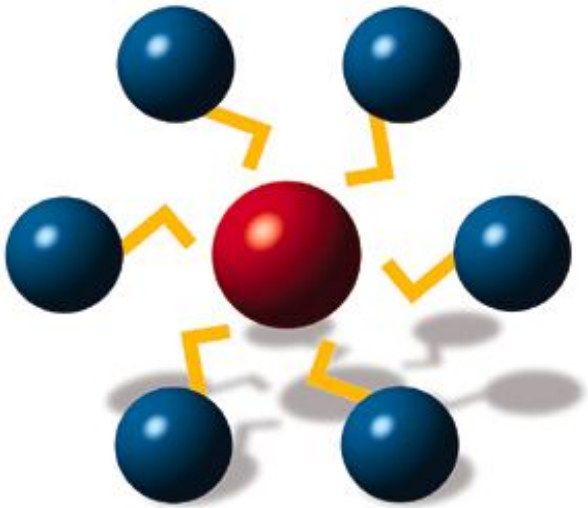
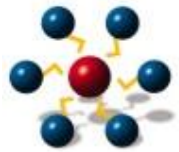
Vibrationer

Matti Hotokka

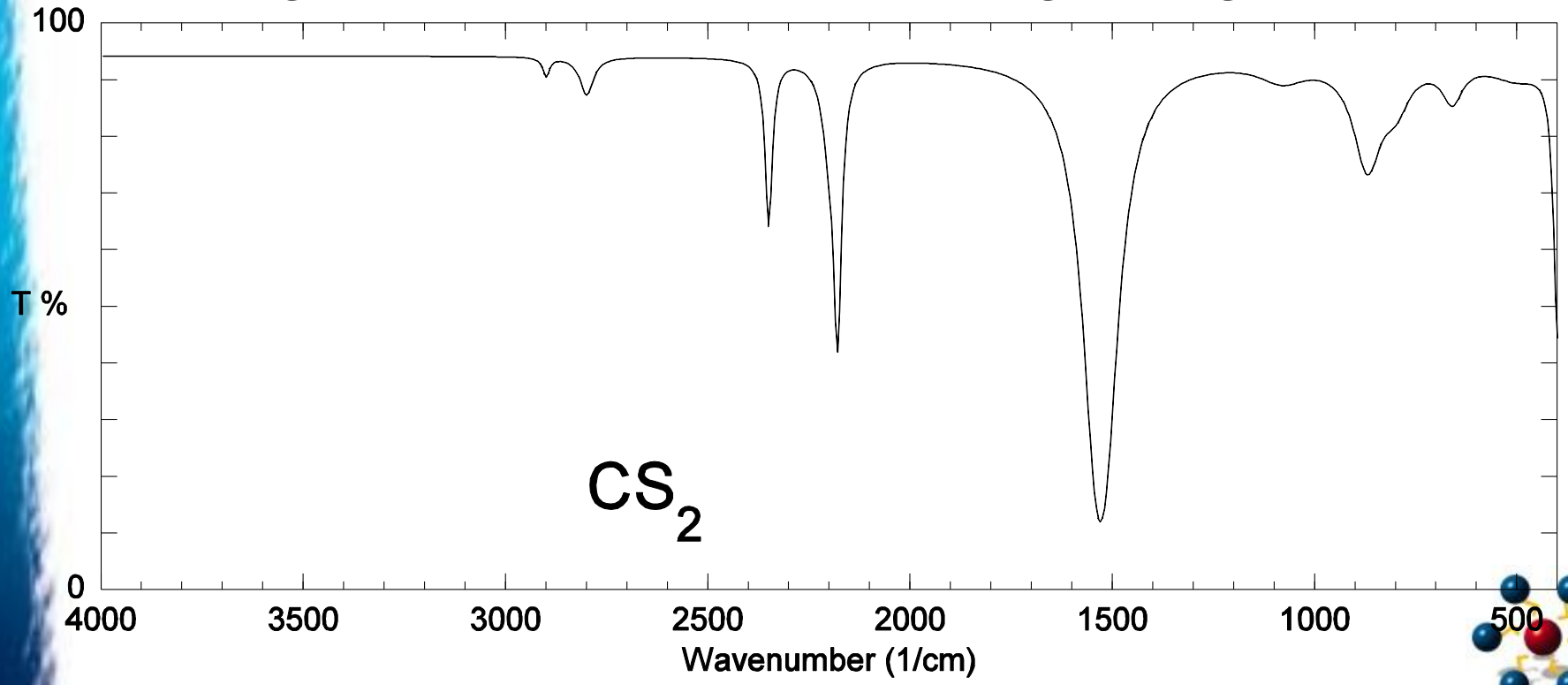




Identifiera ämnet

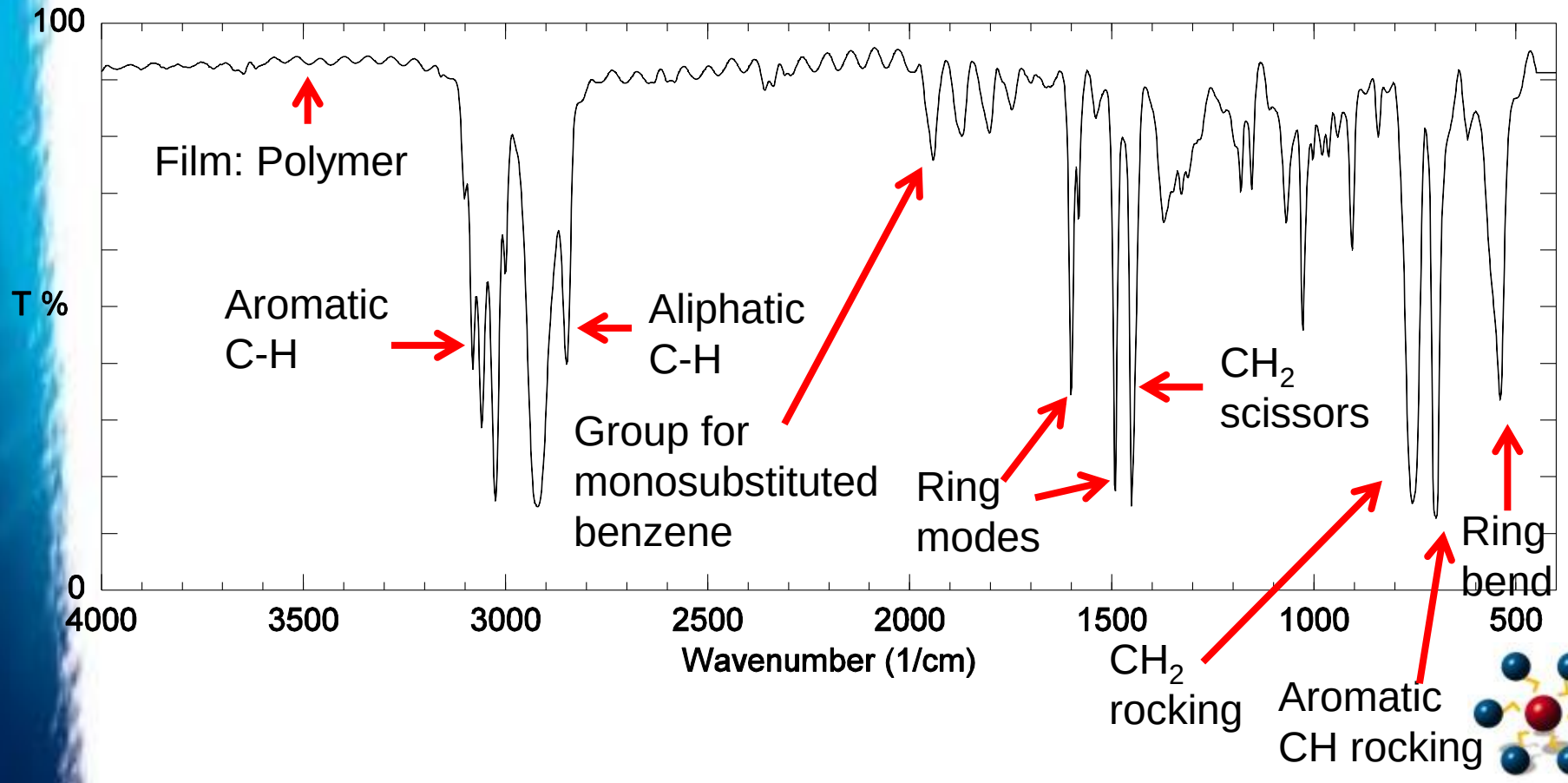
⇨ Det här har jag sett tidigare.

- ➢ Jag vet vad det här är för någonting

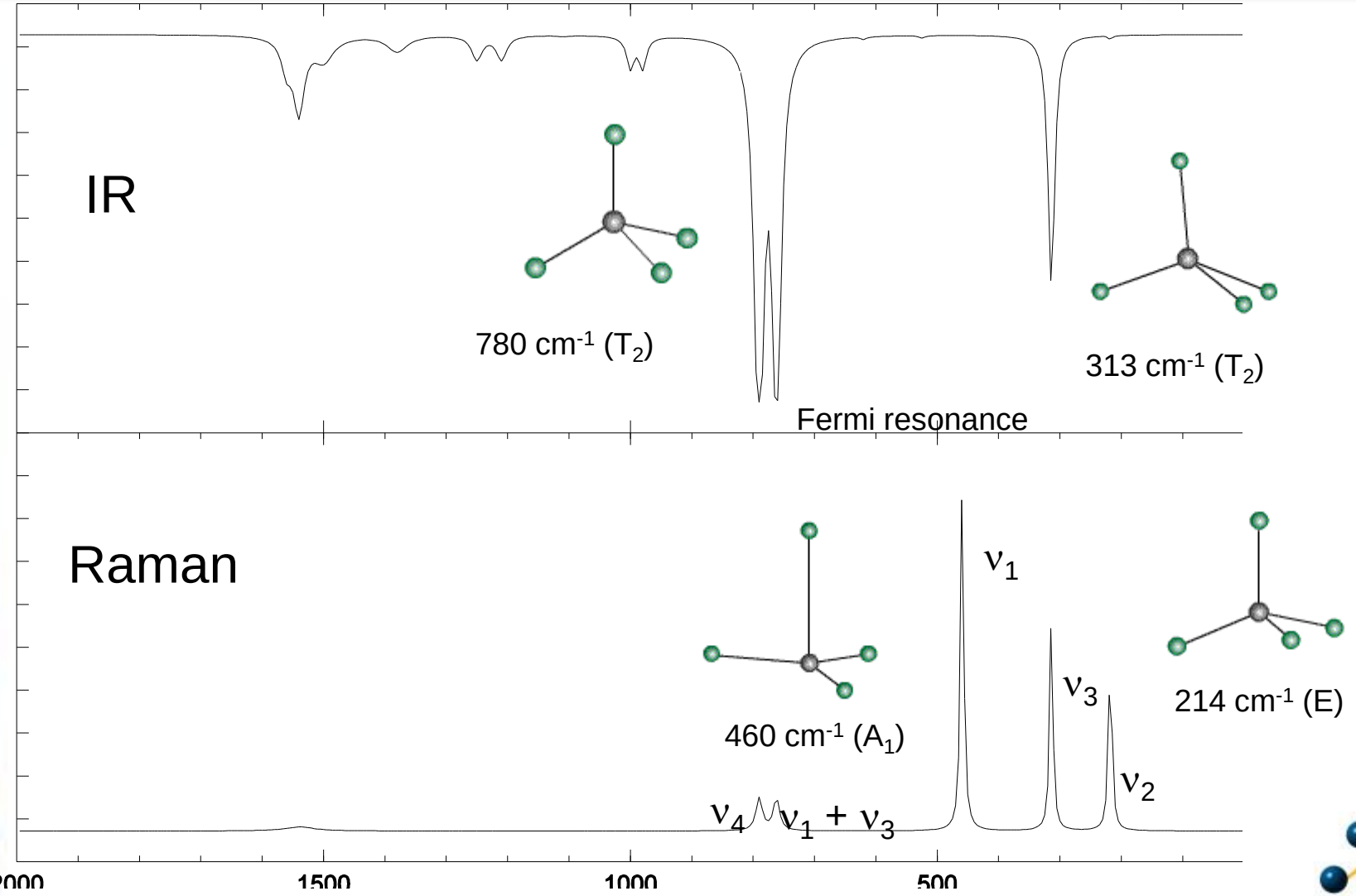


Identifiera ämnet

⇨Låt oss kolla spektralbanden



Identifiera vibrationerna

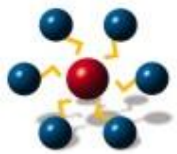


B. Schrader, Raman/Infrared Atlas of Organic Compounds, VCH, 1989.

Symmetri

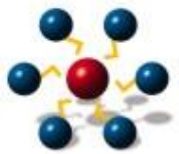
⇨Varje molekyl hör till en punktgrupp

- I varje punktgrupp finns en väl definierad uppsättning symmetrityper
- Varje vibration hör till någon av molekylens symmetrityper
- Vibrationernas symmetrier kan bestämmas
- Urvalsreglerna följer från symmetrityperna



