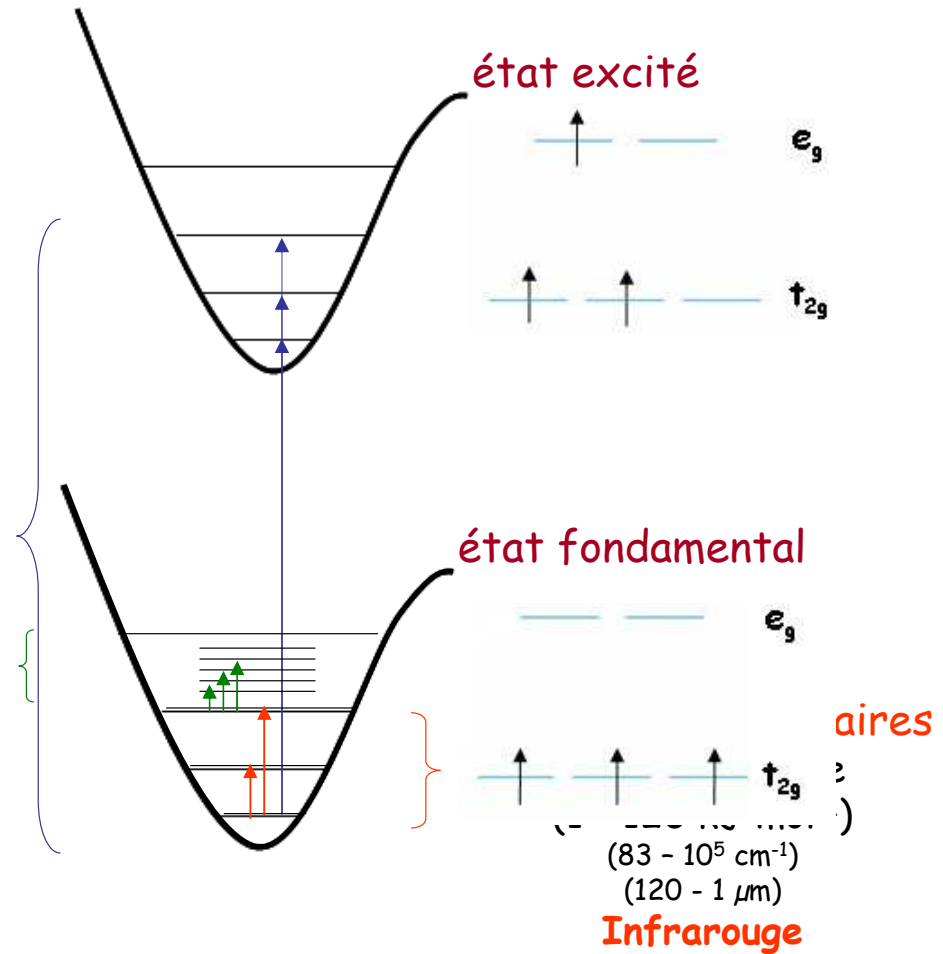
Reposent sur les interactions entre la matière et la lumière
absorption : excitation après absorption d'un quanta d'énergie $h\nu$
 \Rightarrow transitions entre deux niveaux d'énergie



Energies des transitions

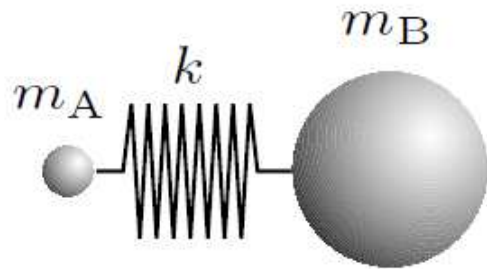


(1200 - 12 nm)
visible et UV
cf. Chapitre 2
rotations moléculaires
 faible énergie
 (0.01 - 1 kJ mol⁻¹)
 (0.83 - 83 cm⁻¹)
 (12 - 0.12 mm)
 micro-ondes



! Absorptions vibrationnelles exprimées en nombre d'onde ν (cm⁻¹)

I - 2. modèle du vibrateur : oscillateur harmonique



Molécule AB

$$\mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$$

$\nu_{c=c}$ en cm^{-1}

k en dynes.cm^{-1} ($1\text{N} = 10^5 \text{ dynes}$)

μ en g ($\mu / 6.023 \cdot 10^{23}$)

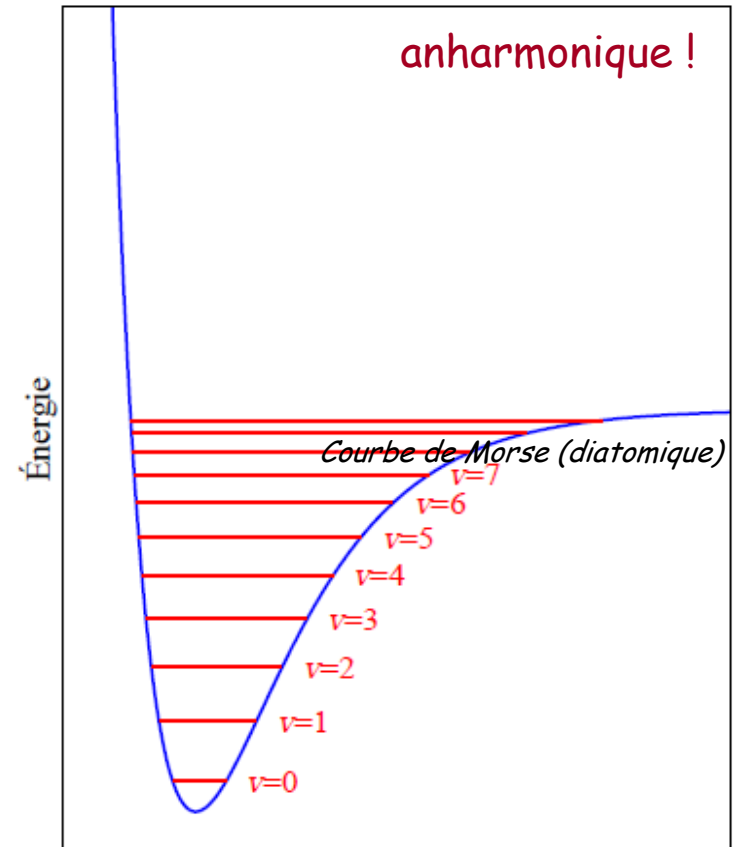
$C = 3 \cdot 10^{10} \text{ cm.s}^{-1}$

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

Absorption : $V = h\nu$

Mécanique classique : infinité de solution

Mécanique quantique : quantification de l'énergie
 \Rightarrow niveaux discrets d'énergie vibrationnelle



Déplacement ($x = R - R_e$)

$$E_v = \left(v + \frac{1}{2}\right) h c \bar{\nu} = \left(v + \frac{1}{2}\right) h \nu$$

où $v = 0, 1, 2, \dots, \infty$

Règles de sélection pour une transition dipolaire électrique

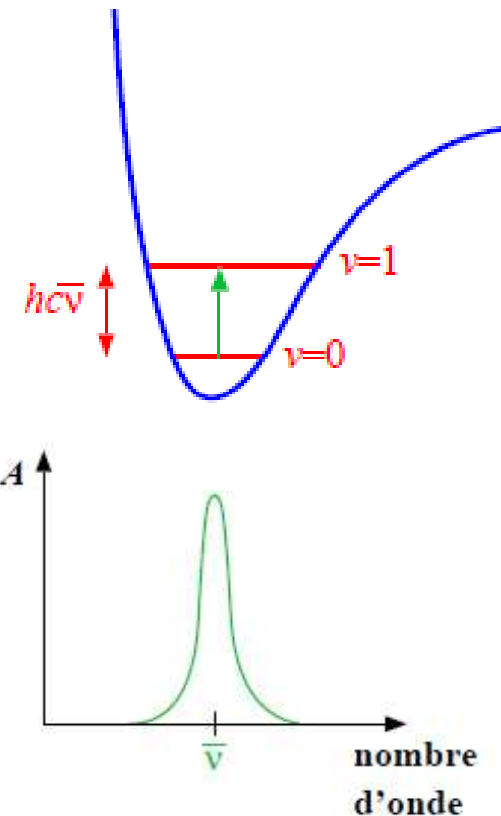
$$transition = \langle \Psi_i | \mu | \Psi_f \rangle = \langle \Psi_i^{orb} | \mu | \Psi_f^{orb} \rangle \langle \Psi_i^{spin} | \Psi_f^{spin} \rangle \neq 0$$

Le moment dipolaire μ doit varier quand les atomes se déplacent les uns par rapport aux autres

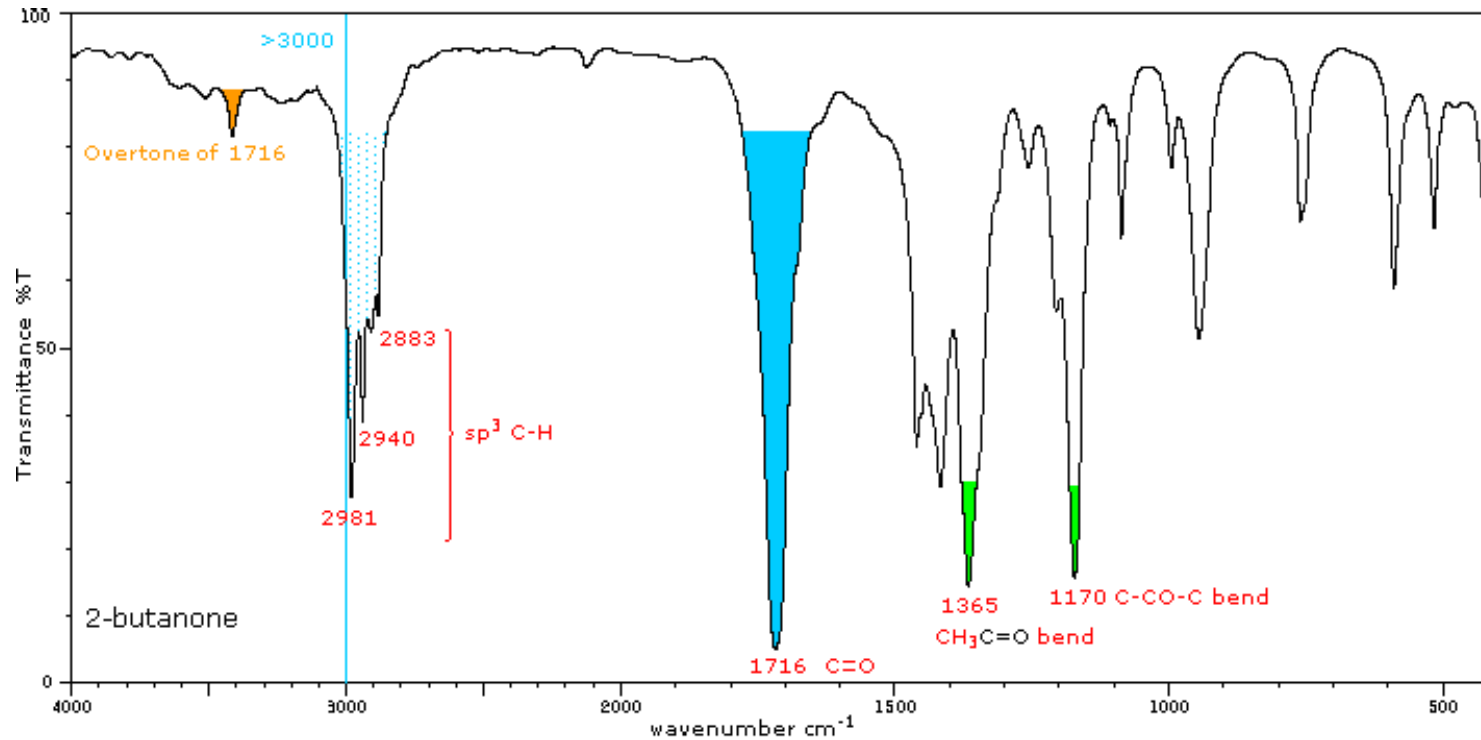
$$\Delta v = \pm 1$$

Conséquences :

- ✓ Le mode normal d'élongation des molécules diatomiques homonucléaires n'est pas observable en IR
⇒ TDG !
- ✓ A RT : la plupart des molécules sont dans leur état fondamental
⇒ **transition fondamentale** $v = 0 \rightarrow v = 1$



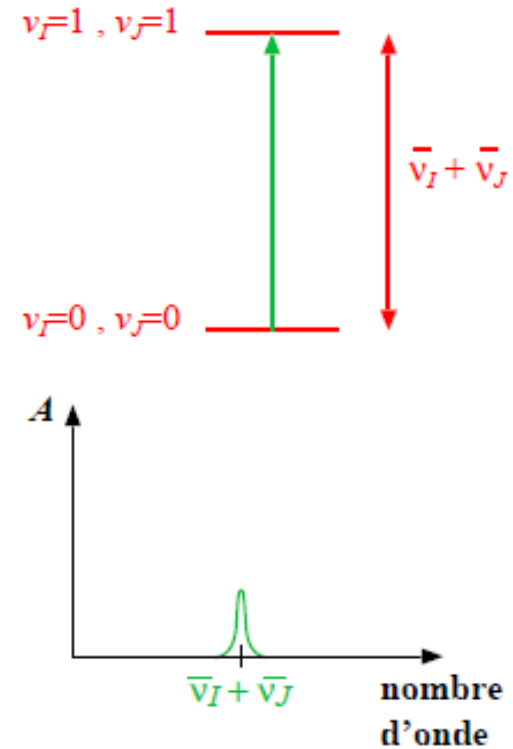
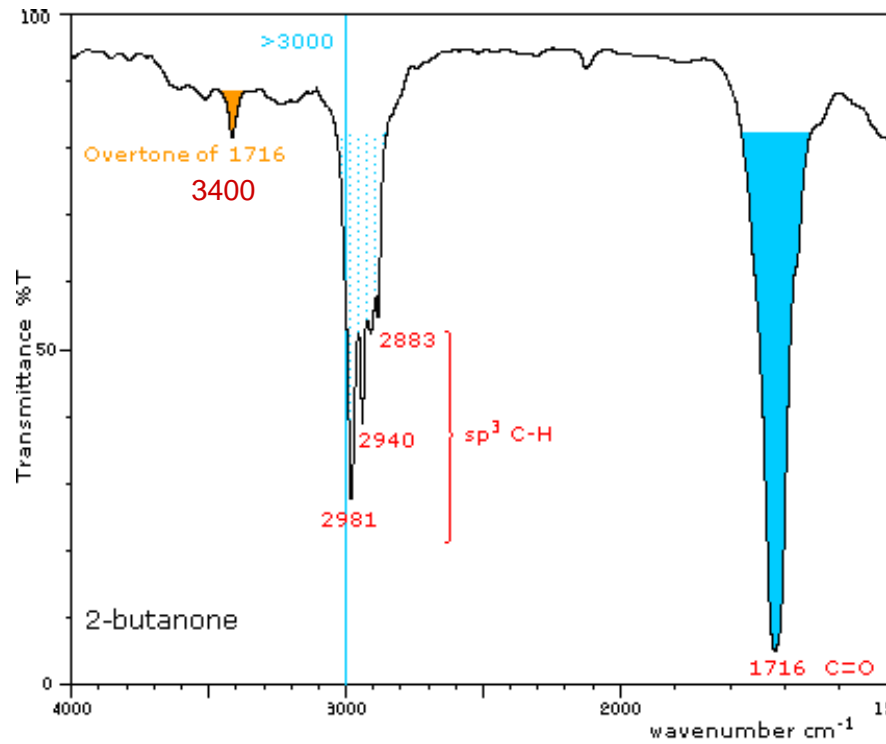
I - 3. Que voit-on sur un spectre IR ?



bandes :

- ✓ fondamentales + autres...
- ✓ différents modes de vibration : élongations + déformations
- ✓ activité dépend de la symétrie (TDG) : varie comme le moment dipolaire

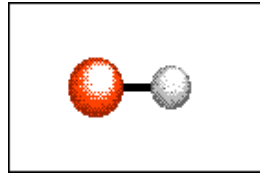
Bandes fondamentales et autres...