Urvalsregler

- ⇨Teoretiskt från symmetrin
- ⇨Tumregel
  - IR: Starkt band om dipolmomentet oscillerar i takt med vibrationen
  - Raman: Starkt band om polariserbarheten oscillerar i takt med vibrationen



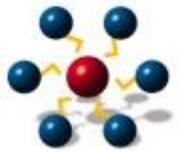
Urvalsregler

Example: Carbon dioxide

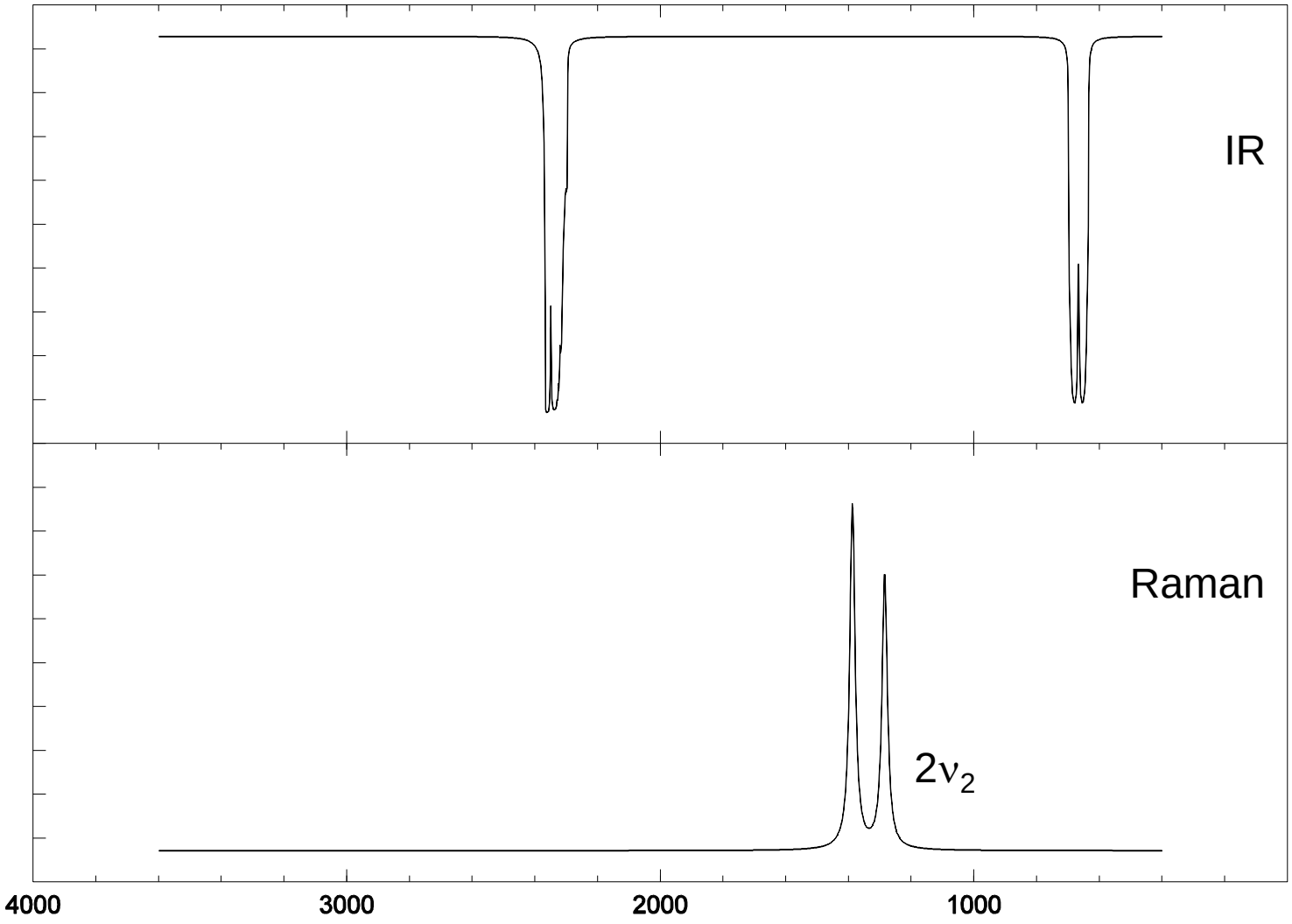
Σ_g^+
1340 cm^{-1}
IR inaktiv
Raman aktiv

Σ_u^+
2349 cm^{-1}
IR aktiv
Raman inaktiv

Π_u
667 cm^{-1}
IR aktiv
Raman inaktiv

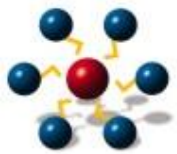


CO_2 spektrum



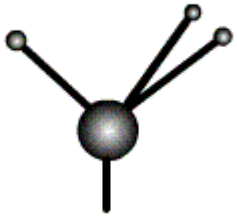
Gruppvibrationer

- ⇨Teoretiskt
  - ➢alla vibrationer strecker sig över hela molekylen
- ⇨I praktiken
  - ➢Många vibrationer berör endast en funktionell grupp och följer den funktionella gruppens symmetri
  - ➢Funktionella grupper kan identifieras

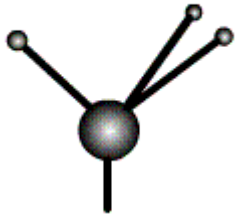


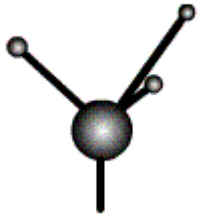
Gruppvibrationer

Exempel: Metylgrupp



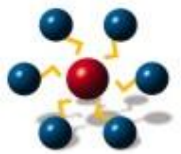
Symmetrisk töjning
2870 cm^{-1}
A_1





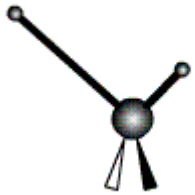
Asymmetrisk töjning
2960 cm^{-1}
E

Alla töjningsvibrationer är tillåtna både i IR och Raman i denna punktgrupp.



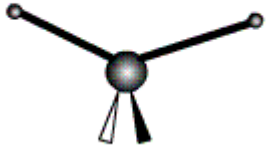
Gruppvibrationer

Exempel: Metylenegrupp



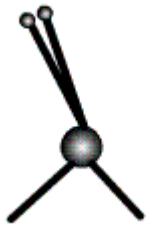
Asymmetric stretch (as)
2925 cm^{-1}

Symmetric stretch (as)
2850 cm^{-1}



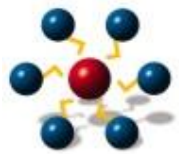
Bending (ρ)
Scissors
1465 cm^{-1}

Rocking (ρ_r)
720 cm^{-1}



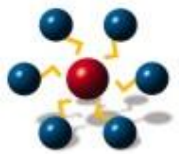
Wagging (ρ_w)
1470 cm^{-1}

Twisting (ρ_w)
1250 cm^{-1}

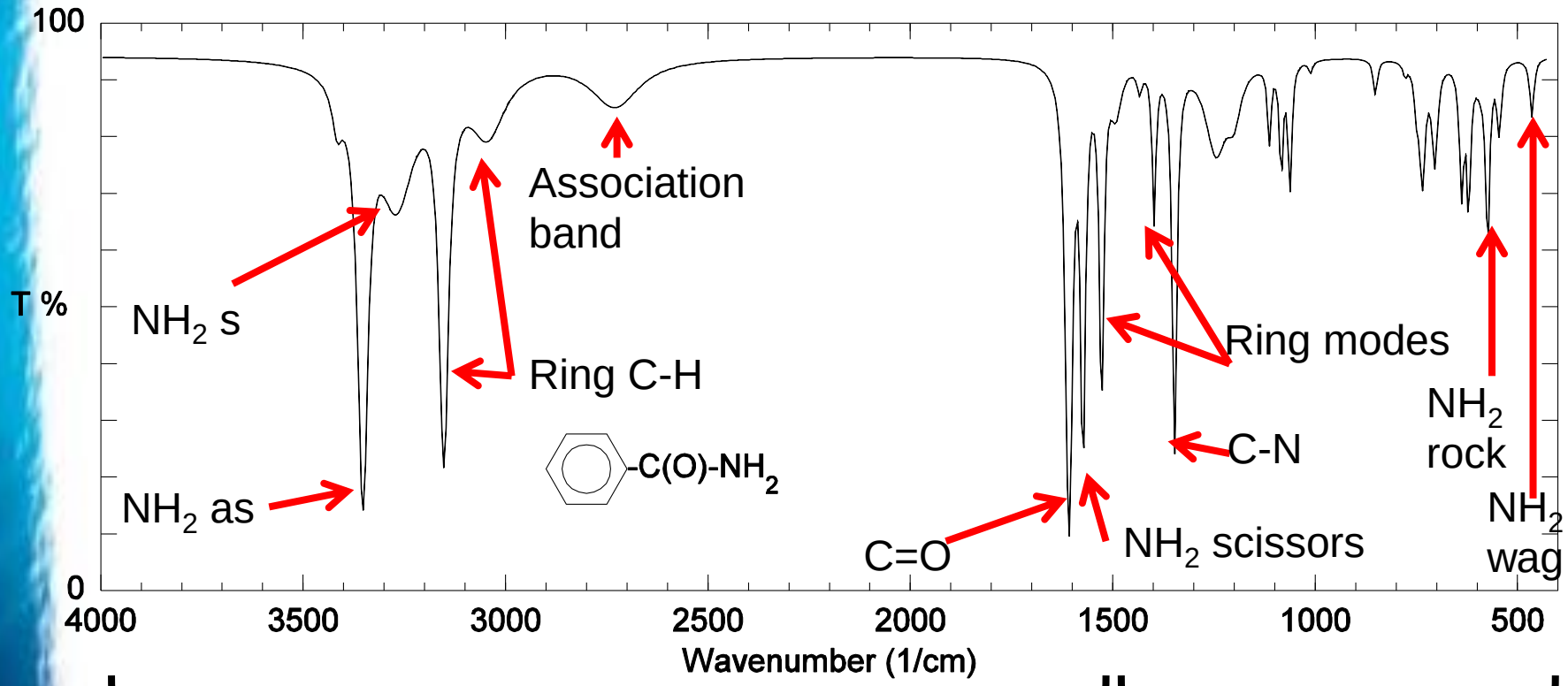


Vad syns i spektret?

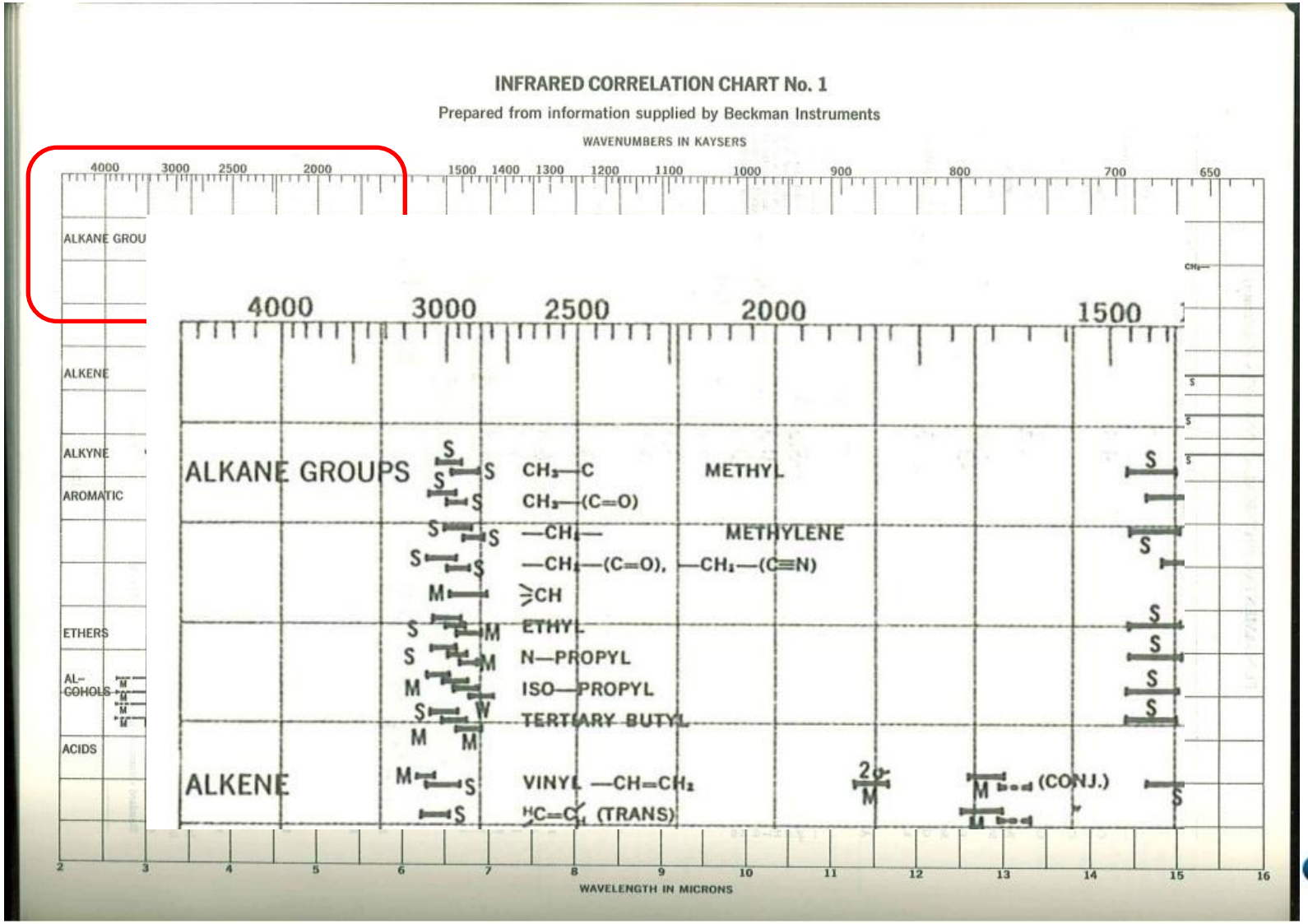
- ⇨De starkaste banden
  - ➢Tillåtna fundamentala övergångar
- ⇨Medelstarka och svaga band
  - ➢Förbjudna fundamentala
  - ➢Tillåtna övertoner och kombinationsband
- ⇨Gruppvibrationer 4000 – 1500 cm^{-1}
- ⇨Fingeravtrycksområdet under 1300 cm^{-1}



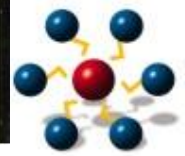
Vad syns i spektret?



Korrelationstabeller

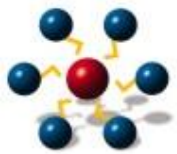


CRC Handbook



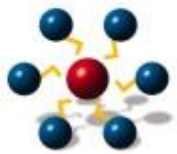
Band som kan lätt identifieras

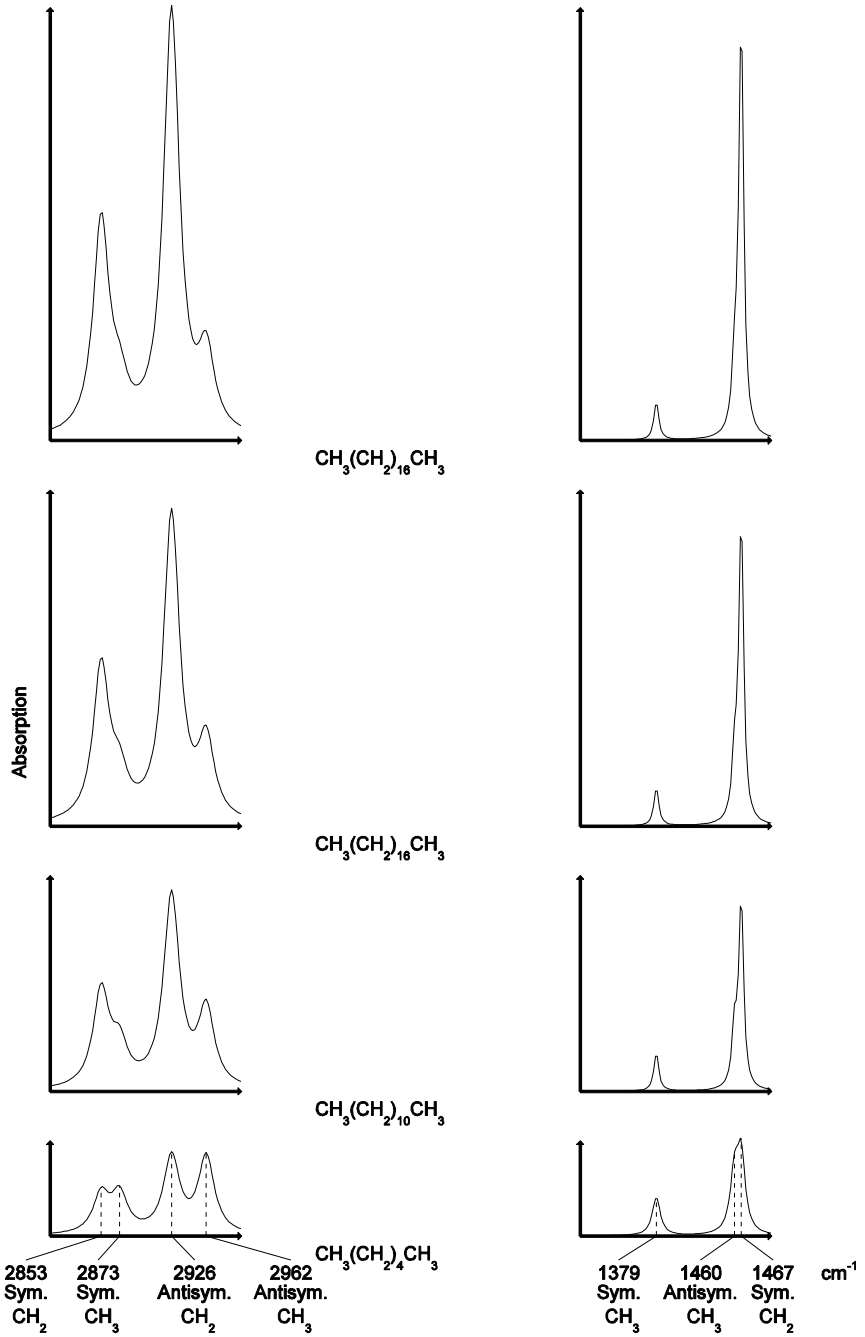
Bandposition [cm-1]	Tillordning
3500-3200	O-H or N-H stretch
3200-2800	C-H stretch
2250-2000	C≡C or N≡C stretch
1800-1600	C=O stretch
<1000	C=C stretch, phenyl ring



Alkaner, C-H moder

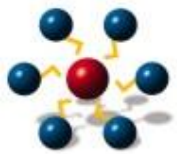
Vibration	CH_3	CH_2
Asym stretch	2970-2950	2935-2915
Sym stretch	2880-2860	2865-2845
CH_3 As bend	1470-1450	
CH_3 Sym bend	1385-1365	
CH_2 Scissors		1465-1445
CH_2 Rock		730-710



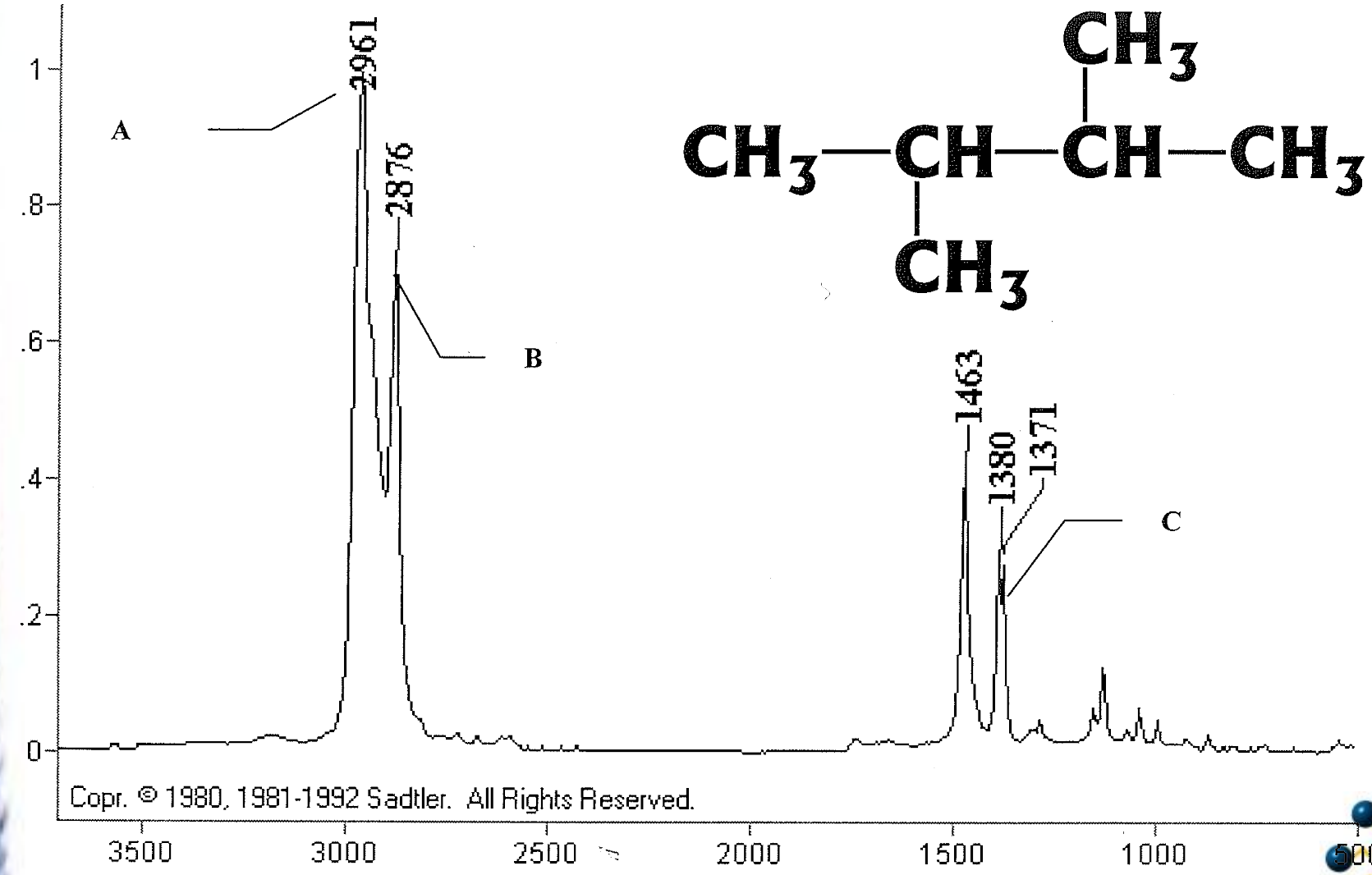

Absorption
$CH_3(CH_2)_{16}CH_3$
$CH_3(CH_2)_{16}CH_3$
$CH_3(CH_2)_{10}CH_3$
$CH_3(CH_2)_4CH_3$
2853 Sym. CH_2
2873 Sym. CH_3
2926 Antisym. CH_2
2962 Antisym. CH_3
1379 Sym. CH_3
1460 Antisym. CH_3
1467 Sym. CH_2
cm^{-1}
Stretching vibrations
Bending vibrations

Grenade alkaner

Methine C-H stretch	~2900 cm^{-1} (w)
Methine C-H bend	1350 (w)
Split umbrella mode	
- Isopropyl and gem dimethyl	1385-1365 (2 bands, intensity ratio 1:1)
- Isobutyl and t-butyl	1395-1365 (2 bands, intensity ratio 1:2)