- ✓ l'harmonique n'est pas exactement 2 fois la fondamentale : anharmonicité !
- ✓ moins intenses car moins probables...
- ✓ harmoniques visibles dans le PIR : 4000 - 12500 cm^{-1}

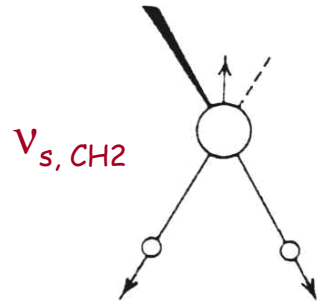
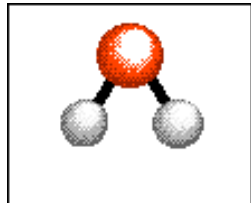
Types de vibrations

① longueurs des liaisons : vibration d'élongation (valence) notée ν_{AB}

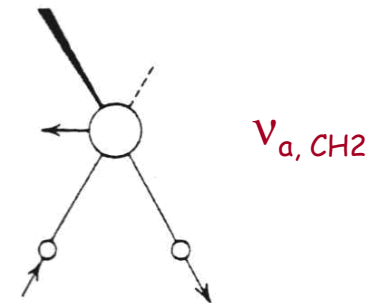
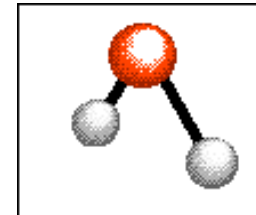


Pour un groupement formé de plusieurs liaisons identiques :

mode symétrique : ν_s

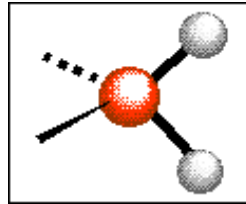


mode antisymétrique : ν_a



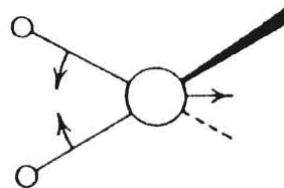
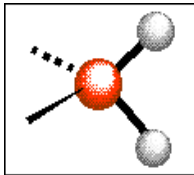
Types de vibrations

② déformation angulaire : vibration de déformation notée δ_{AB}

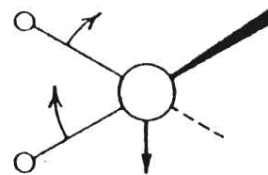
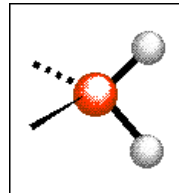


Pour un groupement formé de plusieurs liaisons identiques :

déformation hors du plan : δ_{dp}

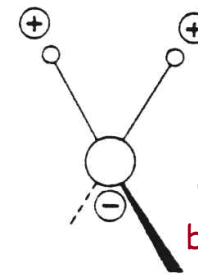
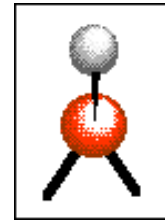


$\delta_{dp, s, CH2}$
cisaillement
(scissoring)

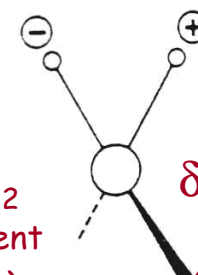
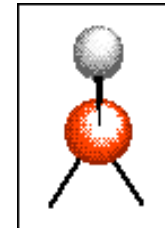


$\delta_{dp, a, CH2}$
rotation plane
(rocking)

déformation hors du plan : δ_{hp} ou γ



$\delta_{hp, s, CH2}$
balancement
(wagging)



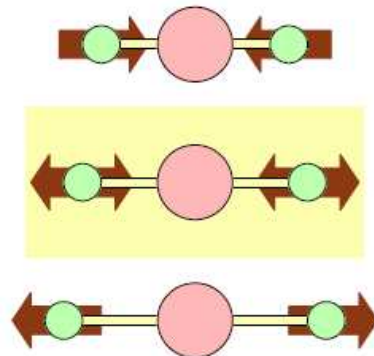
$\delta_{hp, a, CH2}$
torsion
(twisting)

Activité des modes de vibration

mode normal de vibration actif en si le mouvement correspondant s'accompagne d'une variation du moment dipolaire électrique de la molécule

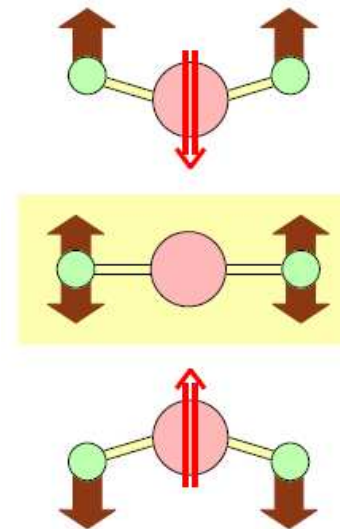
molécule linéaire A-B-A : $\vec{\mu} = 0$

élongation symétrique



$\vec{\mu} = 0 \Rightarrow$ mode **inactif** en IR

déformation angulaire



$\vec{\mu} \neq 0 \Rightarrow$ mode **actif** en IR

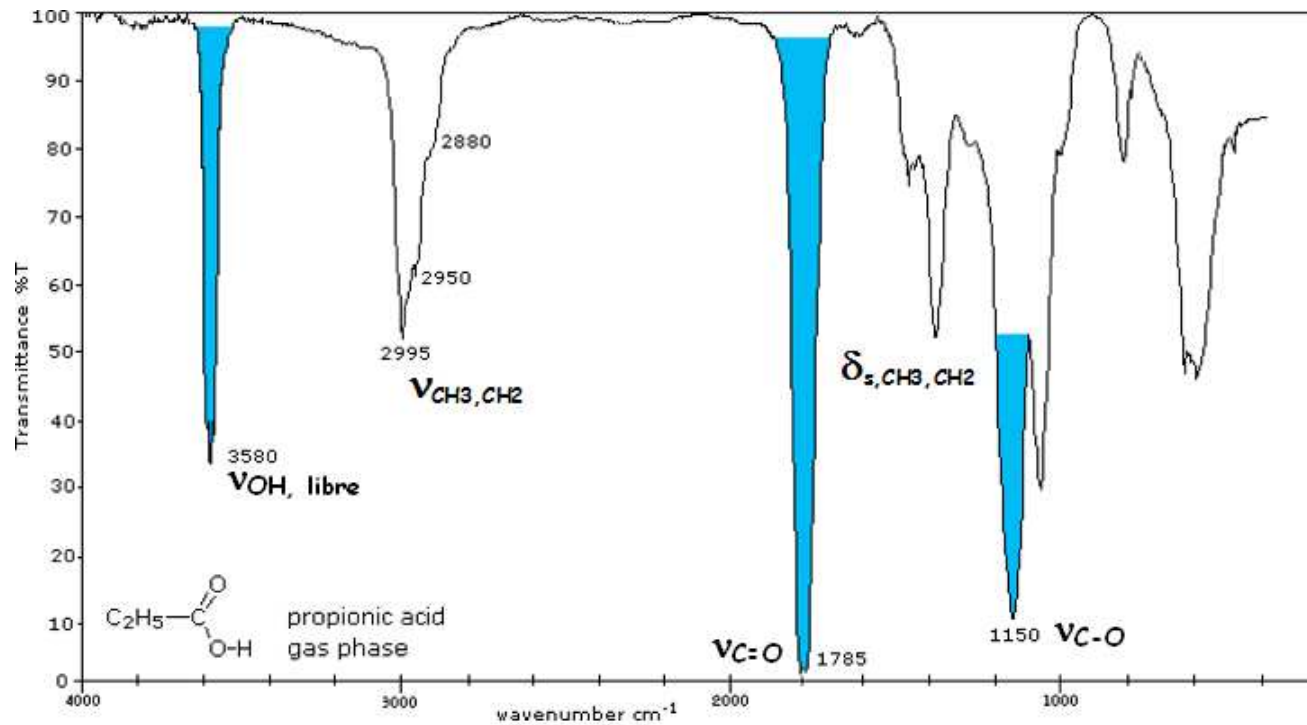
TDG : centre d'inversion !

Principe d'exclusion mutuelle : seuls les modes antisymétriques sont actifs en IR

Intensité des bandes

L'intensité de la bande est liée à la variation du moment dipolaire et à la concentration

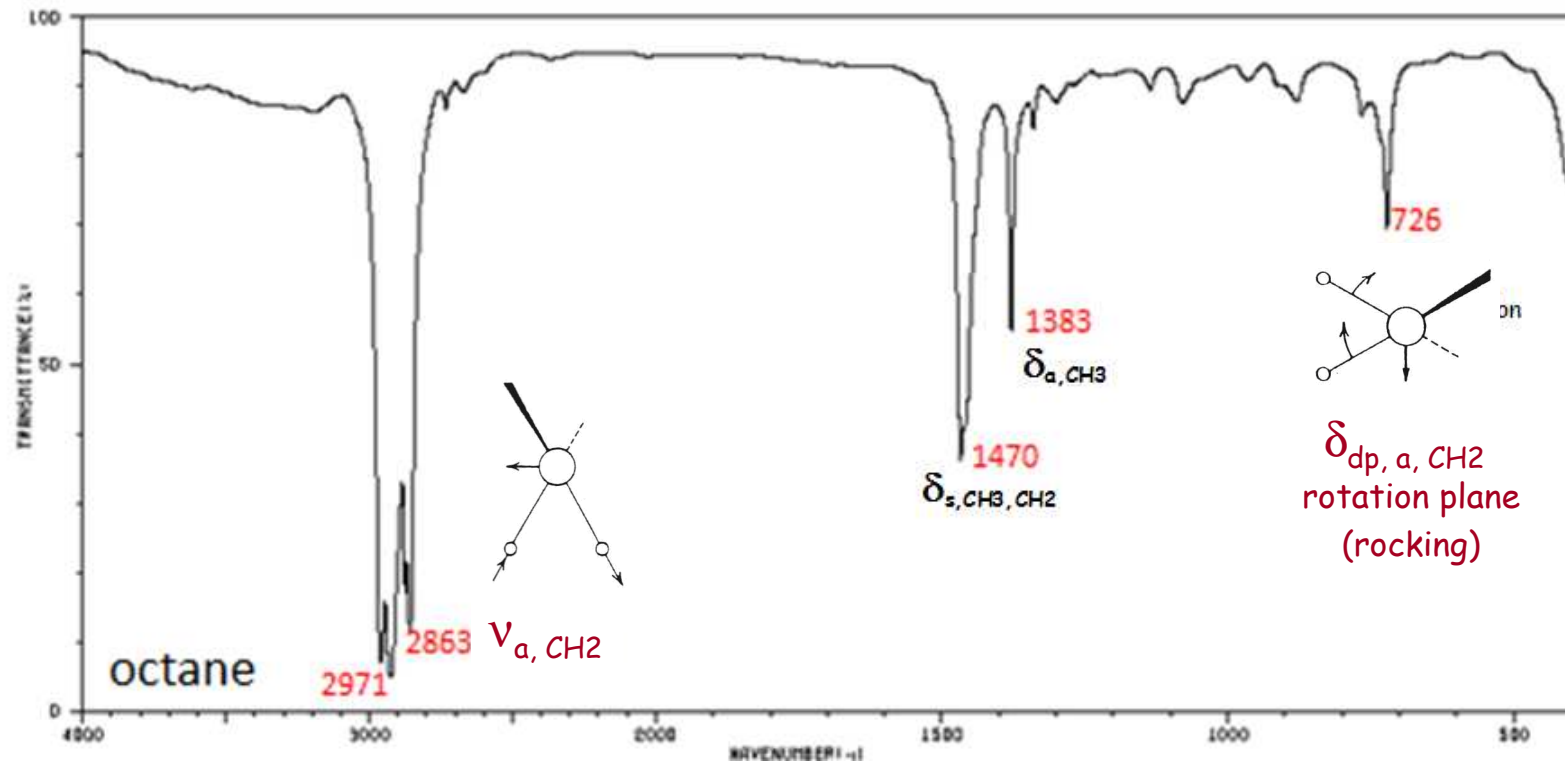
✓ Polarité intrinsèque du vibreur



Intensité des bandes

L'intensité de la bande est liée à la variation du moment dipolaire et à la concentration

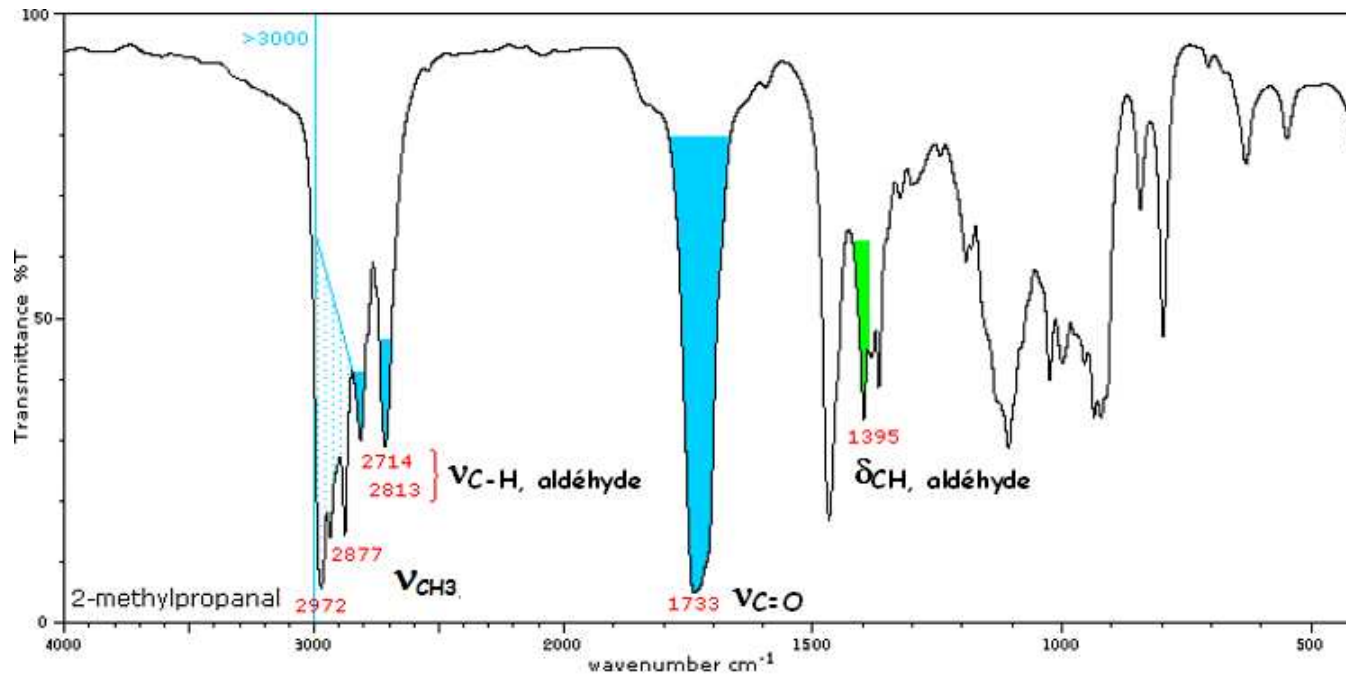
✓ Variation du moment dipolaire pendant la vibration



Intensité des bandes

L'intensité de la bande est liée à la variation du moment dipolaire et à la concentration

✓ « concentration » du vibreur : loi de Beer-Lambert $A = \epsilon lc$



Position des bandes : fréquences de groupe

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

✓ ordre de la liaison $\Rightarrow \nu$ proportionnelle à k

$$\begin{array}{l}
 \nu_{C=C} = 1640 \text{ cm}^{-1} \\
 k_{C\equiv C} = \frac{3}{2} k_{C=C} \quad \Rightarrow \quad \nu_{C\equiv C} = \sqrt{\frac{3}{2}} \nu_{C=C} \quad \nu_{C\equiv C} = 2008 \text{ cm}^{-1} \\
 k_{C-C} = \frac{1}{2} k_{C=C} \quad \Rightarrow \quad \nu_{C-C} = \sqrt{\frac{1}{2}} \nu_{C=C} \quad \nu_{C-C} = 1159 \text{ cm}^{-1}
 \end{array}$$

2100 - 2250 cm^{-1}
 900 - 1200 cm^{-1}

$$\begin{array}{c}
 \nu_{C\equiv C} > \nu_{C=C} > \nu_{C-C} \\
 \leftarrow \quad \quad \quad \rightarrow \\
 \quad \quad \quad k \nearrow
 \end{array}$$

Vibrateurs *indépendants* mais ...