Grenade alkaner

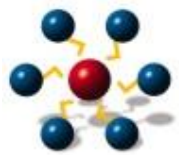


B. Smith, Inrared Spectral Interpretation, CRC 1998.

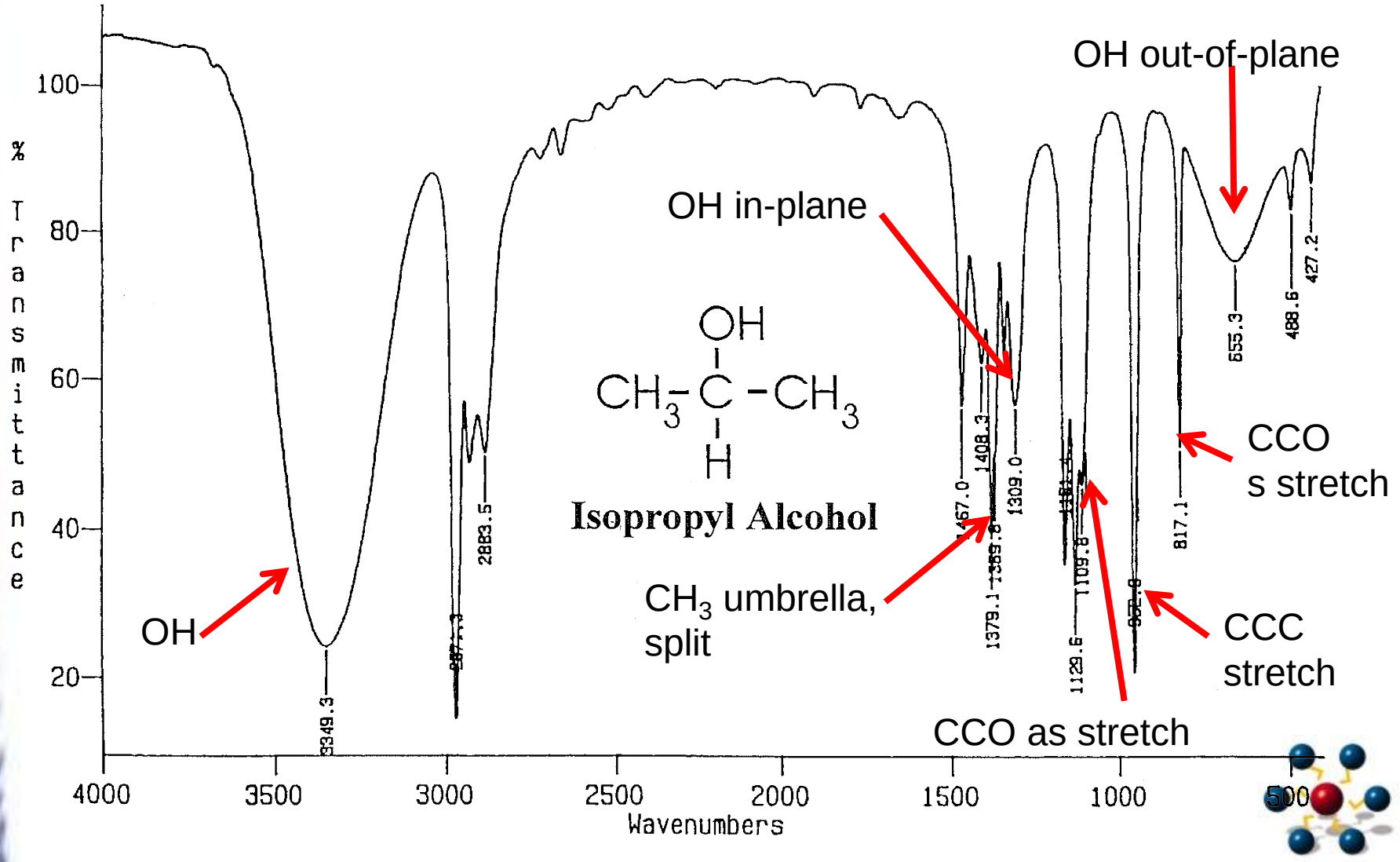
O-H och N-H

- ⇨Vanligtvis vätebundna
  - ➢Alla relaterade band är mycket breda
  - ➢Ifall (exceptionellt) inte vätebundna finns banden vid högre frekvens och är smala

Alcohols	C-O stretch	O-H stretch	O-H bends
All		3350±50	1350±50, 650±50
Primary	1075-1000		
Secondary	1150-1075		
Tertiary	1210-1100		
Phenols	1260-1200		
C-N stretch	1430-1390	NH2 stretch	3370-3170
NH2 scissors	1650-1620	NH2 wagging	750-600

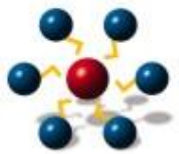


Alkoholspektrum

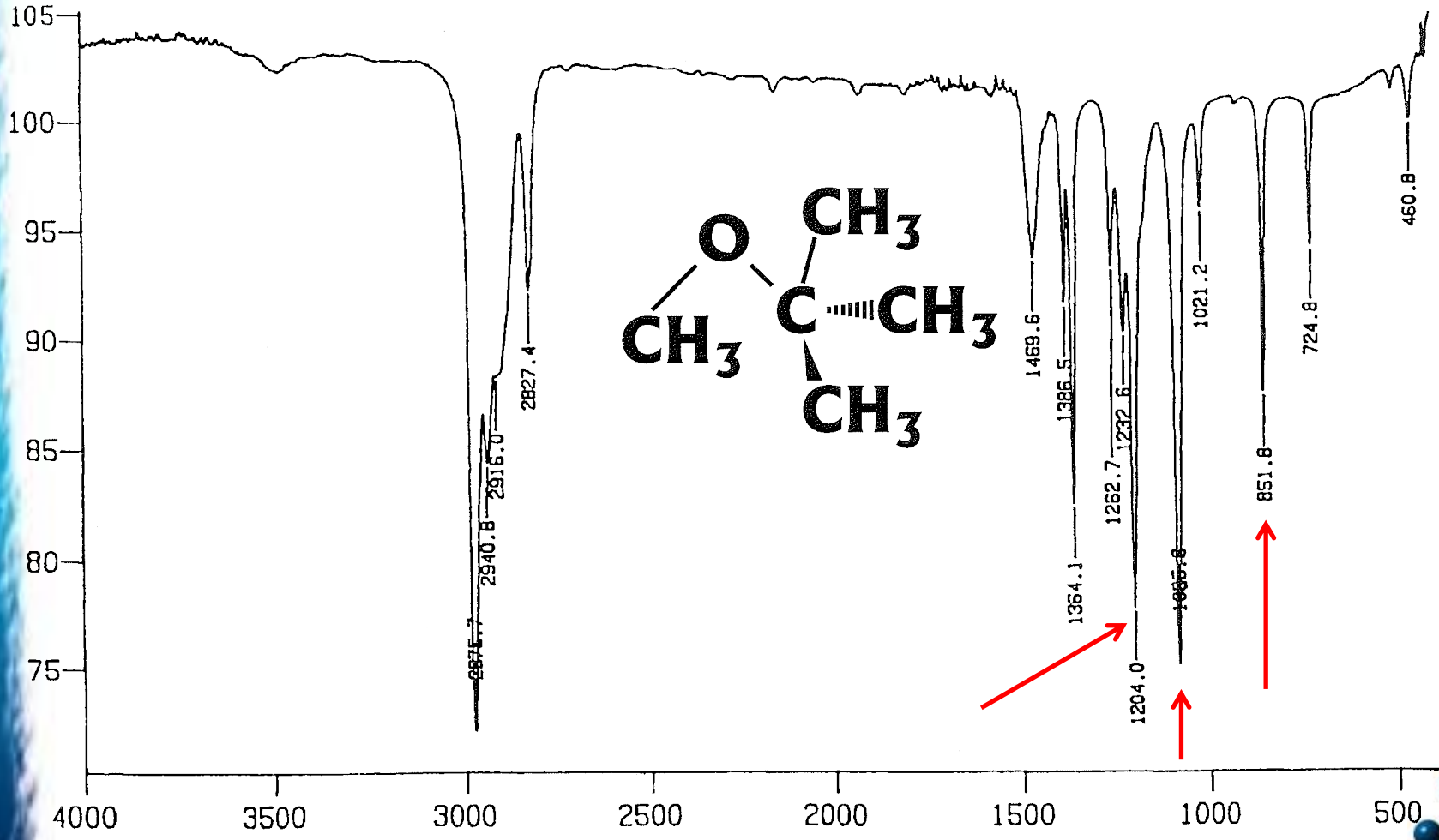


Eter

Ether type	Asymmetric C-O-C	Symmetric C-O-C
Saturated, unbranched	1140-1070 (1 band)	890-820
Saturated, branched	1210-1070 (2 or more bands)	890-820
Alkyl/Aryl (mixed)	1300-1200 and 1050-1010	-
Aryl	1300-1200	-

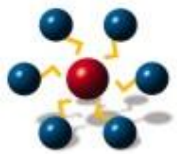


Eter


105
100
95
90
85
80
75
4000
3500
3000
2500
2000
1500
1000
500
2940.8
2916.0
2827.4
1469.6
1386.5
1364.1
1262.7
1232.6
1204.0
1021.2
851.8
724.8
460.8
O
CH3
C
CH3
CH3
CH3

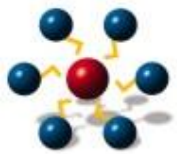
Alkener

Group	C-H stretch	C=C stretch	C-H Out-of-plane
Vinyl	3090-3075	1660-1630	995-984, 915-905
Vinylidine	3090-3075	1660-1630	895-885
Cis	3050-3000	1660-1630	740-640
Trans	3050-3000	1680-1665	970-960
Trisubstituted	3050-3000	1680-1665	840-790
Tetrasubsituted		1680-1665	

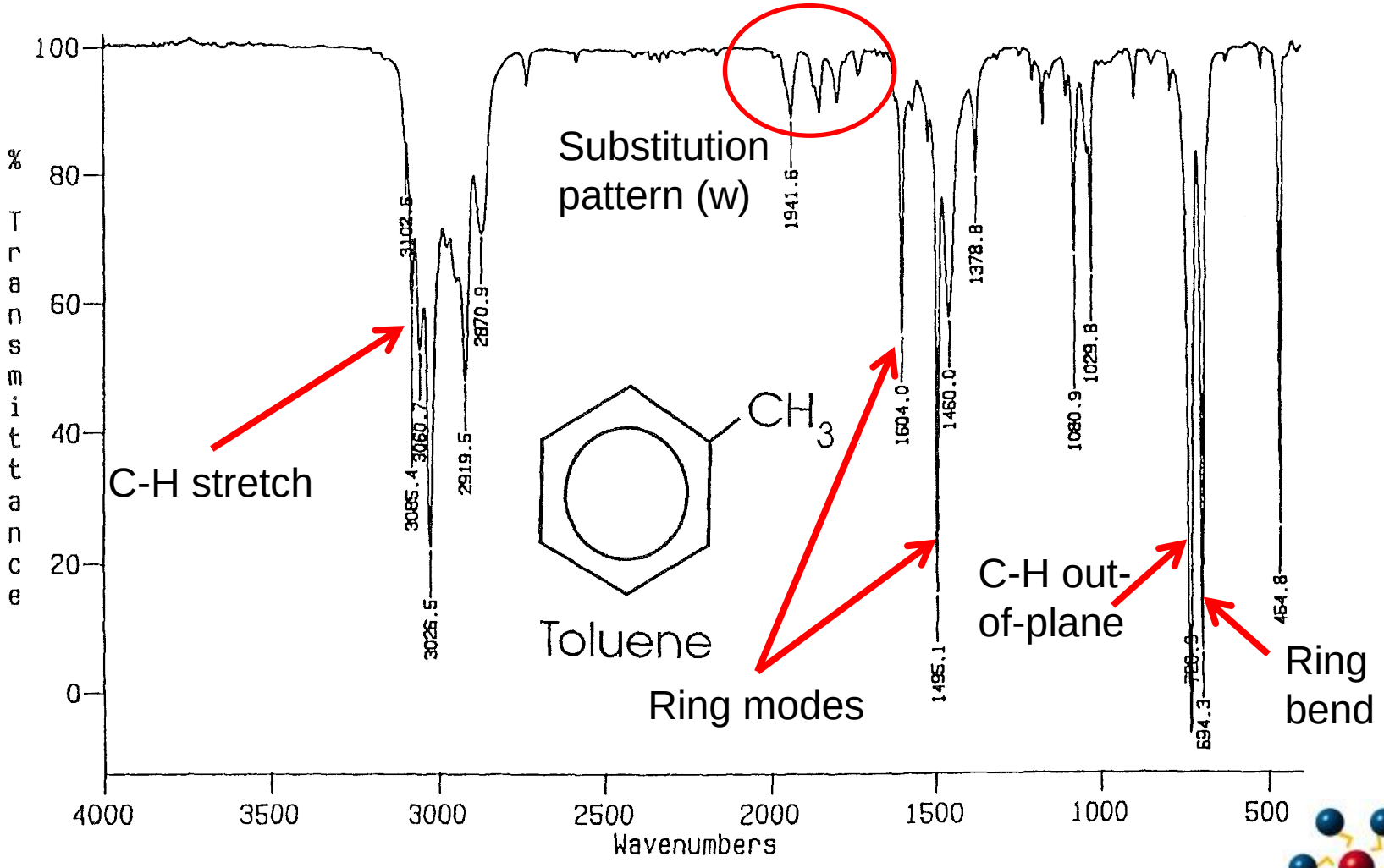


Fenylringar

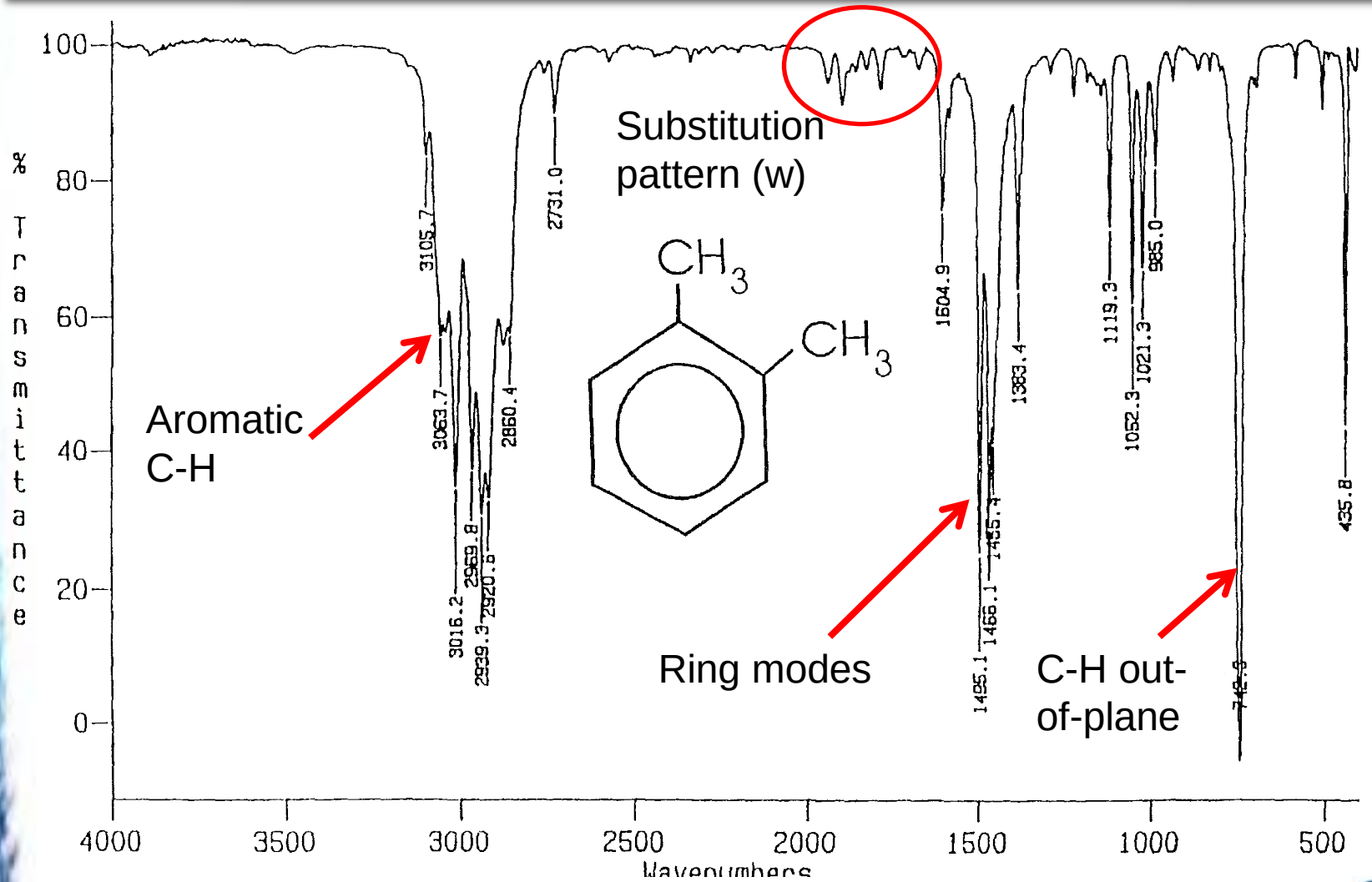
Substitution	C-H out-of-plane	Ring bend 700-680
Mono	770-710	Yes
Ortho	810-750	No
Meta	770-735	Yes
Para	860-790	No



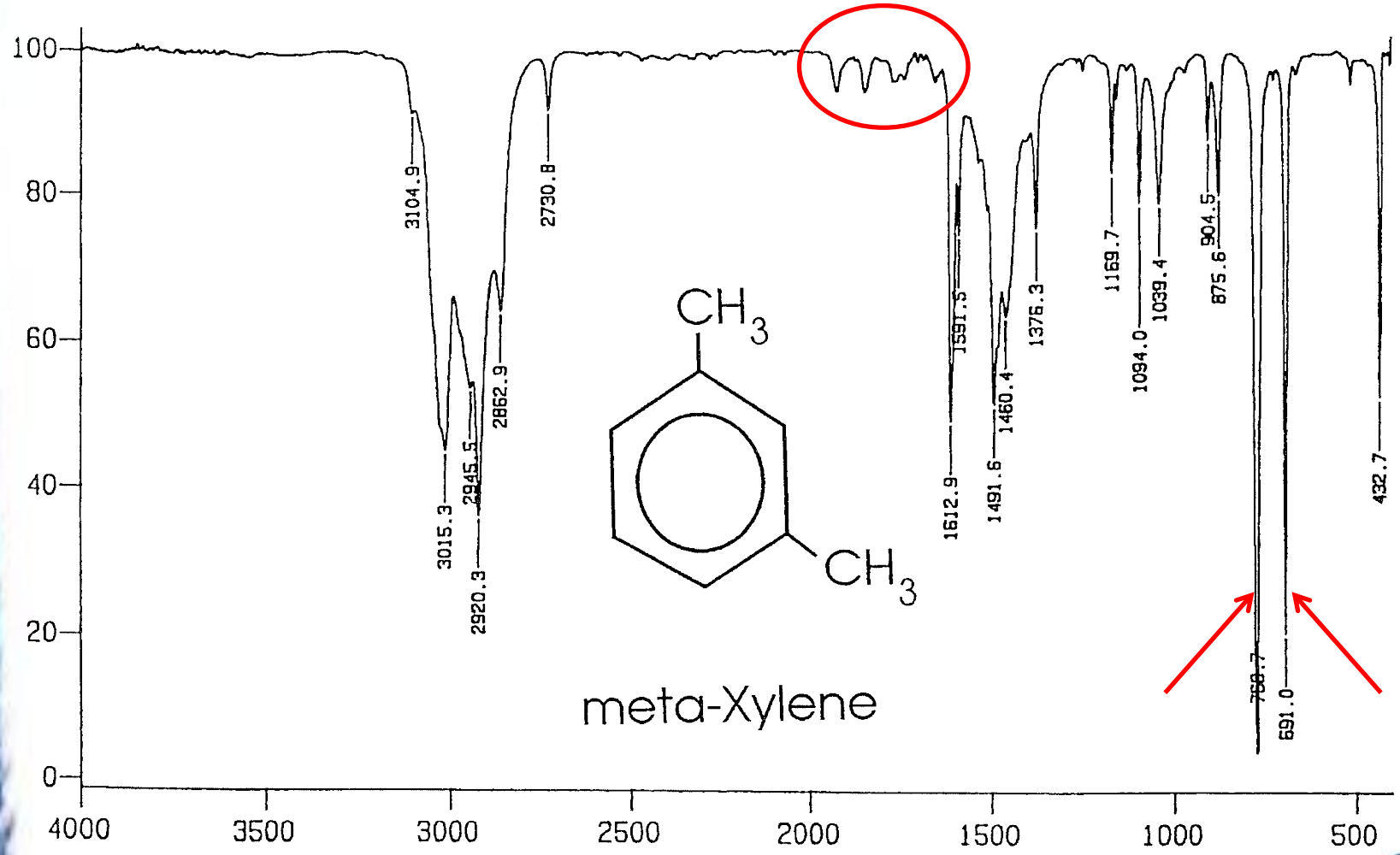
Subsituerad bensen



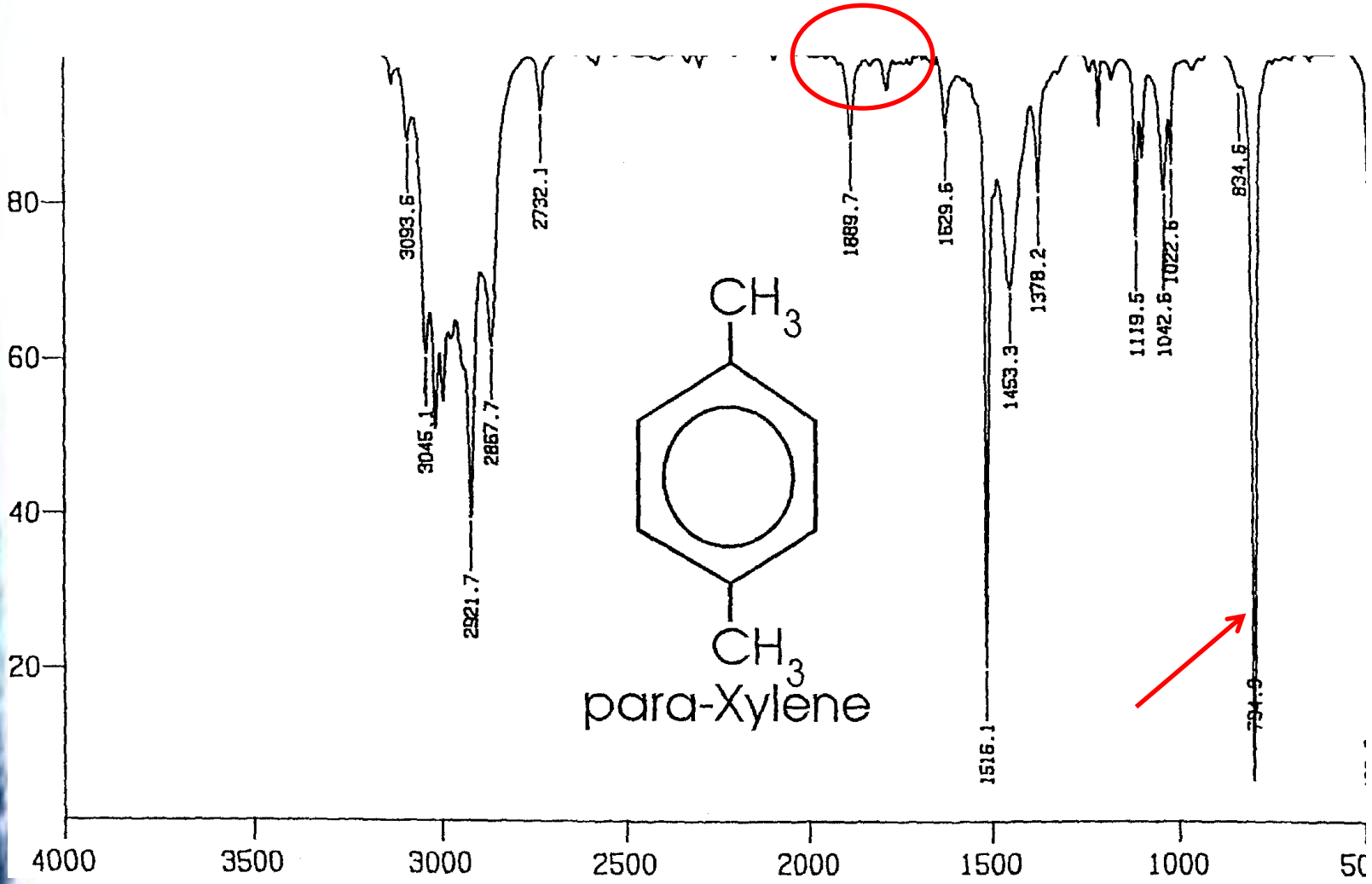
Substituerad bensenring



Substituerad bensenring

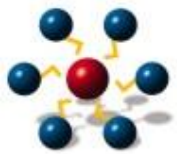


Substituerad bensenring



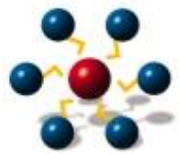
Substitutionsmönster

Substitution Pattern	C-H out-of-plane	Ring bend 690±10 cm^{-1}
Mono	770-710	Yes
Ortho	810-750	No
Meta	770-735	Yes
Para	860-790	No