	$\equiv C-H$	$=C-H$	$-C-H$
ν (cm^{-1})	3300	3100	2900
type de C	sp	sp ²	sp ³
Longueur (\AA)	1.08	1.10	1.12
k (N.m^{-1})	593	523	458

Mais même région IR
 \Rightarrow Fréquence de groupe

Position des bandes : fréquences de groupe

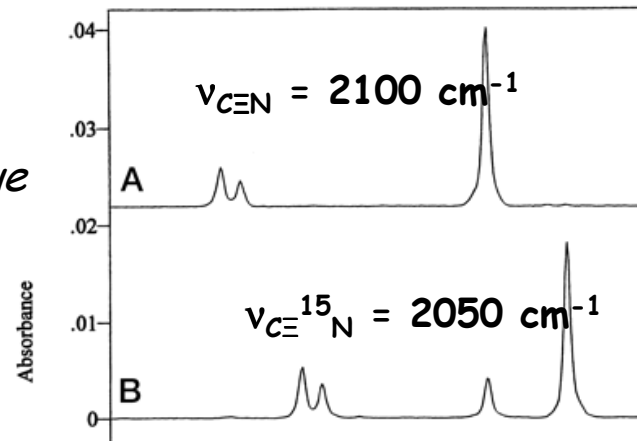
$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

✓ la masse du vibrateur $\Rightarrow \nu$ inversement proportionnelle à μ

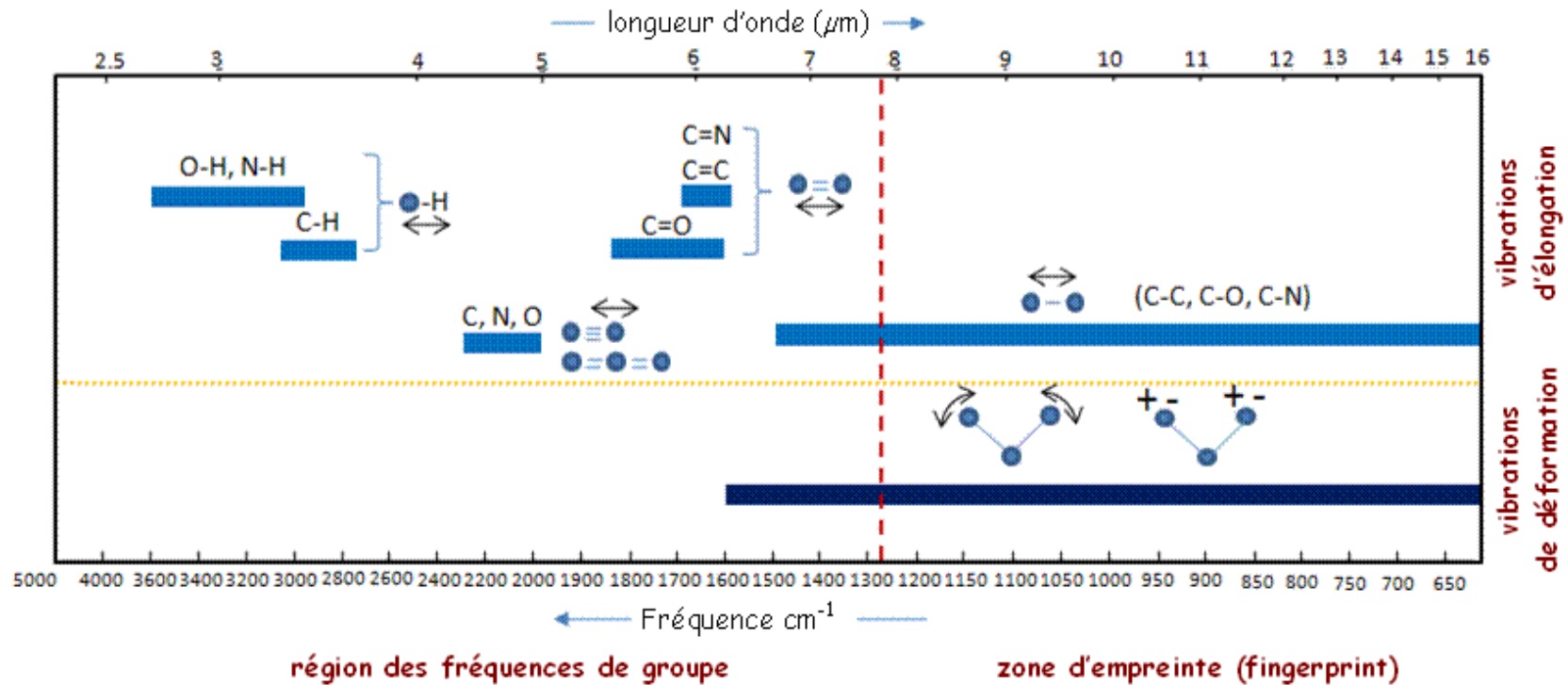
Liaisons	C-H	C-C	C-F	C-Cl	C-Br	C-I
Masses réduites (μ en 10^{-26} kg)	0,15	0,99	1,21	1,48	1,73	1,82
Fréquences de vibration en cm^{-1}	3030	1100	1000	750	600	450

$\leftarrow \mu \rightarrow$

effet isotopique



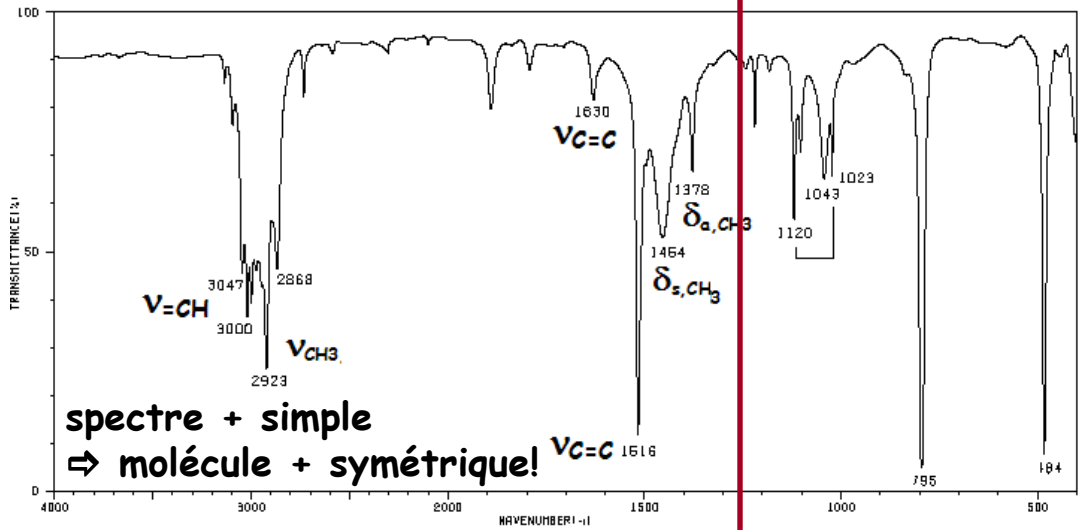
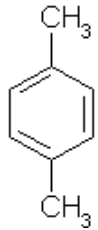
Se repérer dans la gamme infrarouge



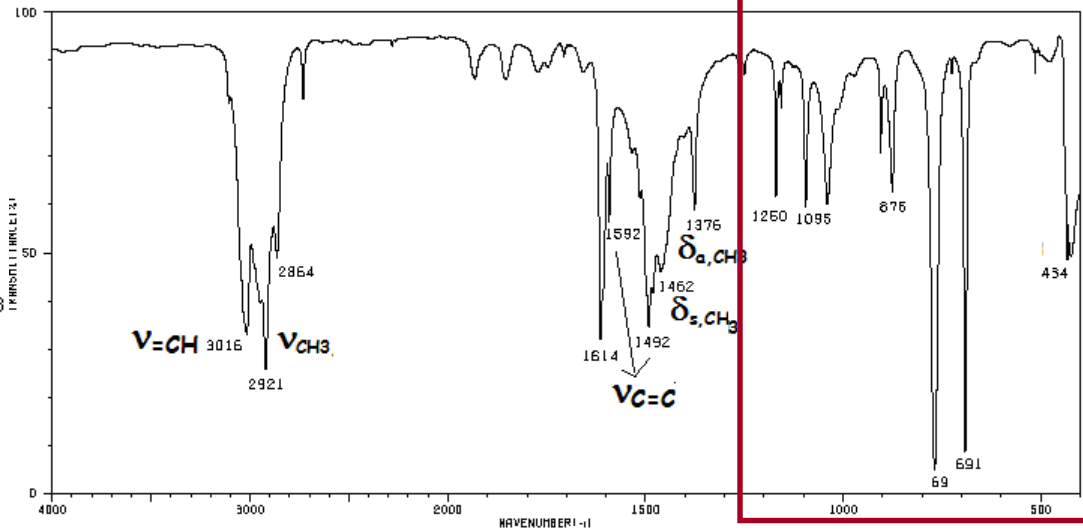
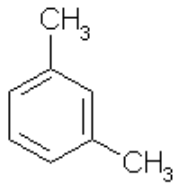
Doit-on apprendre par cœur toutes les fréquences ?

Tables classées par fonctions chimiques

Importante de la zone d'empreinte



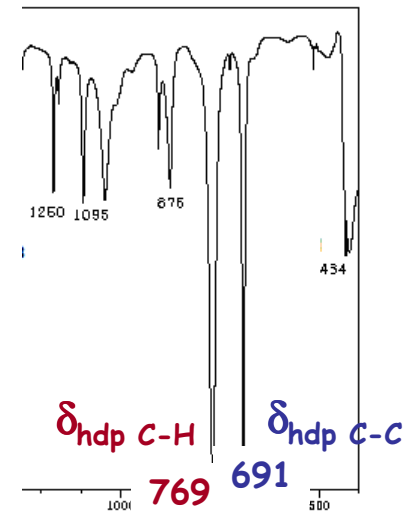
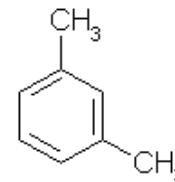
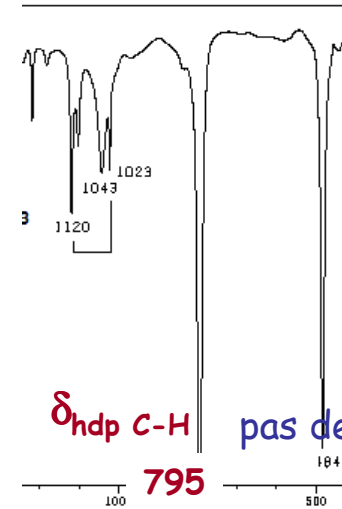
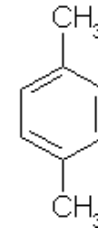
spectre + simple
 ⇒ molécule + symétrique!



Déformations dp et Hdp des C-H et C-C
 ⇒ nombre de bandes différent
 ⇒ caractéristique de la structure des composés

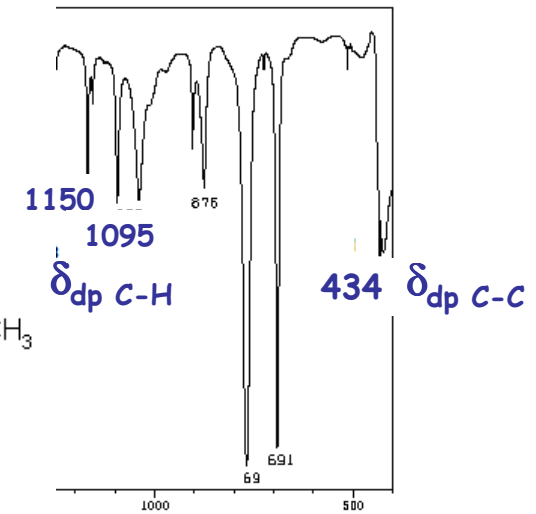
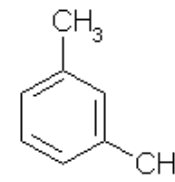
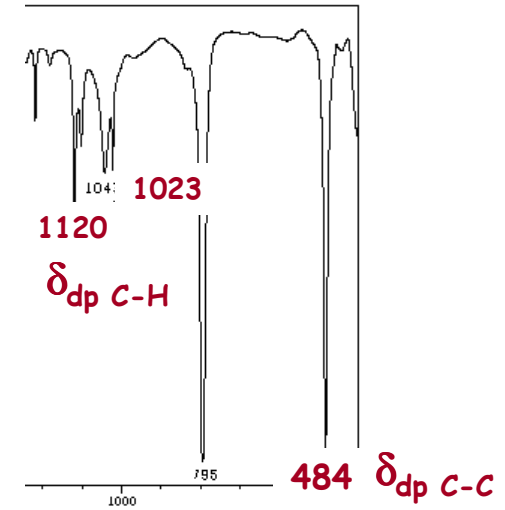
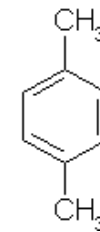
Importante de la zone d'empreinte

Hydrogènes adjacents	Substitution	$\delta_{\text{C-H hdp}}$	$\delta_{\text{C-C hdp}}$
6H 	Néant	ν_{11} 673 ν_5 (995 interdite)	ν_4 (703 interdite)
5H 	1	751 ± 15 (a)	700-675 (F)
4H 	1,2	751 ± 7	inactive (d)
3H 	1,3 meta	782 ± 9	710-665 (F)
	1,2,3	810-750	730-685 (v)
2H 	1,4 para	817 ± 13 (b)	inactive (d)
	1,2,4	860-800	730-685 (v)
	1,2,3,4	860-800	
1H 	1,3,5	865-810	730-665 (F)
	1,2,3,5	$880-840$ (c)	inactive (d)
	1,2,4,5		
	penta		

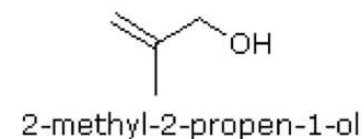
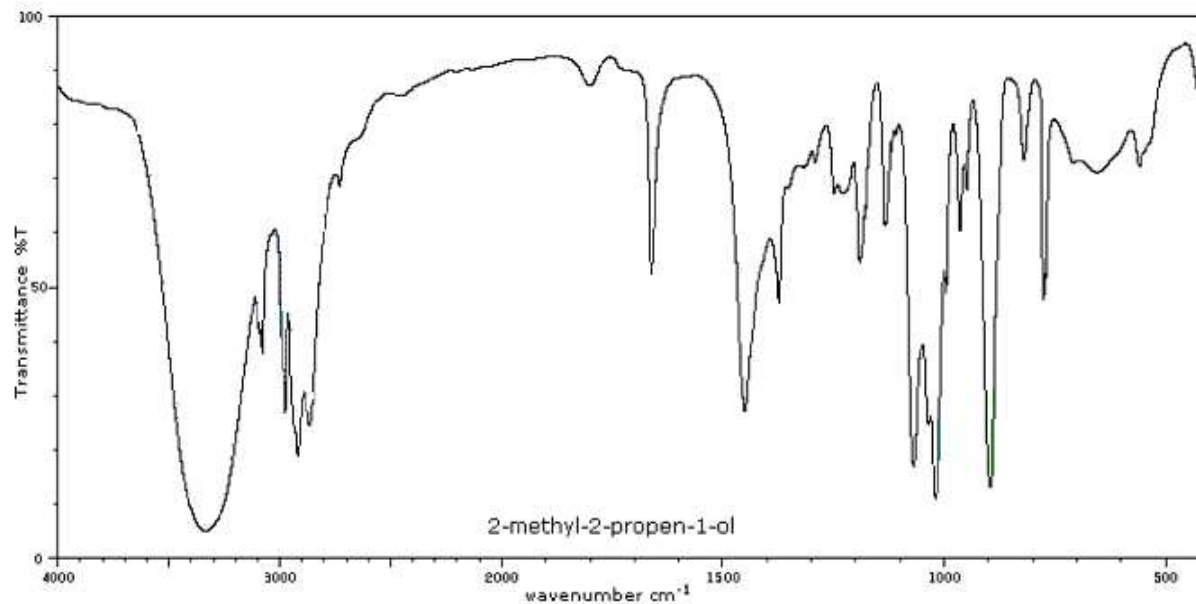


Importante de la zone d'empreinte

	Mono	Ortho	Méta	Para (b)
$\delta_{\text{C-H}}^{\text{dp}}$	1000 ± 5	-	1000 ± 5	-
	1027 ± 3 (a)	1033 ± 11 (a)	1076 ± 7	1013 ± 5 (IR)
	1073 ± 4	1125 ± 14	1096 ± 7	1117 ± 7 (IR)
	1156 ± 5	1160 ± 4	1157 ± 5	1175 ± 6 (R)
	1177 ± 7	-	-	-
$\delta_{\text{C-C}}^{\text{dp}}$	560-418	470-418	490-415	552-446 ..