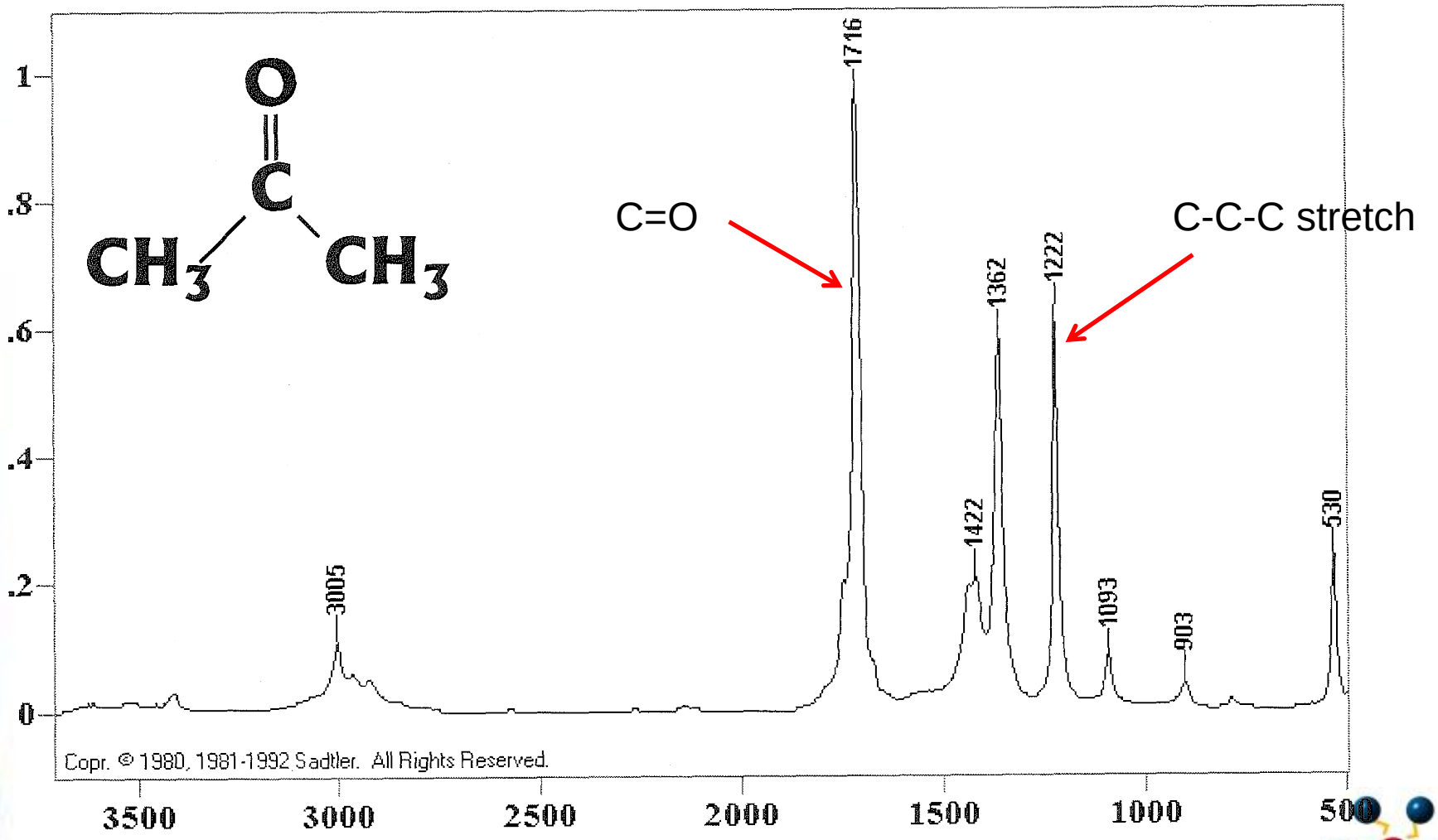


Karboxylgrupp

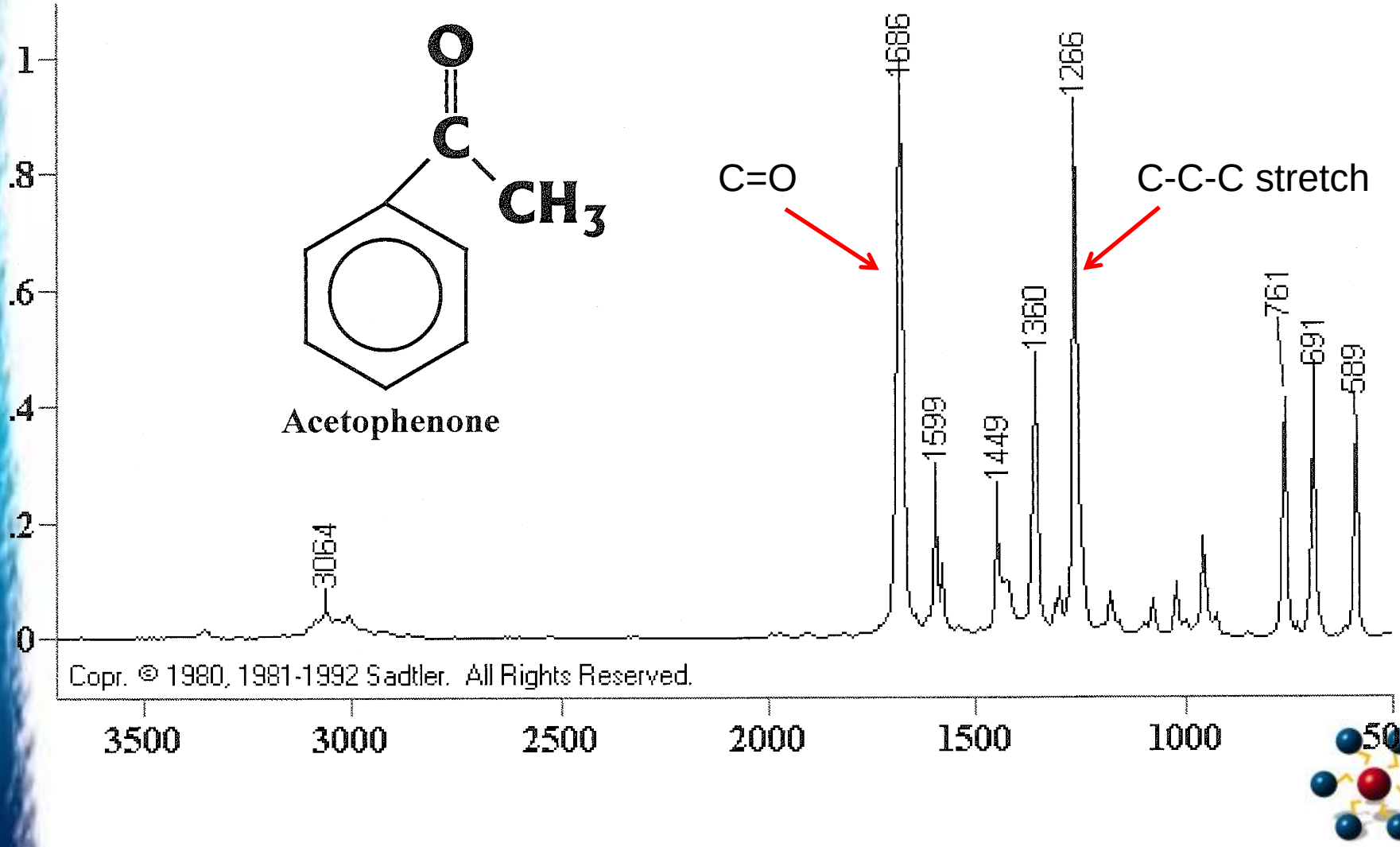
Vibration	
Saturated C=O stretch	1725-1705
Aromatic C=O stretch	1700-1640



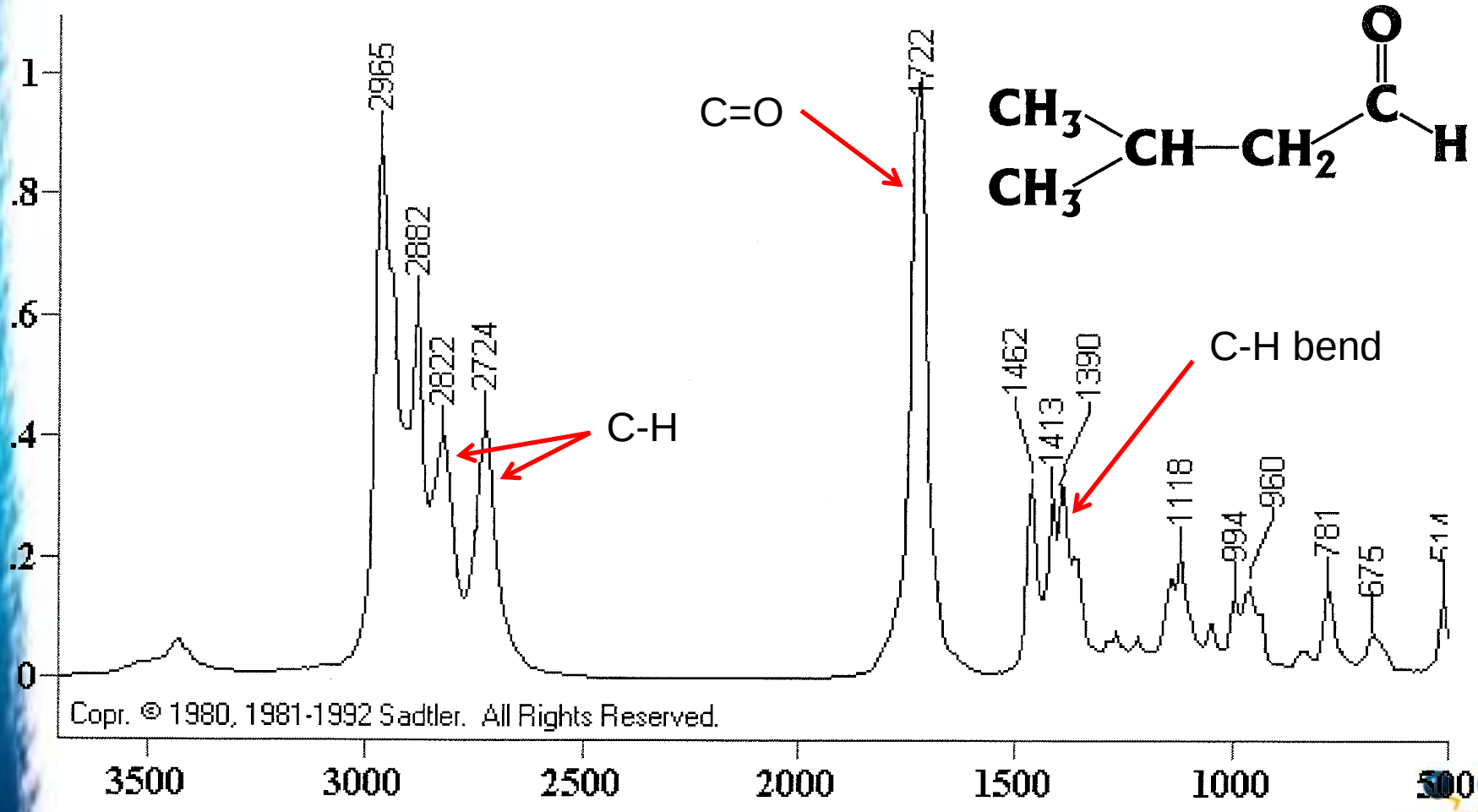
Mättad keton



Aromatisk keton



Aldehyd


2965
2882
2822
2724
1722
1462
1413
1390
1118
994
960
781
675
C=O
C-H
C-H bend
1
.8
.6
.4
.2
0
3500
3000
2500
2000
1500
1000
500
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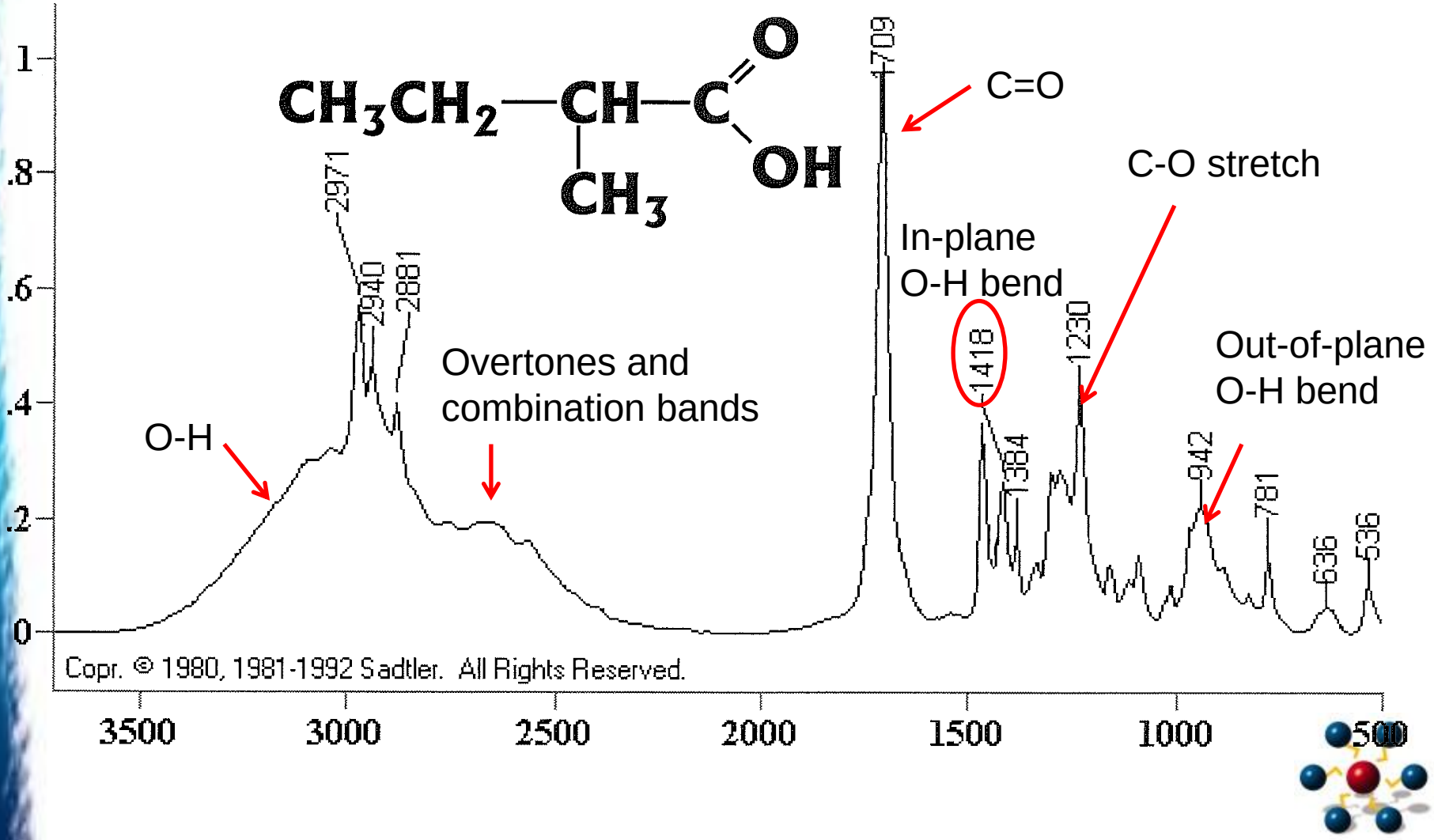
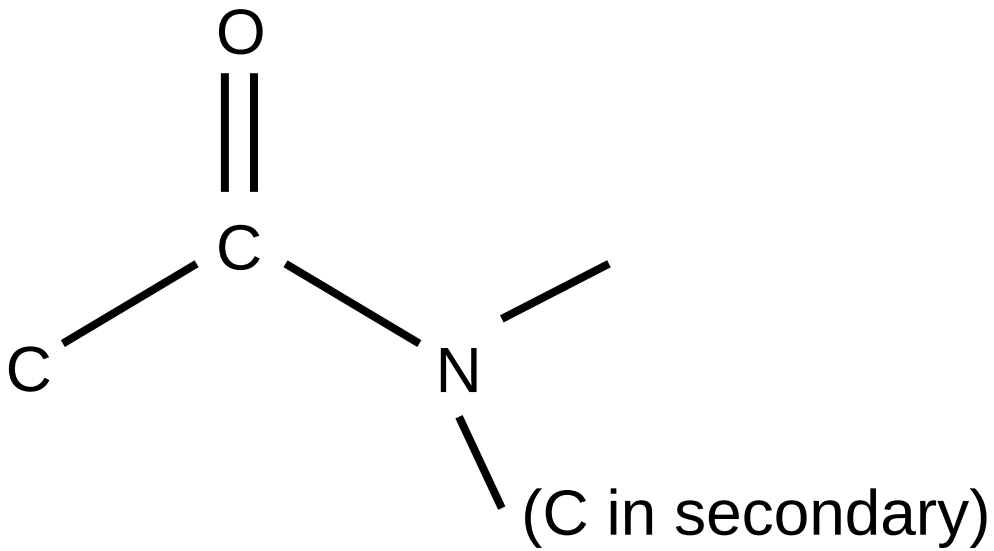
Karboxylsyra

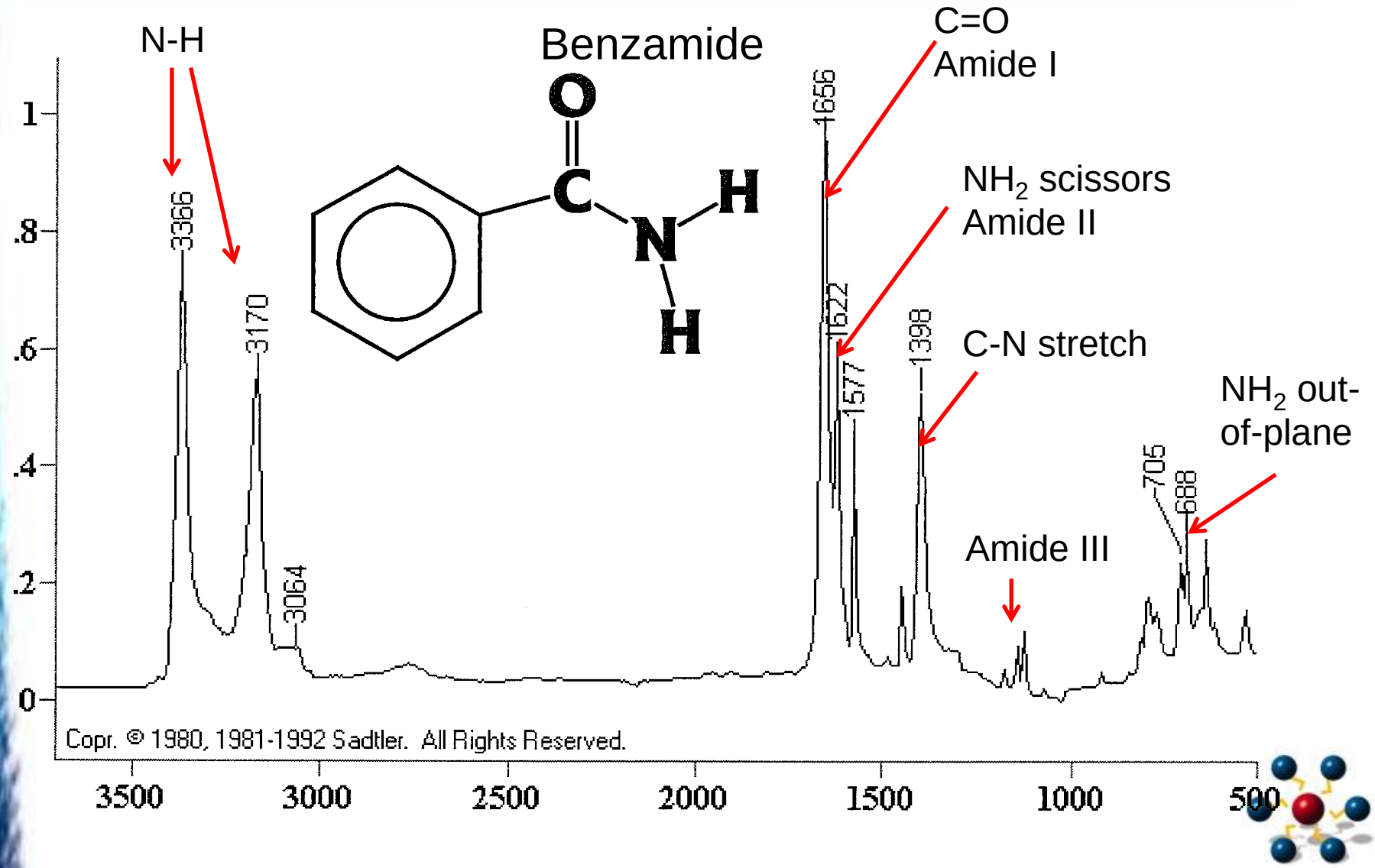


Amider

Amide I band: C=O stretch at 1690-1630
Amide II band: N-H bend (primary) 1650-1590
Amide II band: N-H bend (secondary) 1560-1500