I - 4. Analyse d'un spectre IR : mode d'emploi

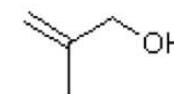


Doit-on attribuer toutes les bandes ?

1. vibrations d'élongation des fonctions chimiques
2. vibrations de déformations des fonctions chimiques

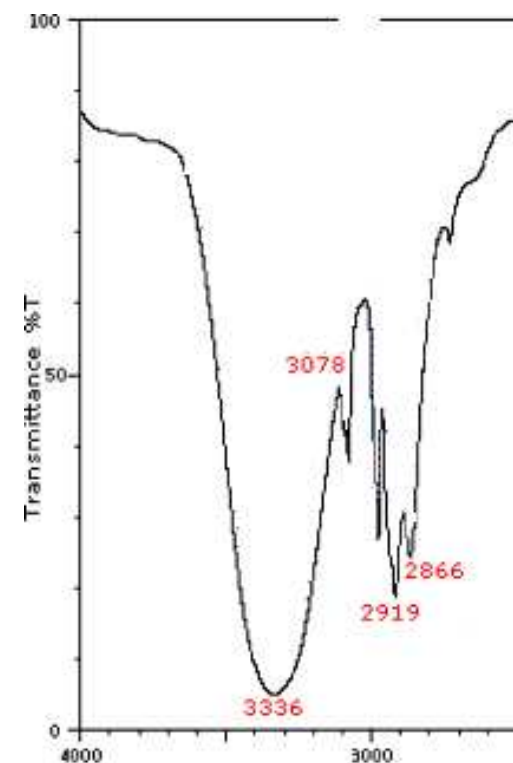
Tables à utiliser : alcools, alcènes, alcanes

(1) repérer les vibrations de valence des fonctions alcools



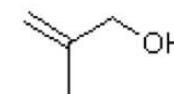
2-methyl-2-propen-1-ol

ALCOHOLS AND PHENOLS				
<i>O—H Stretching Vibrations</i>				
free OH	3,670–3,580	2·73–2·79	v.	sharp band
hydrogen bonded OH				
(a) intermolecular				
dimeric association	3,550–3,450	2·82–2·90	v.	sharp band
polymeric association	3,400–3,230	2·94–3·10	s.	broad band
(b) intramolecular	3,590–3,420	2·79–2·92	v.	sharp band
(c) chelate compounds	3,200–1,700	3·13–5·88	w.	very broad band
tropolones	ca. 3,100	ca. 3·23		
—OD	2,780–2,400	3·60–4·17	v.	O—D str.
<i>C—O Stretching and O—H In-plane Deformations</i>				
primary alcohol	1,075–1,000	9·30–10·00	s.	l.v.
	1,350–1,260	7·40– 7·94	s.	l.v.
secondary alcohol	1,120–1,030	8·93– 9·71	s.	l.v.
	1,350–1,260	7·41– 7·94	s.	l.v.
tertiary alcohol	1,170–1,100	8·55– 9·09	s.	l.v.
	1,410–1,310	7·09– 7·63	s.	l.v.
phenols	1,230–1,140	8·13– 8·77	s.	l.v.
	1,410–1,310	7·09– 7·63	s.	l.v.



ν_{OH} , lié

(2) confirmer avec les vibrations de déformation (empreinte) : alcools

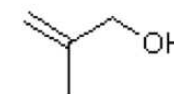


2-methyl-2-propen-1-ol

ALCOHOLS AND PHENOLS				
<i>O—H Stretching Vibrations</i>				
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tertiary alcohol	1,170–1,100	8.55–9.09	s.	l.v.
phenols	1,230–1,140	8.13–8.77	s.	l.v.
	1,410–1,310	7.09–7.63	s.	l.v.



(1) repérer les vibrations de valence des fonctions alcènes



2-methyl-2-propen-1-ol

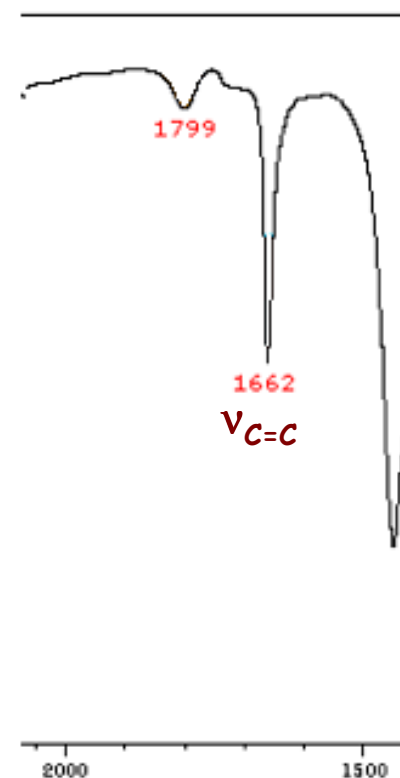
ALKENES

C=C Stretching Vibrations

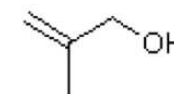
non-conj. C=C	1,680-1,620	5-95-6-17	v.	
CHR=CH ₂	1,645-1,640	6-08-6-10	v.	
CHR ₁ =CHR ₂ (cis)	1,665-1,635	6-01-6-12	v.	
CHR ₁ =CHR ₂ (trans)	1,675-1,665	5-97-6-00	v.	
CR ₁ R ₂ =CH ₂	1,660-1,640	6-02-6-10	v.	
CR ₁ R ₂ =CHR ₃	1,675-1,665	5-97-6-00	v.	
CR ₁ R ₂ =CR ₃ R ₄	1,690-1,670	5-92-5-99	w.	Lv.
phenyl conj. C=C	ca. 1,625	ca. 6-16	s.	enh. int.
C=O or C=C conj. C=C	1,660-1,580	6-02-6-33	s.	cisoid form int. often more enh. than transoid

C-H Stretching and Deformation Vibrations

CHR ₁ =CH ₂	3,040-3,010	3-29- 3-32	m.	CH str. (CHR ₁)
	3,095-3,075	3-23- 3-25	m.	CH str. (CH ₂)
	995- 985	10-05-10-15	m.	CH o.o.p. def.
	915- 905	10-93-11-05	s.	CH ₂ o.o.p. def.
	1,850-1,800	5-41- 5-56	m.	overtone
	1,420-1,410	7-04- 7-09	w.	CH ₂ i.p. def.
CHR ₁ =CHR ₂ (cis)	1,300-1,290	7-69- 7-75	v.	CH i.p. def.
	3,040-3,010	3-29- 3-32	m.	CH str.
CHR ₁ =CHR ₂ (trans)	1,420-1,400	7-04- 7-14	w.	CH i.p. def.
	> 730- 665	13-70-15-04	s.	CH o.o.p. def.
	3,040-3,010	3-29-3-32	m.	CH str.
CR ₁ R ₂ =CH ₂	> 980- 960	10-20-10-42	s.	CH o.o.p. def.
	1,310-1,290	7-63- 7-75	w.	CH i.p. def.
	3,095-3,075	3-23- 3-25	m.	CH str.
	895- 885	11-17-11-30	s.	o.o.p. def.
CR ₁ R ₂ =CHR ₃	1,800-1,780	5-56- 5-62	m.	overtone
	1,420-1,410	7-04- 7-09	w.	CH ₂ i.p. def.
	3,040-3,010	3-29- 3-32	m.	CH str.
	850- 790	11-76-12-66	m.	CH o.o.p. def.



(1) repérer les vibrations de valence des fonctions alcènes



2-methyl-2-propen-1-ol

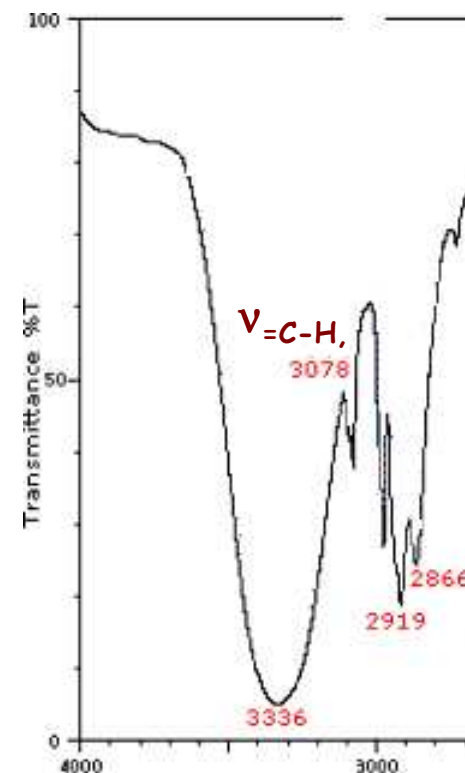
ALKENES

C=C Stretching Vibrations

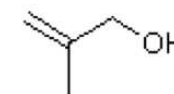
non-conj. C=C	1,680-1,620	5-95-6-17	v.	
CHR=CH ₂	1,645-1,640	6-08-6-10	v.	
CHR ₁ =CHR ₂ (cis)	1,665-1,635	6-01-6-12	v.	
CHR ₁ =CHR ₂ (trans)	1,675-1,665	5-97-6-00	v.	
CR ₁ R ₂ =CH ₂	1,660-1,640	6-02-6-10	v.	
CR ₁ R ₂ =CHR ₃	1,675-1,665	5-97-6-00	v.	
CR ₁ R ₂ =CR ₃ R ₄	1,690-1,670	5-92-5-99	w.	Lv.
phenyl conj. C=C	ca. 1,625	ca. 6-16	s.	enh. int.
C=O or C=C conj. C=C	1,660-1,580	6-02-6-33	s.	cisoid form int. often more enh. than transoid

C-H Stretching and Deformation Vibrations

CHR ₁ =CH ₂	3,040-3,010	3-29- 3-32	m.	CH str. (CHR ₁)
	3,095-3,075	3-23- 3-25	m.	CH str. (CH ₂)
	995- 985	10-05-10-15	m.	CH o.o.p. def.
	915- 905	10-93-11-05	s.	CH ₂ o.o.p. def.
	1,850-1,800	5-41- 5-56	m.	overtone
CHR ₁ =CHR ₂ (cis)	1,420-1,410	7-04- 7-09	w.	CH ₂ i.p. def.
	1,300-1,290	7-69- 7-75	v.	CH i.p. def.
	3,040-3,010	3-29- 3-32	m.	CH str.
CHR ₁ =CHR ₂ (trans)	1,420-1,400	7-04- 7-14	w.	CH i.p. def.
	> 730- 665	13-70-15-04	s.	CH o.o.p. def.
	3,040-3,010	3-29-3-32	m.	CH str.
CR ₁ R ₂ =CH ₂	> 980- 960	10-20-10-42	s.	CH o.o.p. def.
	1,310-1,290	7-63- 7-75	w.	CH i.p. def.
	3,095-3,075	3-23- 3-25	m.	CH str.
CR ₁ R ₂ =CHR ₃	895- 885	11-17-11-30	s.	o.o.p. def.
	1,800-1,780	5-56- 5-62	m.	overtone
	1,420-1,410	7-04- 7-09	w.	CH ₂ i.p. def.
CR ₁ R ₂ =CHR ₃	3,040-3,010	3-29- 3-32	m.	CH str.
	850- 790	11-76-12-66	m.	CH o.o.p. def.



(2) confirmer avec les vibrations de déformation (empreinte) : alcènes



2-methyl-2-propen-1-ol

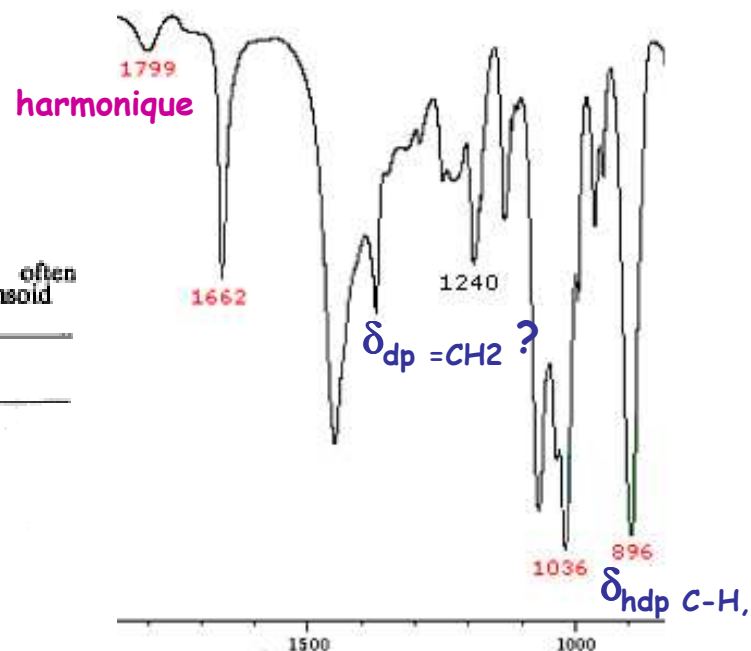
ALKENES

C=C Stretching Vibrations

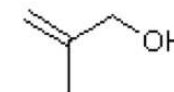
non-conj. C=C	1,680-1,620	5-95-6-17	v.	
CHR=CH ₂	1,645-1,640	6-08-6-10	v.	
CHR ₁ =CHR ₂ (cis)	1,665-1,635	6-01-6-12	v.	
CHR ₁ =CHR ₂ (trans)	1,675-1,665	5-97-6-00	v.	
CR ₁ R ₂ =CH ₂	1,660-1,640	6-02-6-10	v.	
CR ₁ R ₂ =CHR ₃	1,675-1,665	5-97-6-00	v.	
CR ₁ R ₂ =CR ₃ R ₄	1,690-1,670	5-92-5-99	w.	Lv.
phenyl conj. C=C	ca. 1,625	ca. 6-16	s.	enh. int.
C=O or C=C conj. C=C	1,660-1,580	6-02-6-33	s.	cisoid form int. often more enh. than transoid

C-H Stretching and Deformation Vibrations

CHR ₁ =CH ₂	3,040-3,010	3-29- 3-32	m.	CH str. (CHR ₁)
	3,095-3,075	3-23- 3-25	m.	CH str. (CH ₂)
	995- 985	10-05-10-15	m.	CH o.o.p. def.
	915- 905	10-93-11-05	s.	CH ₂ o.o.p. def.
	1,850-1,800	5-41- 5-56	m.	overtone
CHR ₁ =CHR ₂ (cis)	1,420-1,410	7-04- 7-09	w.	CH ₂ i.p. def.
	1,300-1,290	7-69- 7-75	v.	CH i.p. def.
	3,040-3,010	3-29- 3-32	m.	CH str.
CHR ₁ =CHR ₂ (trans)	1,420-1,400	7-04- 7-14	w.	CH i.p. def.
	> 730- 665	13-70-15-04	s.	CH o.o.p. def.
	3,040-3,010	3-29-3-32	m.	CH str.
CR ₁ R ₂ =CH ₂	> 980- 960	10-20-10-42	s.	CH o.o.p. def.
	1,310-1,290	7-63- 7-73	w.	CH i.p. def.
	3,095-3,075	3-23- 3-25	m.	CH str.
CR ₁ R ₂ =CHR ₃	895- 885	11-17-11-30	s.	o.o.p. def.
	1,800-1,780	5-56- 5-62	m.	overtone
	1,420-1,410	7-04- 7-09	w.	CH ₂ i.p. def.
CR ₁ R ₂ =CR ₃ R ₄	3,040-3,010	3-29- 3-32	m.	CH str.
	850- 790	11-76-12-66	m.	CH o.o.p. def.



(1) repérer les vibrations de valence des fonctions alcanes



2-methyl-2-propen-1-ol

ALKANES

C—H Stretching Vibrations

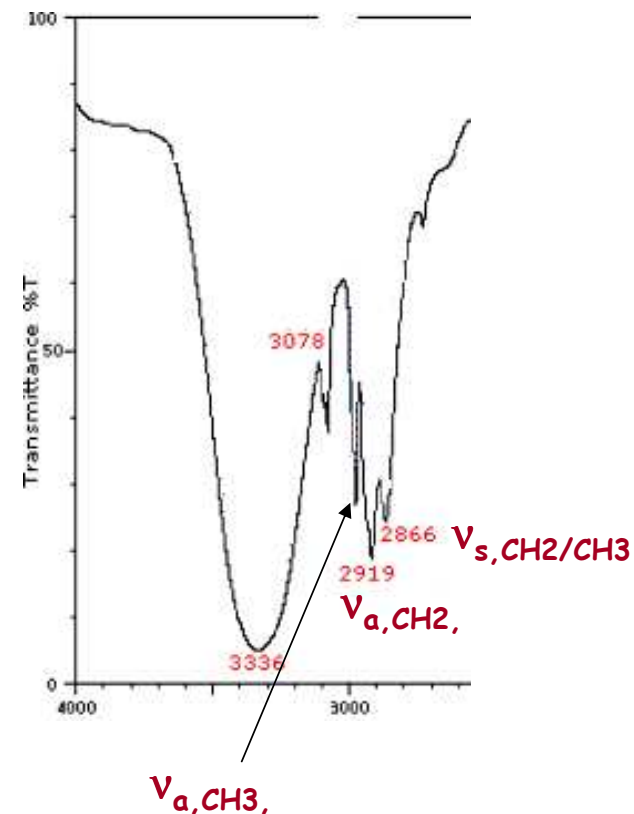
—CH ₃	2,975–2,950	3·36–3·39	m.	} The presence of several of these groups gives strong absorption
	2,885–2,860	3·47–3·50	m.	
—CH ₂ —	2,940–2,915	3·40–3·45	m.	
	2,870–2,845	3·49–3·52	m.	
—CH ₂ — (cyclopropane)	3,080–3,040	3·25–3·29	v.	l.v.
—CH—	2,900–2,880	3·45–3·47	w.	l.v.
OCH ₃ , NCH ₃ etc.				see ethers, amines etc.

C—H Deformation Vibrations

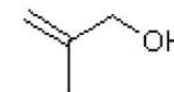
C—CH ₃	1,470–1,435	6·80–6·97	m.	asym. def.
	1,385–1,370	7·22–7·30	s.	sym. def.
C(CH ₃) ₂	1,385–1,380	7·22–7·25	s.	} doublet of approx. equal int.
	1,370–1,365	7·30–7·33	s.	
C(CH ₃) ₃	1,395–1,385	7·17–7·22	m.	doublet
	1,365	7·33	s.	int. ratio ca. 1:2
—CH ₂ —	1,480–1,440	6·76–6·94	m.	CH ₂ scissor
—CH—	ca. 1,340	ca. 7·46	w.	l.v.

Skeletal Vibrations

C(CH ₃) ₂	1,175–1,165	8·51–8·58	s.	
	1,170–1,140	8·55–8·77	s.	
	840–790	11·90–12·66	m.	l.v.
C(CH ₃) ₃	1,255–1,245	7·97–8·03	s.	
	1,250–1,200	8·00–8·33	s.	
—(CH ₂) ₄	750–720	13·33–13·89	s.	
—CH ₂ — (cyclopropane)	1,020–1,000	9·80–10·00	m.	l.v.



(2) confirmer avec les vibrations de déformation (empreinte) : alcanes



2-methyl-2-propen-1-ol

ALKANES

C—H Stretching Vibrations

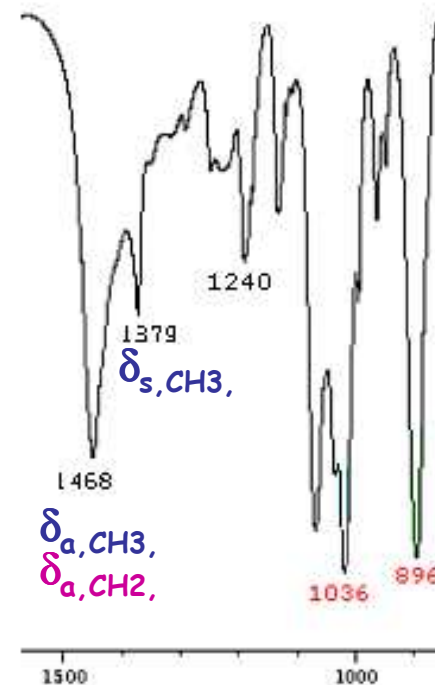
—CH ₃	2,975–2,950	3·36–3·39	m.	} The presence of several of these groups gives strong absorption
	2,885–2,860	3·47–3·50	m.	
—CH ₂ —	2,940–2,915	3·40–3·45	m.	
	2,870–2,845	3·49–3·52	m.	
—CH ₂ — (cyclopropane)	3,080–3,040	3·25–3·29	v.	
—CH—	2,900–2,880	3·45–3·47	w.	l.v.
OCH ₃ , NCH ₃ etc.				l.v. see ethers, amines etc.

C—H Deformation Vibrations

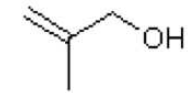
C—CH ₃	1,470–1,435	6·80–6·97	m.	asym. def.
	1,385–1,370	7·22–7·30	s.	sym. def.
C(CH ₃) ₂	1,385–1,380	7·22–7·25	s.	} doublet of approx. equal
	1,370–1,365	7·30–7·33	s.	
C(CH ₃) ₃	1,395–1,385	7·17–7·22	m.	} doublet
	1,265	7·33	s.	
—CH ₂ —	1,480–1,440	6·76–6·94	m.	CH ₂ scissor
—CH—	ca. 1,340	ca. 7·46	w.	l.v.

Skeletal Vibrations

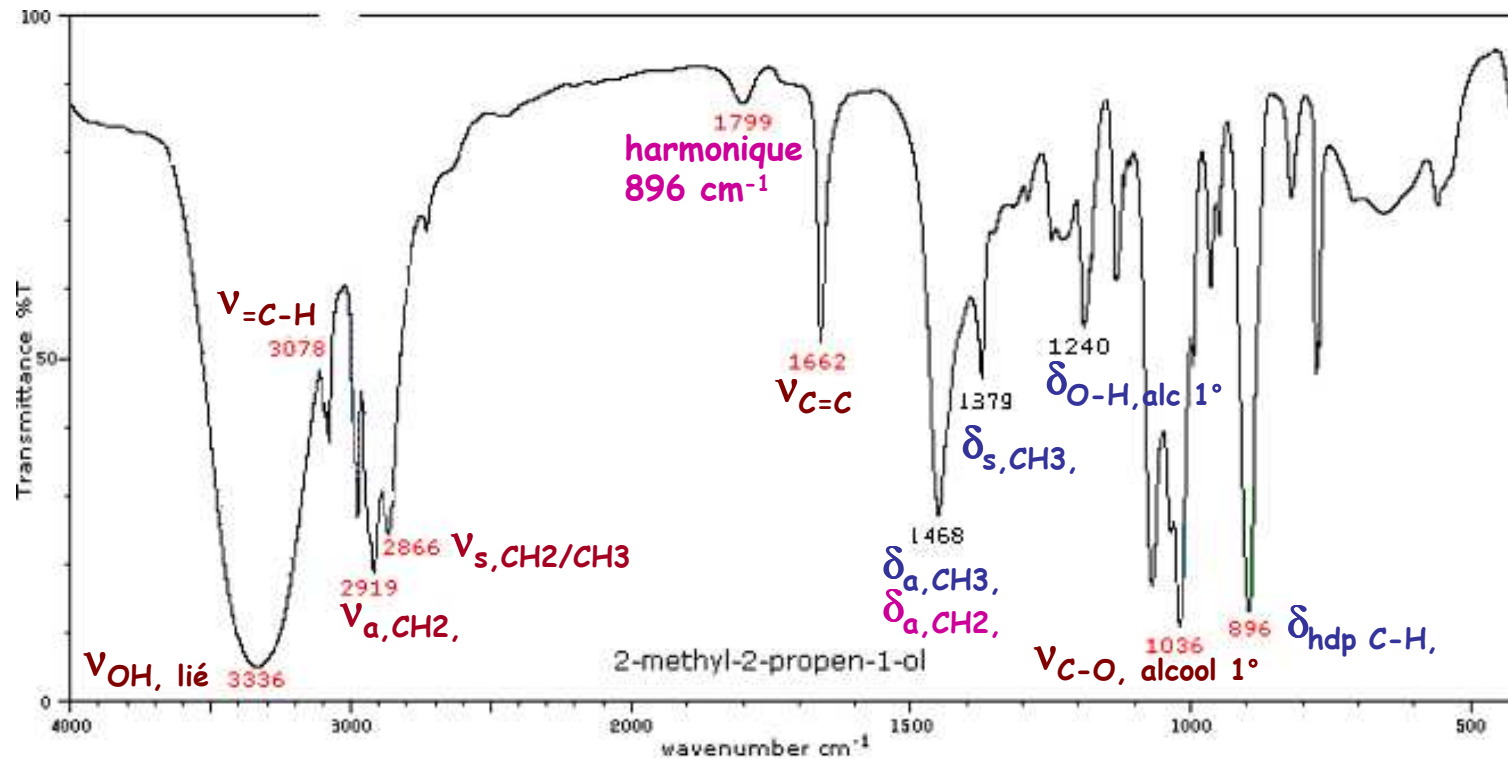
C(CH ₃) ₂	1,175–1,165	8·51–8·58	s.	l.v.
	1,170–1,140	8·55–8·77	s.	
	840–790	11·90–12·66	m.	
C(CH ₃) ₃	1,255–1,245	7·97–8·03	s.	l.v.
	1,250–1,200	8·00–8·33	s.	
	750–720	13·33–13·89	s.	
—(CH ₂) ₄				
—CH ₂ — (cyclopropane)	1,020–1,000	9·80–10·00	m.	l.v.



Analyse du spectre



2-methyl-2-propen-1-ol

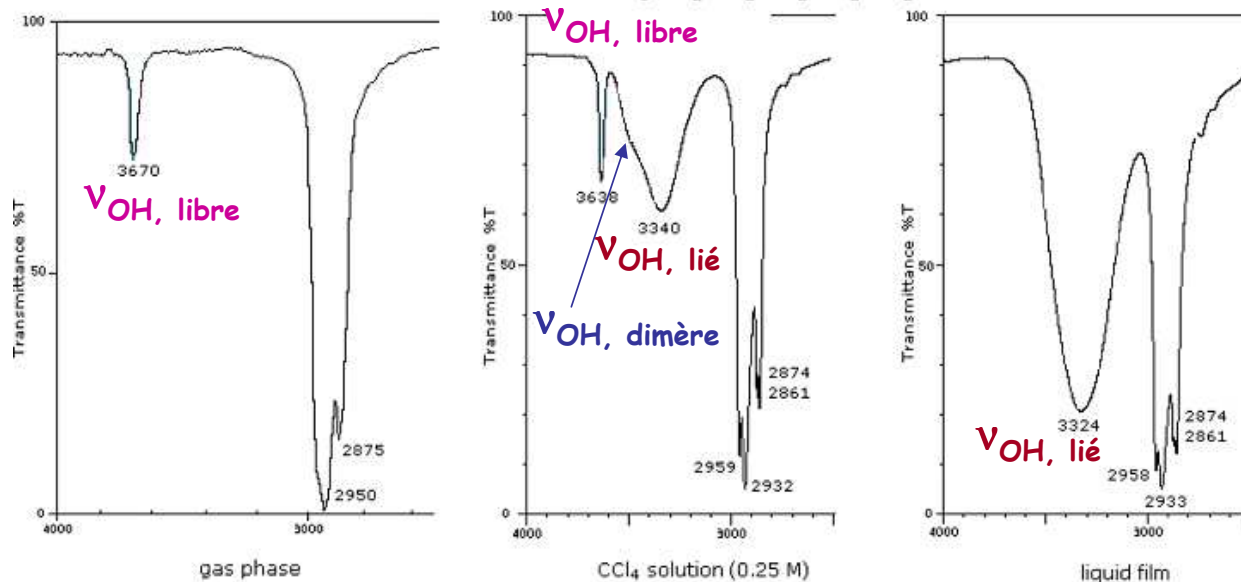


I - 5. Paramètres influant sur les fréquences de groupe

Largeur des bandes : interactions intermoléculaires

La largeur de bande dépend du nombre d'environnements chimiques du vibrateur
 ⇒ la force des liaisons intermoléculaires, comme la liaison hydrogène, influence la force de liaison k du vibrateur, donc sa fréquence de vibration

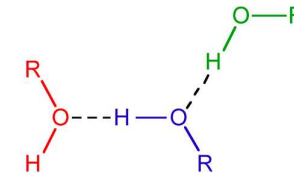
1-hexanol



conditions
 expérimentales !
 T° , [ROH], solvant

O—H Stretching Vibrations				
free OH	3,670–3,580	2·73–2·79	v.	sharp band
hydrogen bonded OH				
(a) intermolecular dimeric association	3,550–3,450	2·82–2·90	v.	sharp band
(a) intermolecular polymeric association	3,400–3,230	2·94–3·10	s.	broad band
(b) intramolecular	3,590–3,420	2·79–2·92	v.	sharp band
(c) chelate compounds	3,200–1,700	3·13–5·88	w.	very broad band

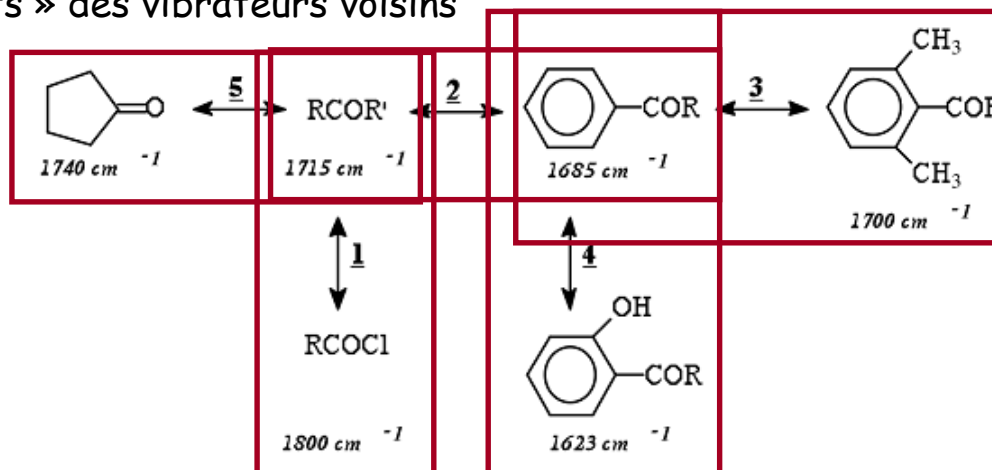
int. changes and frequency shifts on dilution
 unaffected by dilution



Facteurs moléculaires

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

la force de liaison k du vibrateur, donc sa fréquence de vibration, peut être influencée par les « effets » des vibrateurs voisins



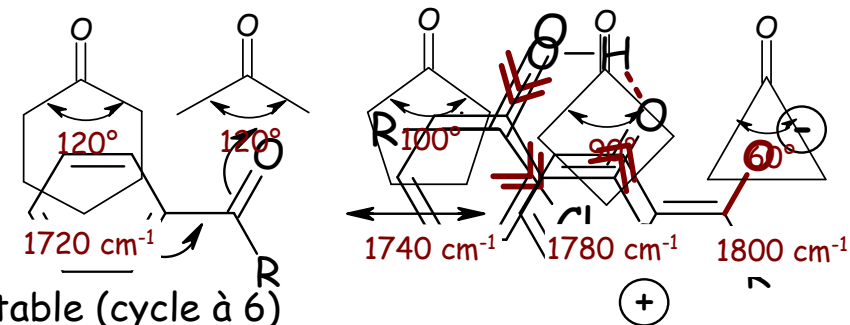
1. effet inductif attracteur (-I) du chlore

2. conjugaison avec le cycle aromatique

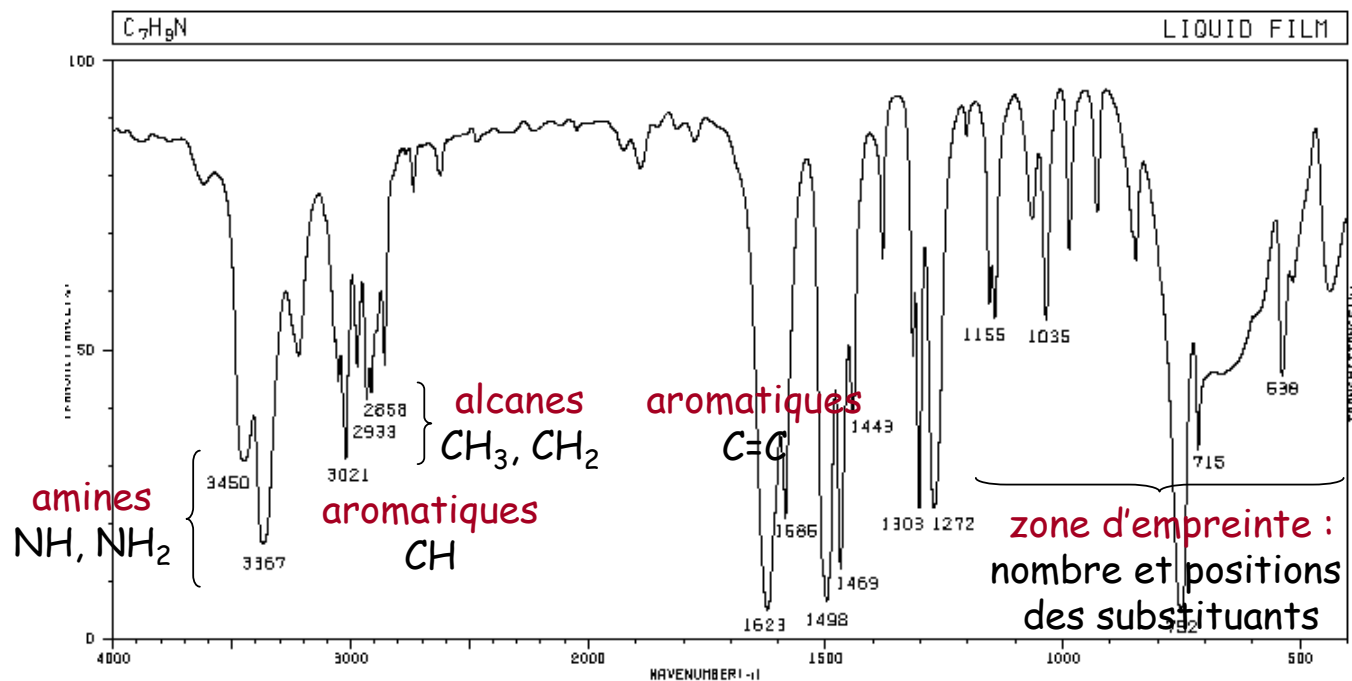
3. gêne stérique

4. liaison hydrogène intramoléculaire très stable (cycle à 6)

5. effet mécanique du cycle qui provoque la rigidification du vibrateur C=O



I - 6. Analyse d'un composé inconnu : mode d'emploi



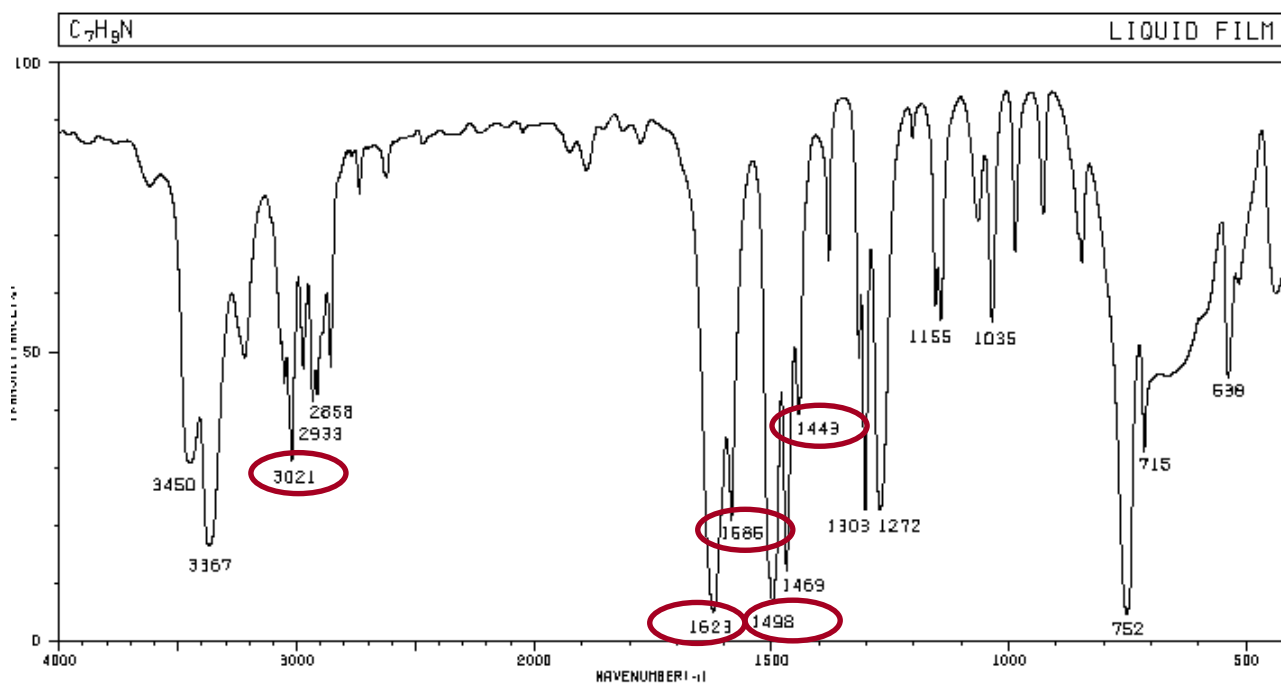
Composé de formule : $C_xH_yN_tO_z$; $2i = 2x + t + 2 - y$

$$i = (2 \cdot 7 + 1 + 2 - 9) / 2 = 4$$

noyau aromatique : 4 insaturations

⇒ reste un C : CH_3 ou CH_2

(1) vérifier les informations structurales (insaturations) obtenues

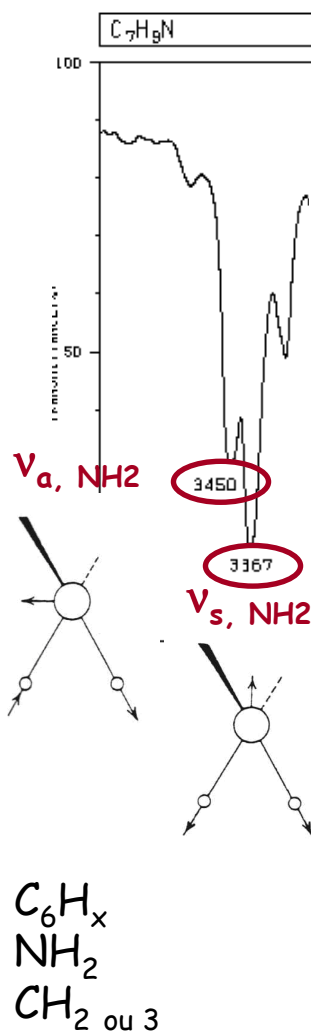


AROMATIC HOMOCYCLIC COMPOUNDS

Stretching Vibrations

=C—H str.	3,080–3,030	3·25–3·30	w.-m.	multiple peaks may appear usually close to 1,600 cm ⁻¹ usually close to 1,500 cm ⁻¹ strong band for conj. rings
C=C i.p. vib.	1,625–1,575	6·16–6·35	v.	
	1,525–1,475	6·56–6·78	v.	
	1,590–1,575	6·29–6·36	v.	
	1,465–1,440	6·38–6·94	v.	

(2) *rechercher les bandes d'élongations caractéristiques des fonctions chimiques envisagées*



LIQUID FILM

AMINES AND IMINES

N—H Stretching Vibrations

primary amines	3,500–3,300	2.86–3.03	v.	2 bands appear in this range
secondary amines	3,500–3,300	2.86–3.03	v.	
imines	3,400–3,300	2.94–3.03	v.	l.v.
associated N—H	3,400–3,100	2.94–3.23	m.	
free N—D	2,600–2,400	3.85–4.15	v.	

N—H Deformation Vibrations

primary amines	1,650–1,580	6.06–6.33	m.-s.	
secondary amines	1,650–1,550	6.06–6.45	w.	

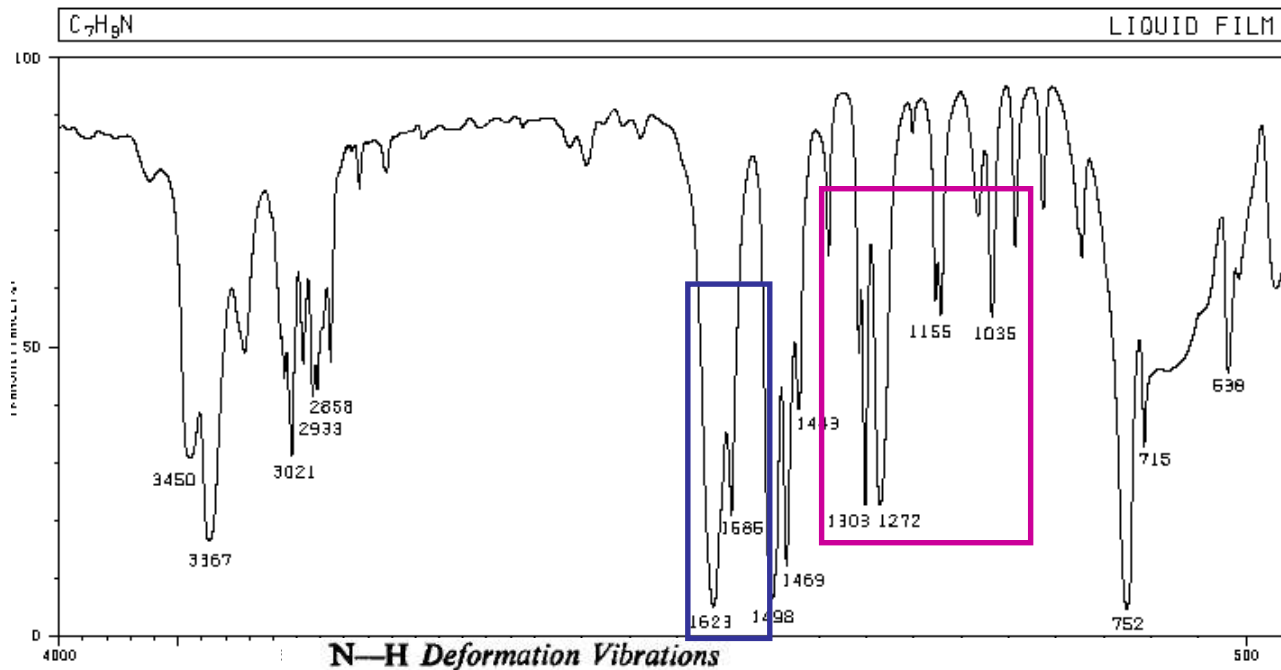
C—N Stretching Vibrations

aliphatic amines	1,220–1,020	8.20–9.80	w.-m.	l.v.
aromatic amines:				
primary	1,340–1,250	7.46–8.00	s.	
secondary	1,350–1,280	7.41–7.81	s.	
tertiary	1,360–1,310	7.35–7.63	s.	

Other Vibrations

N-Methyl	2,820–2,760	3.55–3.62	m.-s.	C—H str.
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(3) confirmer avec la recherche des bandes de déformation

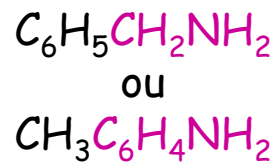


N—H Deformation Vibrations

primary amines	1,650–1,580	6·06–6·33	m.-s.
secondary amines	1,650–1,550	6·06–6·45	w.

C—N Stretching Vibrations

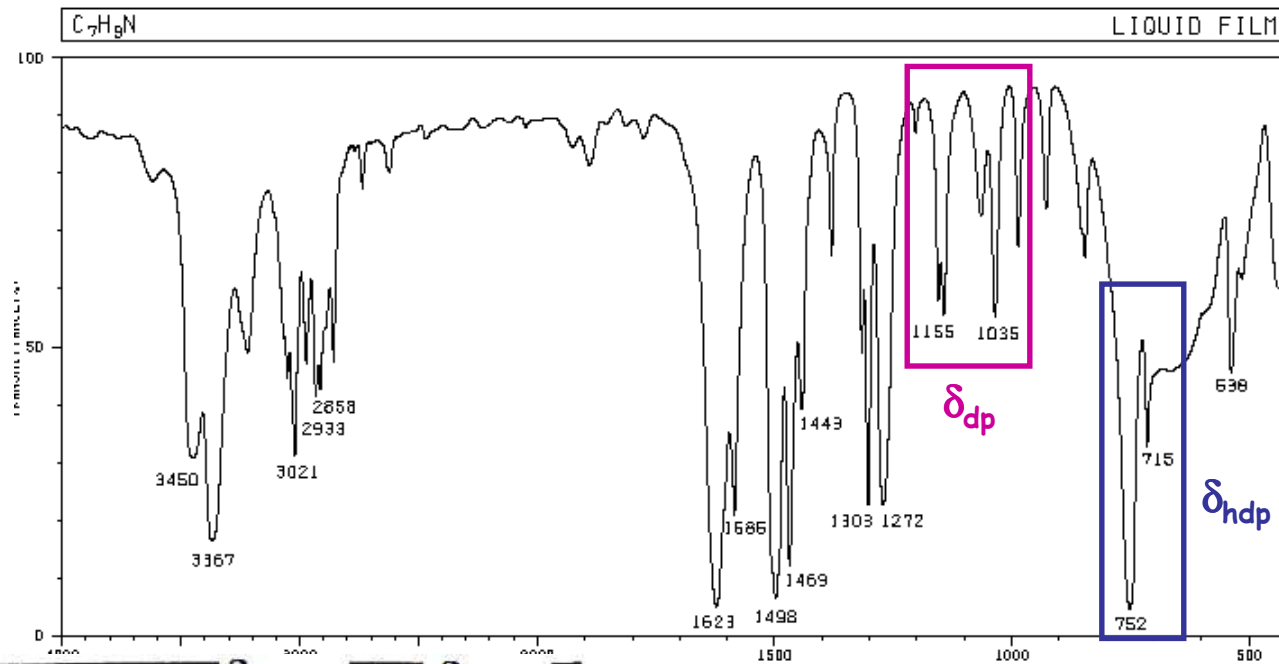
aliphatic amines	1,220–1,020	8·20–9·80	w.-m.
aromatic amines:			
primary	1,340–1,250	7·46–8·00	s.
secondary	1,350–1,280	7·41–7·81	s.
tertiary	1,360–1,310	7·35–7·63	s.



l.v. pas concluant

(3) confirmer avec la recherche des bandes de déformation

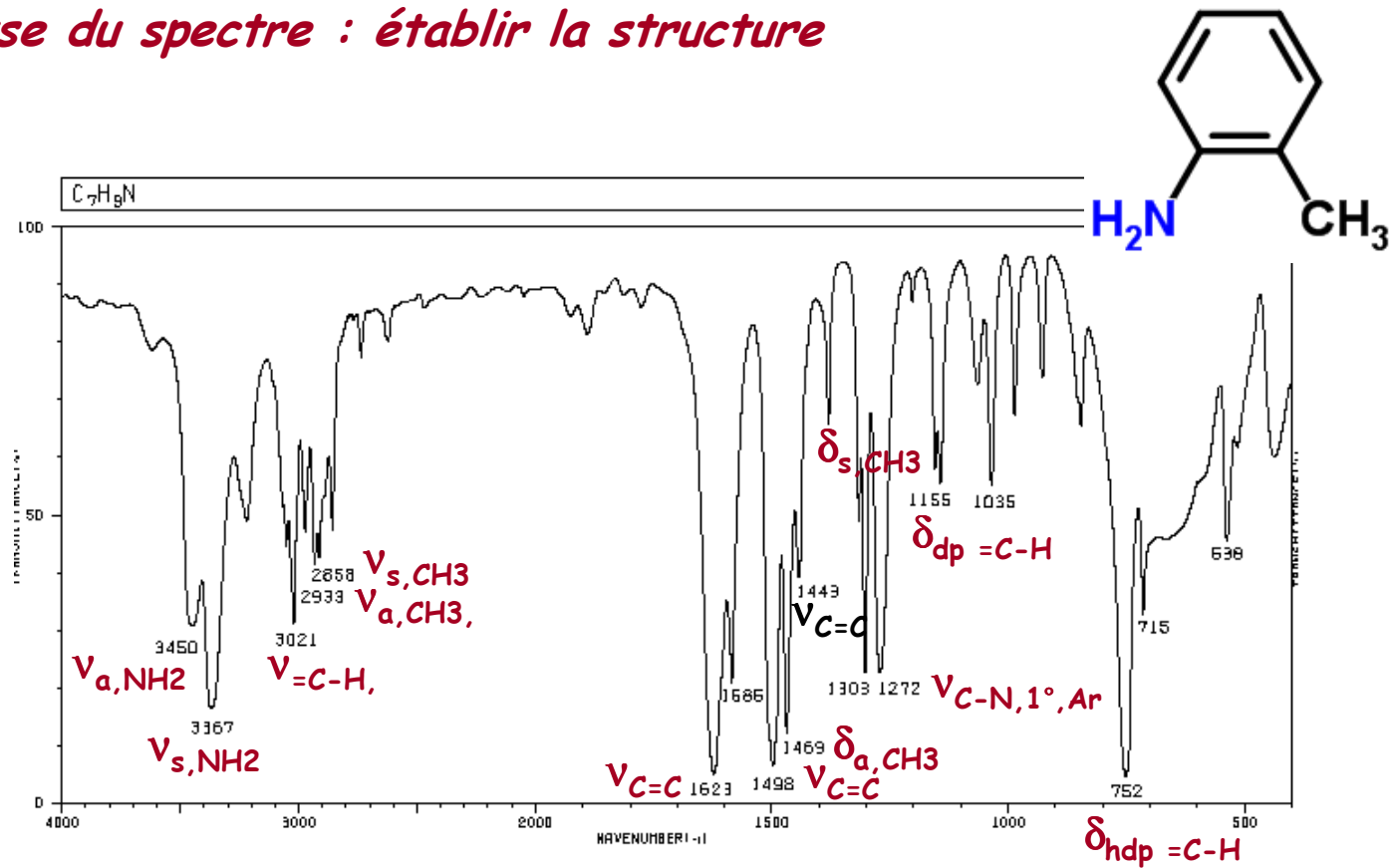
aromatique mono ou disubstitué : zone d'empreinte



Hydrogènes adjacents	Substitution	$\delta_{=CH \text{ hdp}}$	$\delta_{CC \text{ hdp}}$
5H	1	751 ± 15 (a)	700-675 (F)
4H	1,2	751 ± 7	inactive (d)
3H	1,3	782 ± 9	710-665 (F)
2H	1,4	817 ± 13 (b)	inactive (d)

	Mono	Ortho	Méta	Para (b)
$\partial \text{ CH}$	1000 ± 5	-	1000 ± 5	-
	1027 ± 3 (a)	1033 ± 11 (a)	1076 ± 7	1013 ± 5 (IR)
	1073 ± 4	1125 ± 14	1096 ± 7	1117 ± 7 (IR)
	1156 ± 5	1160 ± 4	1157 ± 5	1175 ± 6 (R)
	1177 ± 7	-	-	-
$\partial \text{ CC}$	560-418	470-418	490-415	552-446 ..

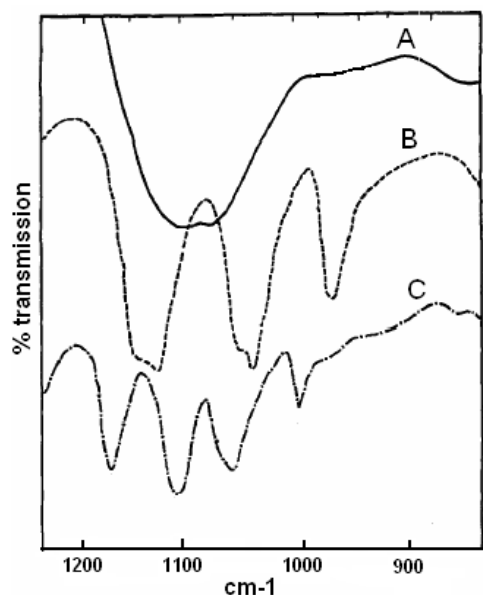
Analyse du spectre : établir la structure



! Toujours confirmer la structure par d'autres analyses spectroscopiques :
RMN, CP-MAS

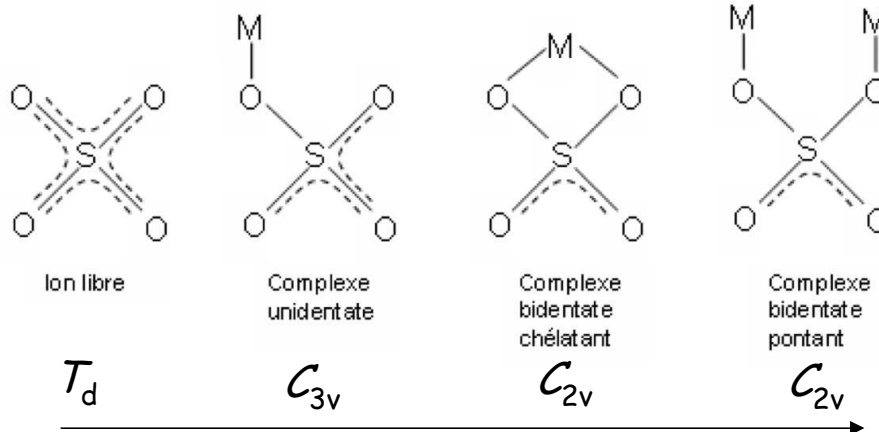
II - Spectroscopie infrarouge des complexes de coordination

1. Information sur le mode de complexation des ligands



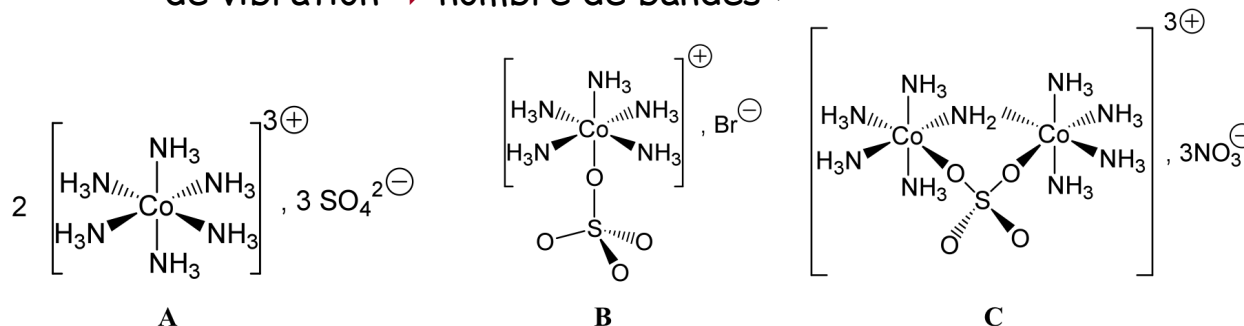
- A** = $\text{Co}_2(\text{NH}_3)_{12}(\text{SO}_4)_3$
B = $\text{Co}(\text{NH}_3)_5\text{SO}_4\text{Br}$
C = $\text{Co}_2(\text{NH}_3)_9(\text{NH}_2)\text{SO}_4(\text{NO}_3)_3$

$$\nu_{\text{SO}_4^{2-}} = 1080 \text{ cm}^{-1}$$

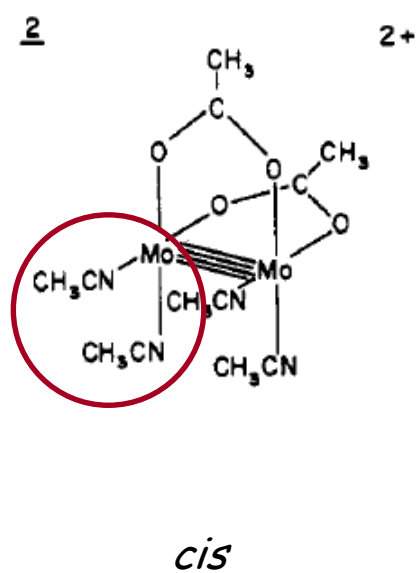
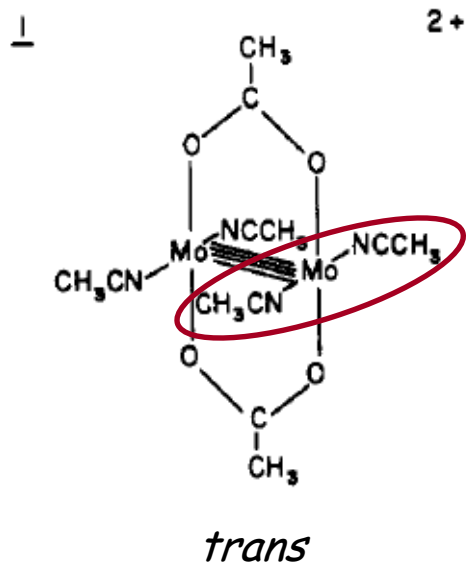


TDG

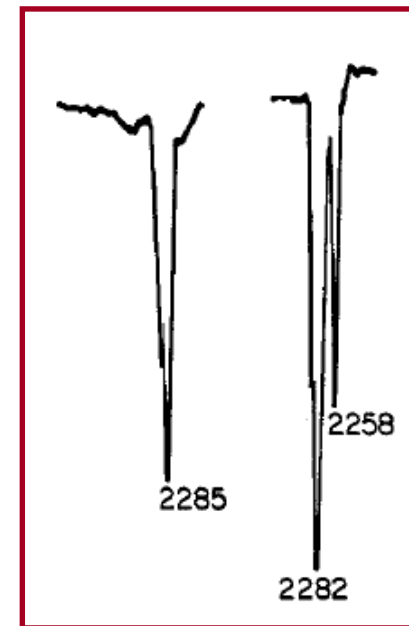
symétrie $\searrow \Rightarrow$ levée de dégénérescence des modes normaux
 de vibration \Rightarrow nombre de bandes \nearrow



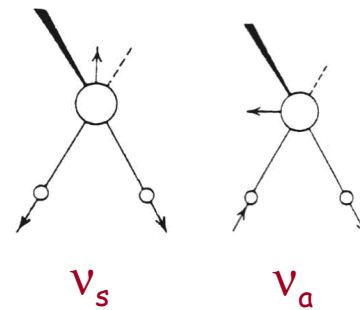
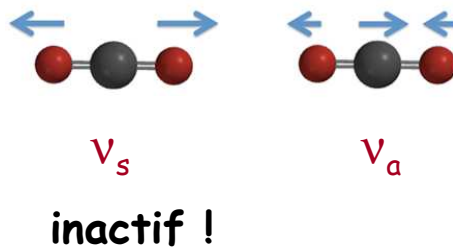
I - 2. Information sur la structure des complexes (isomères)



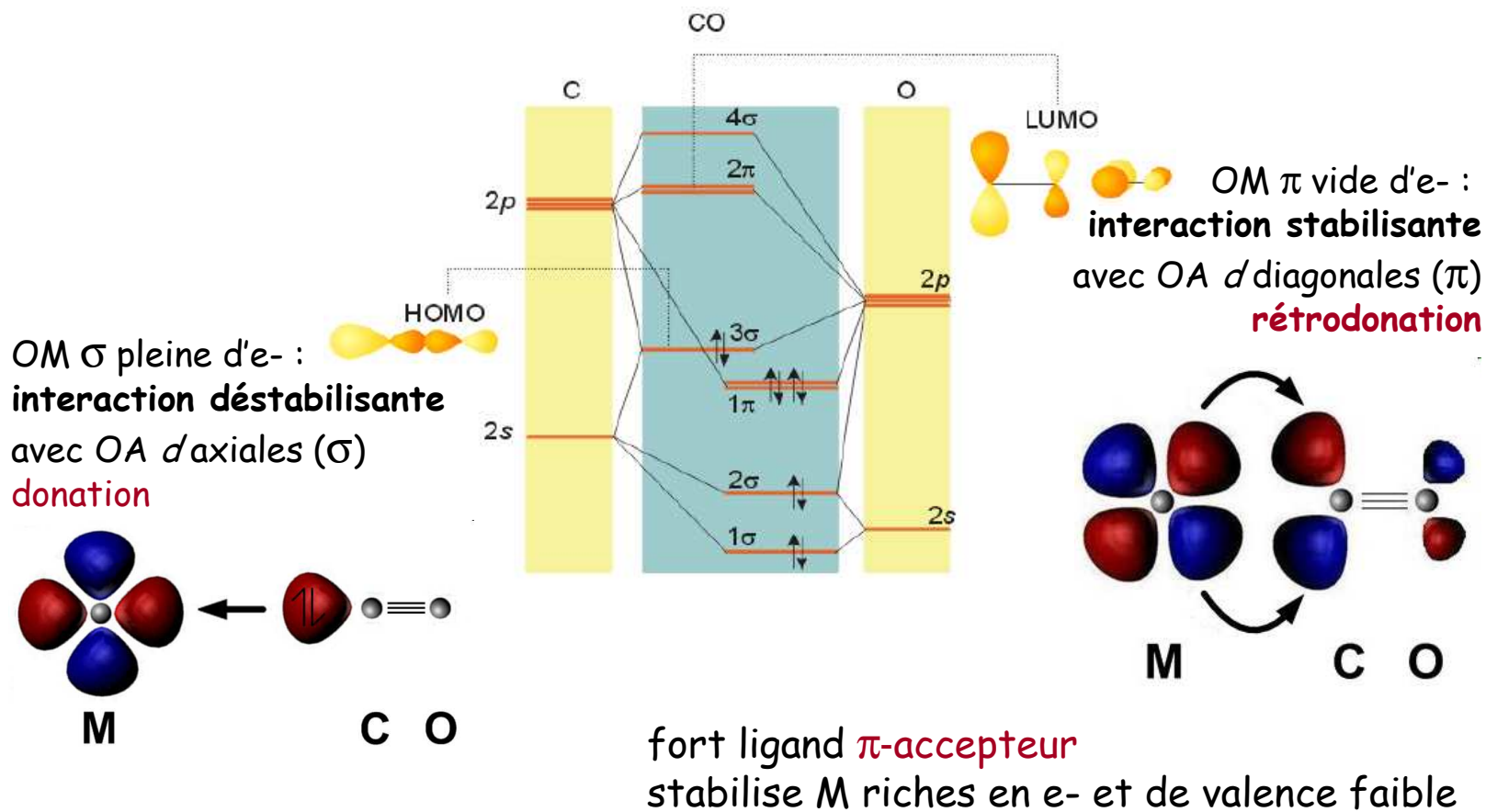
$$\nu_{\text{CN}^-} = 2280 \text{ cm}^{-1}$$



Pour un groupement formé de plusieurs liaisons identiques :

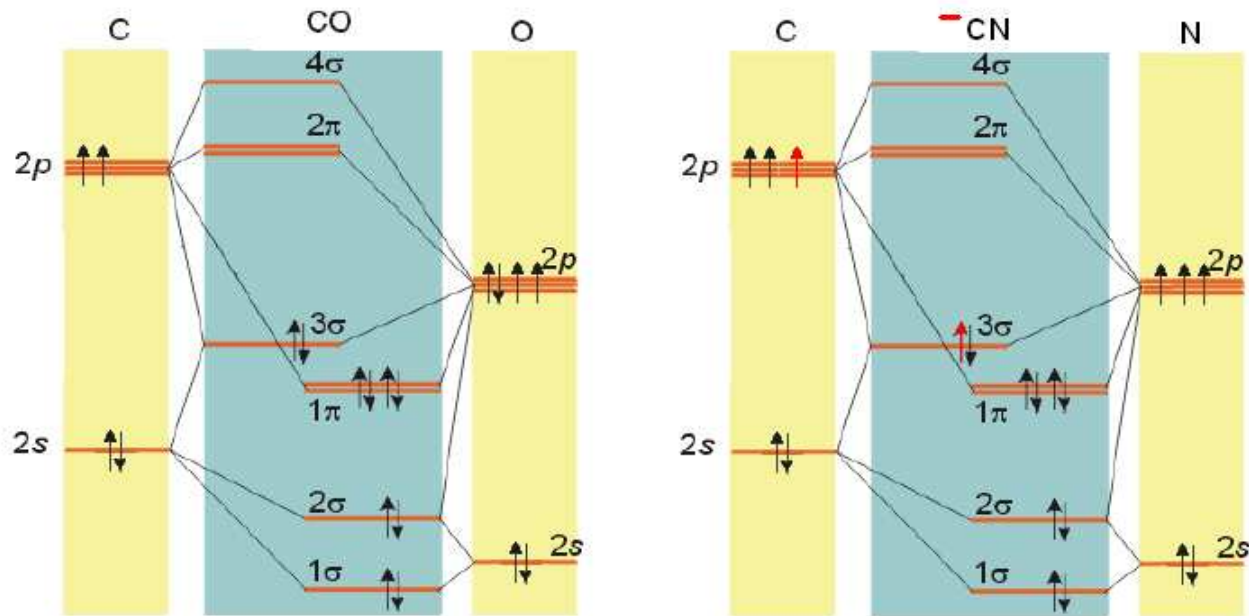


I - 3. Evaluer la rétrodonation : fréquence des ligands π -accepteurs



rétrodonation remplit les OM^* \Rightarrow ordre liaison $\searrow \Rightarrow k \searrow, V_{CO} \searrow$

Evaluer la rétrodonation : CO vs ⁻CN



rétrodonation se fait par les OM côté C
⁻CN : la charge porté par le C limite la rétrodonation

⁻CN est fort σ -donneur, faible π -accepteur : $\nu_{\text{CN, libre}} = 2080 \text{ cm}^{-1}$, $\nu_{\text{CN, complexe}} = 2150 \text{ cm}^{-1}$

CO est faible σ -donneur, fort π -accepteur : $\nu_{\text{CO, libre}} = 2143 \text{ cm}^{-1}$, $\nu_{\text{CO, complexe}} = 2000 \text{ cm}^{-1}$

Evaluer la rétrodonation

Densité de charge du métal

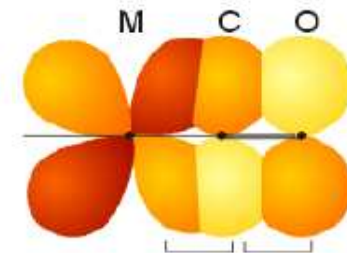
3	4	5	6	7	8	9	10	11	12
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Scandium 3d ¹ 4s ²	Titane 3d ² 4s ²	Vanadium 3d ³ 4s ²	Chrome 3d ⁴ 4s ²	Manganèse 3d ⁵ 4s ²	Fer 3d ⁶ 4s ²	Cobalt 3d ⁷ 4s ²	Nickel 3d ⁸ 4s ²	Cuivre 3d ⁹ 4s ¹	Zinc 3d ¹⁰ 4s ¹

$\nu_{CO} / \text{cm}^{-1}$	
CO (g)	2143
[Mn(CO) ₆] ⁺	2090
Cr(CO) ₆	2000
[V(CO) ₆] ⁻	1860
[Ti(CO) ₆] ²⁻	1750
Fe ₂ (CO) ₉	2082, 2019, 1829

ν_{CN}	$K_4[Fe^{(II)}(CN)_6]$ 2100 cm ⁻¹	$K_3[Fe^{(III)}(CN)_6]$ 2135 cm ⁻¹
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Electronégativité du métal

	χ_M	$\nu_{CN} (\text{cm}^{-1})$
[Ni(CN) ₄] ²⁻	1.91	2130
[Pd(CN) ₄] ²⁻	2.20	2140
[Pt(CN) ₄] ²⁻	2.28	2150



+ forte - forte
 $\nu_{MC} \nearrow$ $\nu_{CO} \searrow$

charge - \nearrow rétrodonation $\nearrow \nu_{CO} \searrow$
 charge + \nearrow donation $\nearrow \nu_{CN} \nearrow$

électronégativité \nearrow donation $\nearrow \nu_{CN} \nearrow$

Evaluer la rétrodonation

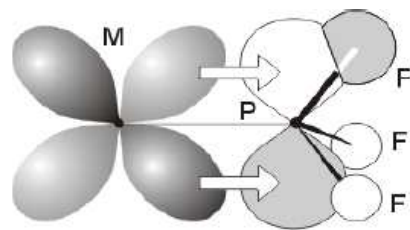
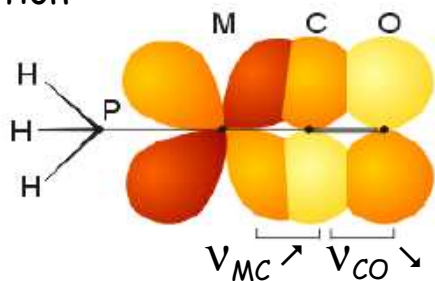
Nature du ligand en *trans*

L *trans* σ -donneur

densité ϵ ique ↗

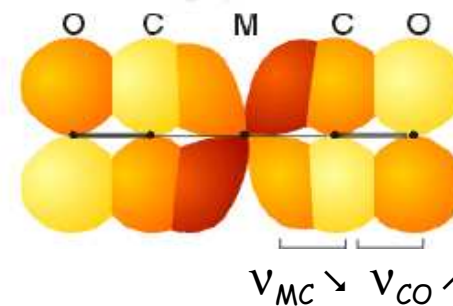
rétrodonation ↗

"O=C=M"



PF_3 , ligand π -accepteur aussi fort que CO

Complex	$\nu_{\text{CO}} \text{ cm}^{-1}$
$\text{Mo}(\text{CO})_3(\text{PF}_3)_3$	2090, 2055
$\text{Mo}(\text{CO})_3(\text{PCl}_3)_3$	2040, 1991
$\text{Mo}(\text{CO})_3[\text{P}(\text{OMe})_3]_3$	1977, 1888
$\text{Mo}(\text{CO})_3(\text{PPh}_3)_3$	1934, 1835
$\text{Mo}(\text{CO})_3(\text{NCCH}_3)_3$	1915, 1783
$\text{Mo}(\text{CO})_3(\text{triamine})_3$	1898, 1758
$\text{Mo}(\text{CO})_3(\text{pyridine})_3$	1888, 1746



L *trans* π -accepteur

densité ϵ ique M ↘

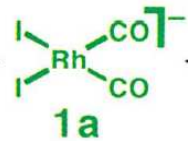
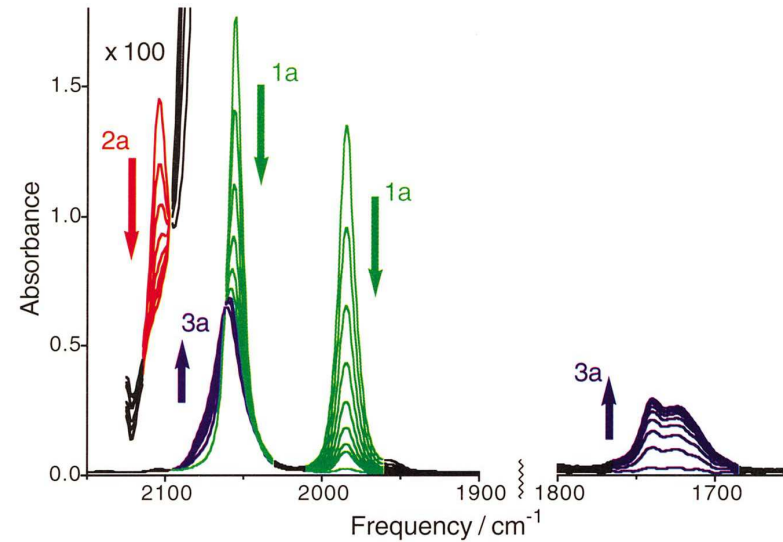
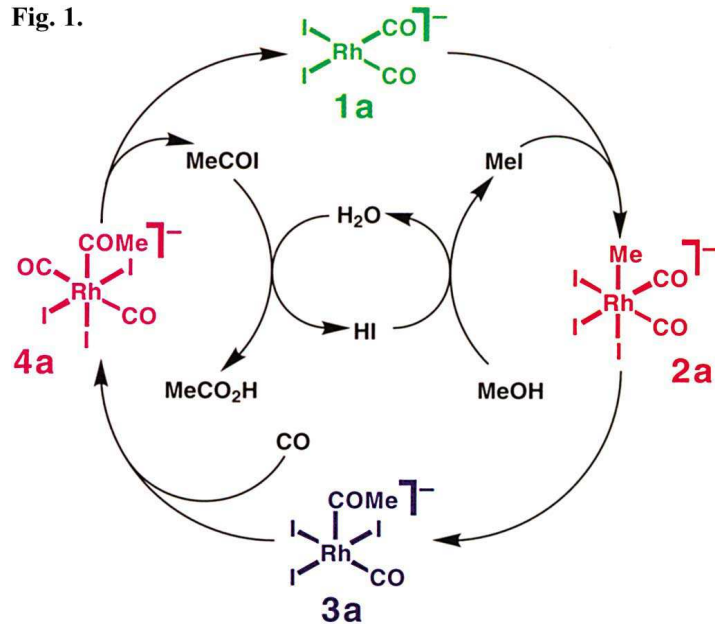
rétrodonation ↘

$\text{O} \equiv \text{C} \rightarrow \text{M}$

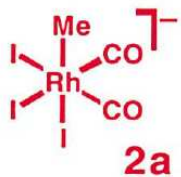
Spectres infrarouge des complexes de coordination

Etude mécanistique : procédé Monsanto

Fig. 1.



cis: $\nu_{CO} = 2055 \text{ cm}^{-1}$ et 1990 cm^{-1} , bandes bien visibles = consommation lente !

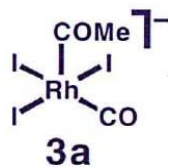
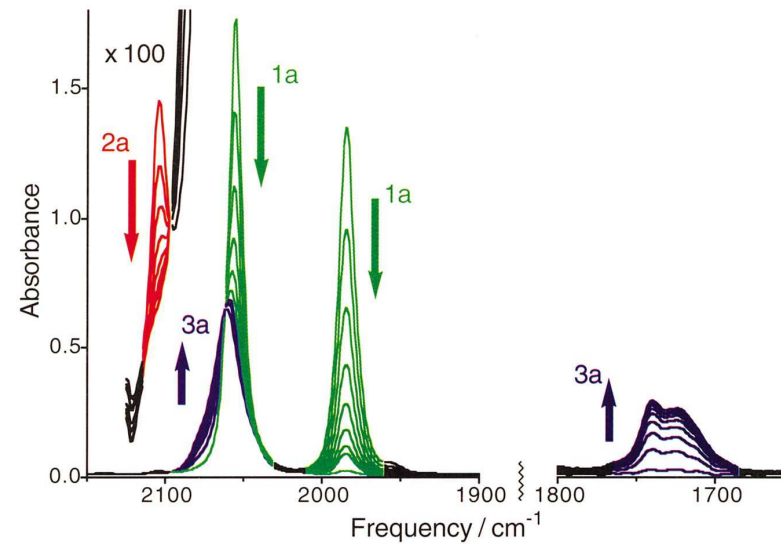
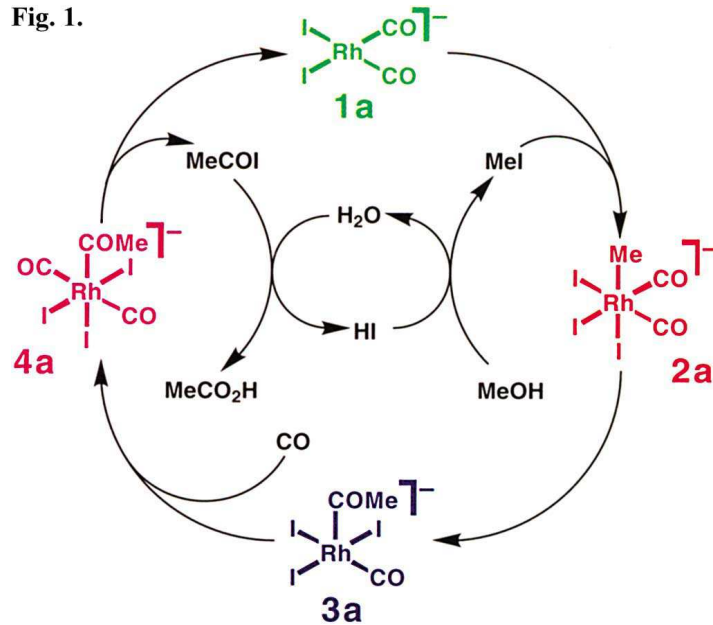


Addition oxydante $\Rightarrow \text{Rh}^{\text{III}}$: $\nu_{CO} = 2104 \text{ cm}^{-1}$ (2065 cm^{-1} non visible)

Spectres infrarouge des complexes de coordination

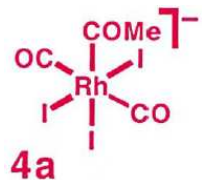
Etude mécanistique : procédé Monsanto

Fig. 1.



insertion-migration : $\nu_{CO} = 1745 \text{ cm}^{-1}$ caractéristique de C=O

$\nu_{CO} = 2060 \text{ cm}^{-1}$ caractéristique de $C\equiv O$ (1 seul vibrateur)

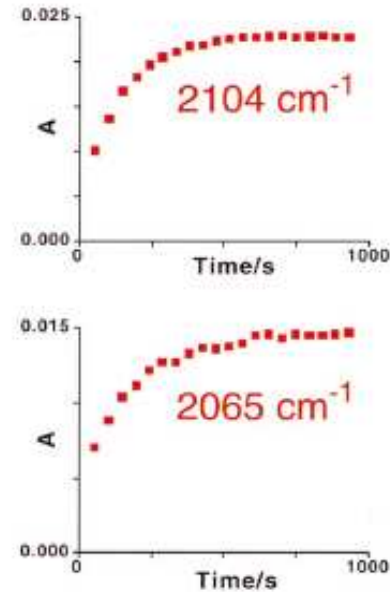
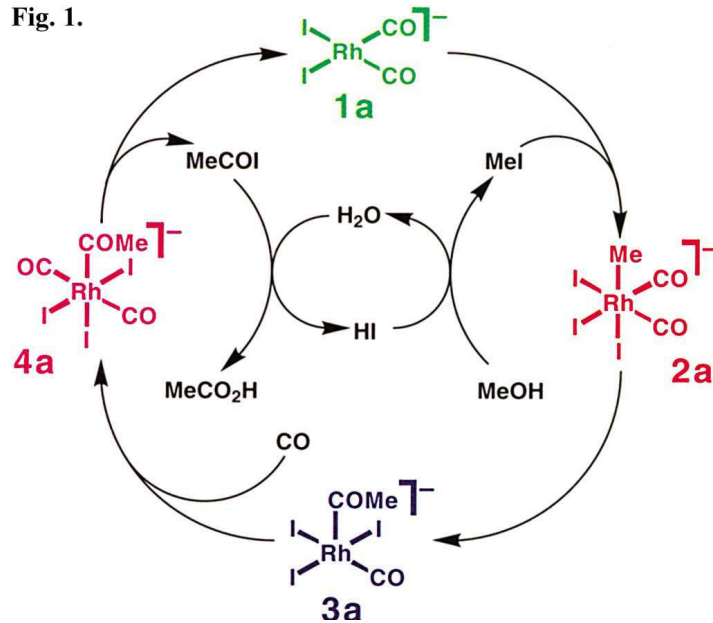


non détectable sur le spectre IR \Rightarrow temps de vie trop court

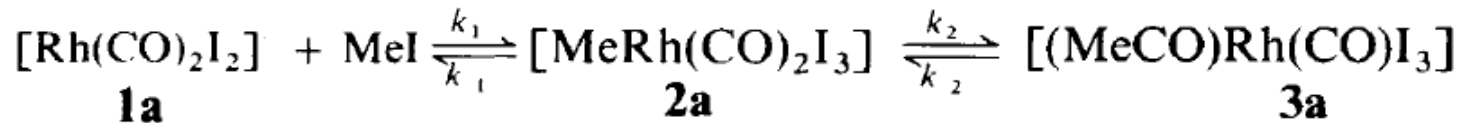
Spectres infrarouge des complexes de coordination

Etude mécanistique : procédé Monsanto

Fig. 1.



Absorption IR proportionnelle à la concentration !



Si $[\text{MeI}]$ très élevée, réaction du pseudo-premier ordre : $k_{\text{obs}} = \frac{k_1 k_2 [\text{MeI}]}{k_{-1} + k_2}$

Or, d'après les réactions : $\frac{[\mathbf{2a}]}{[\mathbf{1a}]} = \frac{k_1 [\text{MeI}]}{k_{-1} + k_2}$ donc : $k_2 = k_{\text{obs}} \frac{[\mathbf{1a}]}{[\mathbf{2a}]}$

Spectres infrarouge des complexes de coordination

Etude mécanistique : procédé Monsanto

Mesure de k_2 sur l'élimination réductrice de **3a** en **1a** en présence d'un excès de MeI

Mesure de k_2/k_1 sur l'élimination de **3a** en **2a** en l'absence de MeI

Pour mieux suivre les réactions d'élimination, le réactif **3a** est marqué avec ^{13}CO