Primär amid


N-H
Benzamide
C=O
Amide I
NH_2 scissors
Amide II
C-N stretch
NH_2 out-of-plane
Amide III
3366
3170
3064
1656
1622
1577
1398
705
688
1
.8
.6
.4
.2
0
3500
3000
2500
2000
1500
1000
500
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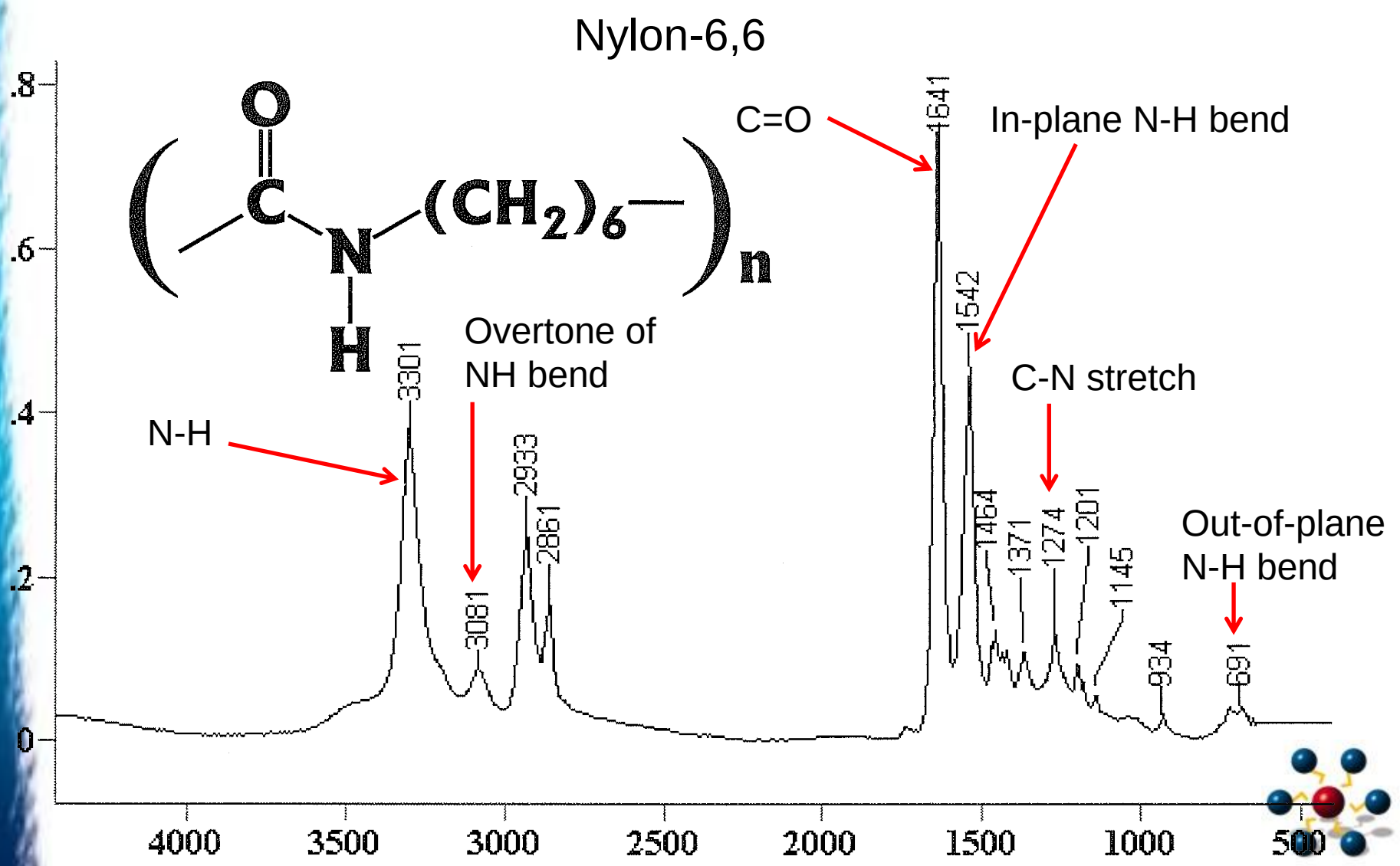
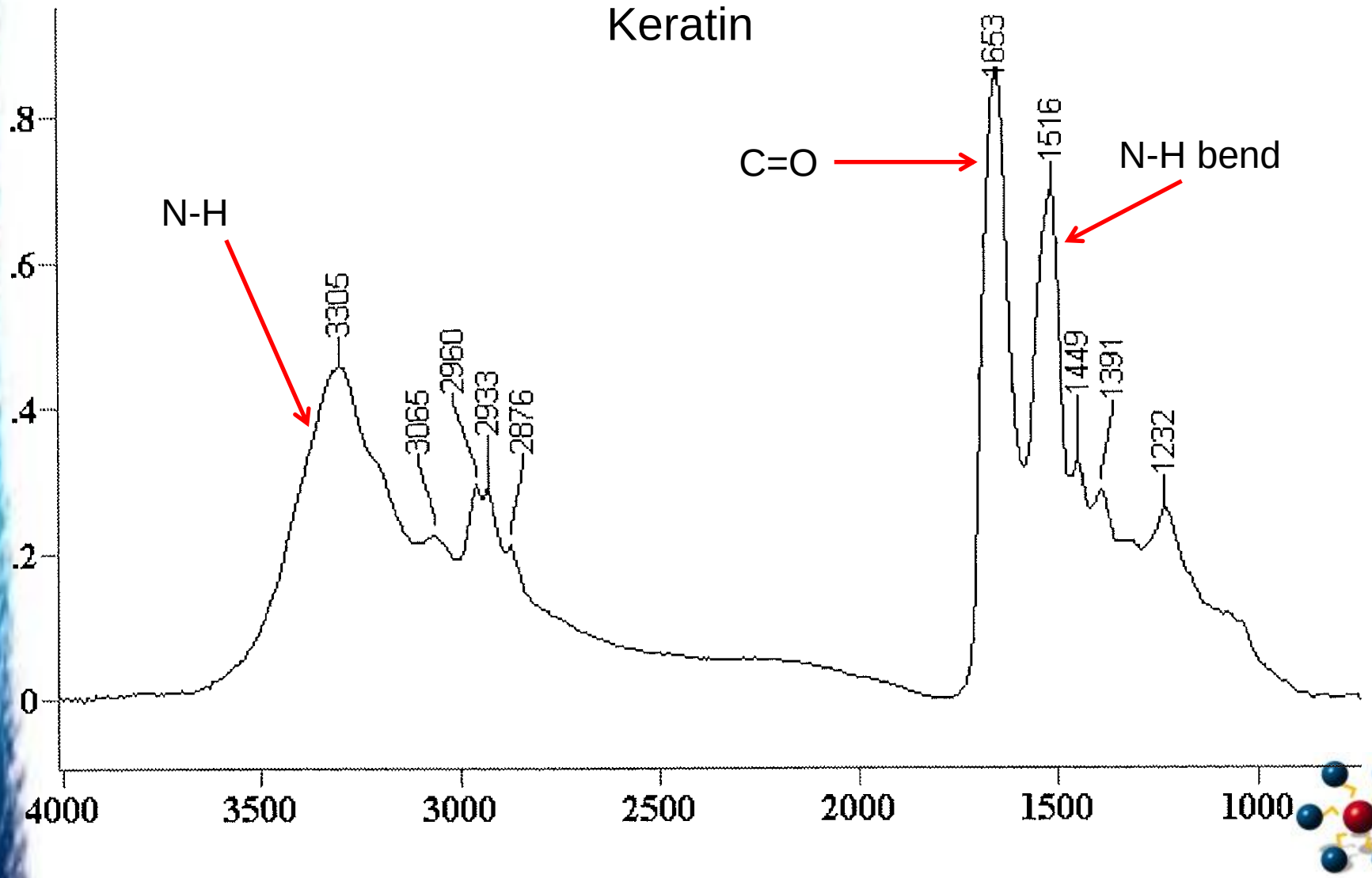
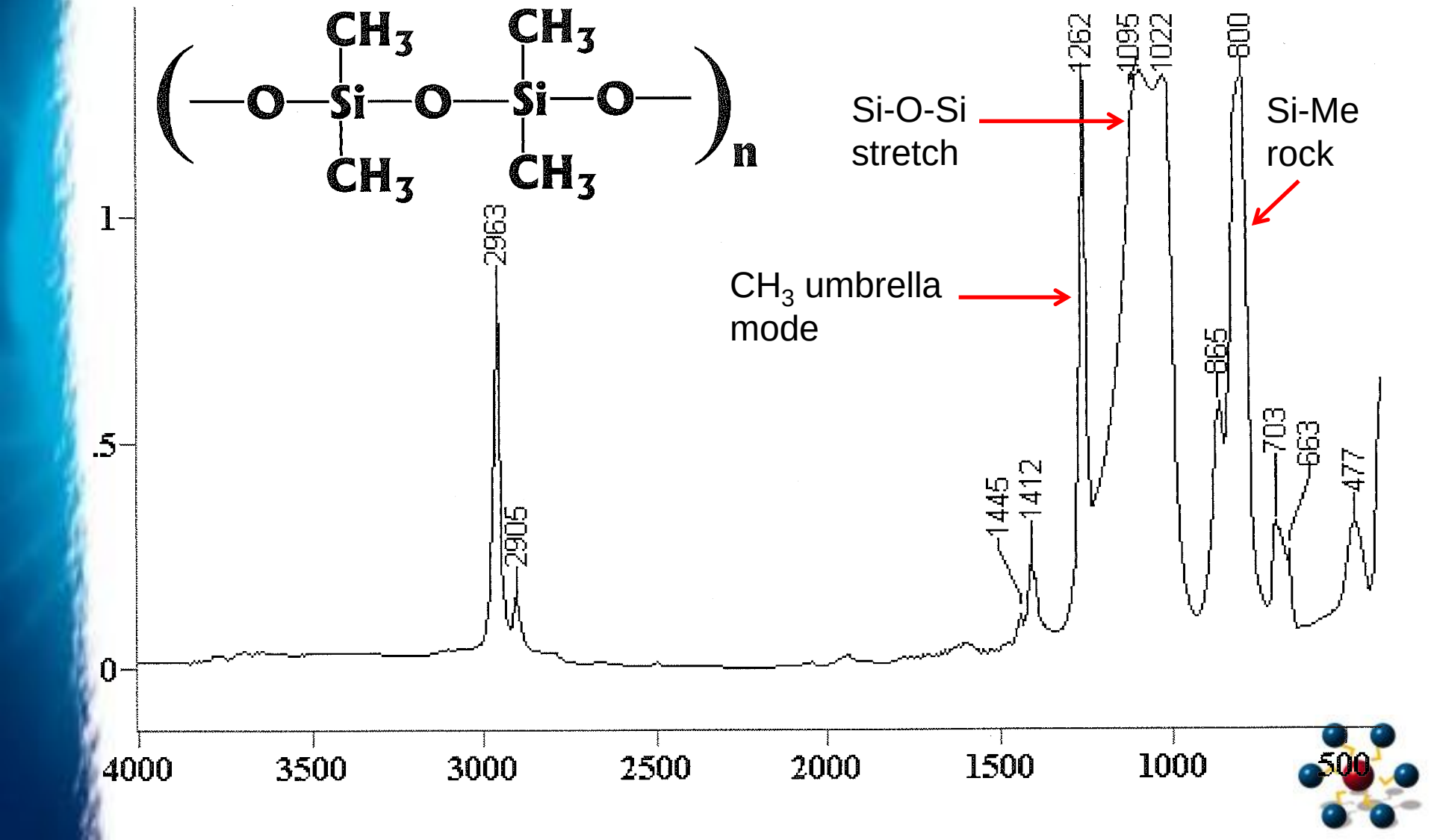
Sekundär amid



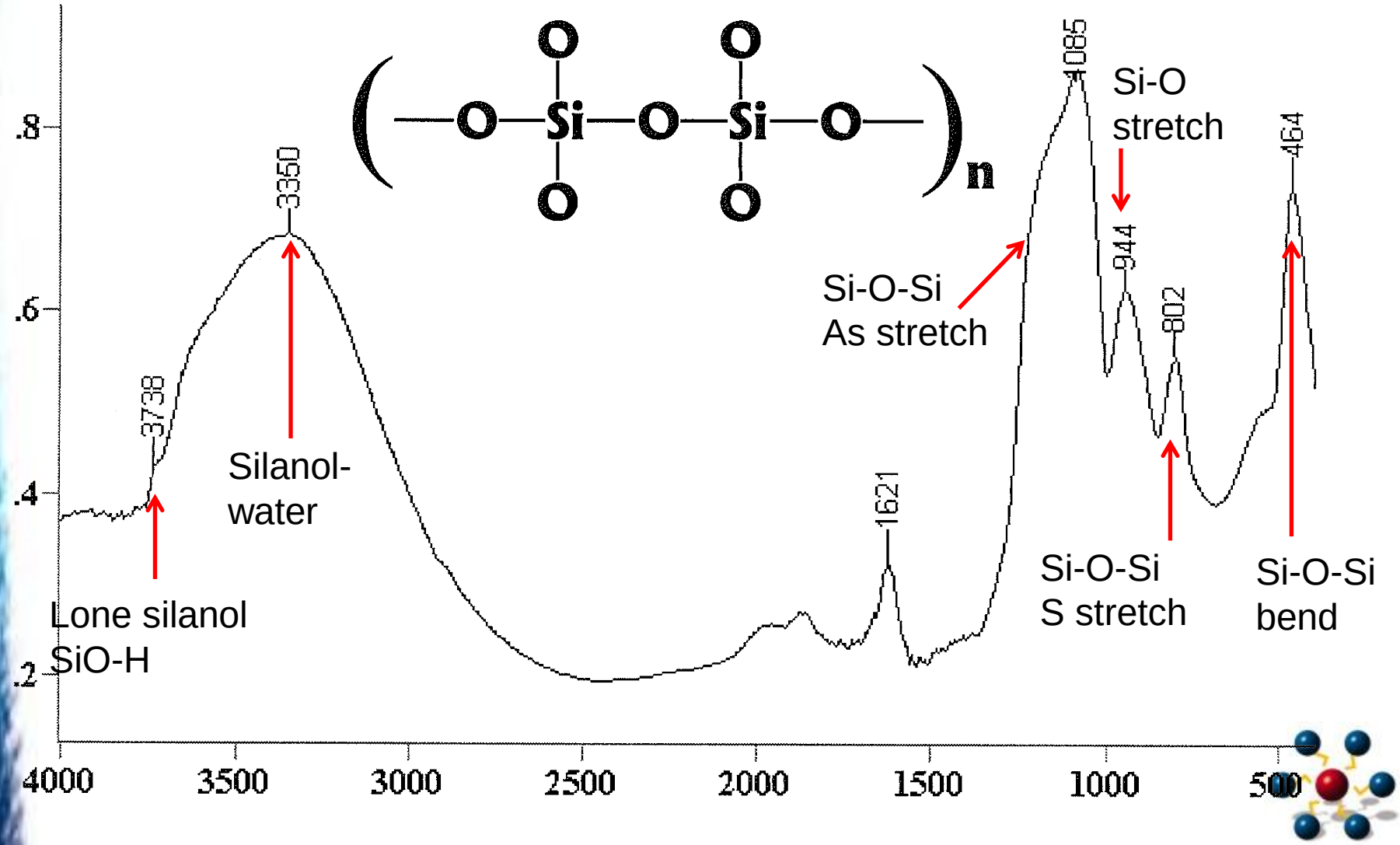
Protein


Keratin
N-H
C=O
N-H bend
3305
3065
2960
2933
2876
1653
1516
1449
1391
1232
.8
.6
.4
.2
0
4000
3500
3000
2500
2000
1500
1000

Silikon


Si-O-Si stretch
Si-Me rock
CH_3 umbrella mode
1262
1095
1022
800
2963
2905
1445
1412
865
703
663
477
1
.5
0
4000
3500
3000
2500
2000
1500
1000
500

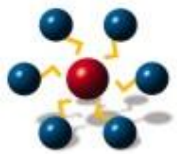
Kiseloxid


.8
.6
.4
.2
3738
3350
1621
1085
944
802
464
4000
3500
3000
2500
2000
1500
1000
500
Lone silanol
SiO-H
Silanol-
water
Si-O-Si
As stretch
Si-O
stretch
Si-O-Si
S stretch
Si-O-Si
bend

Ramanspektrum

⇨Vibrationsrörelserna är desamma

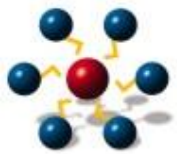
- Urvalsreglerna och då intensiteterna är annorlunda
- Använd korrelationstabeller för Raman
- Övertoner och kombinationsband oftas mycket svaga
  - Enkla spektra



Urvalsreglerna

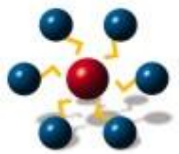
⇨Raman: polariserbarhet bestämmer

- Molekyler med lätt polariserat elektronhölje har ett stort spridningstvärsnitt
- Koltetraklorid, fenylring osv
- Vatten sprider dåligt och kan alltså användas som lösningsmedel



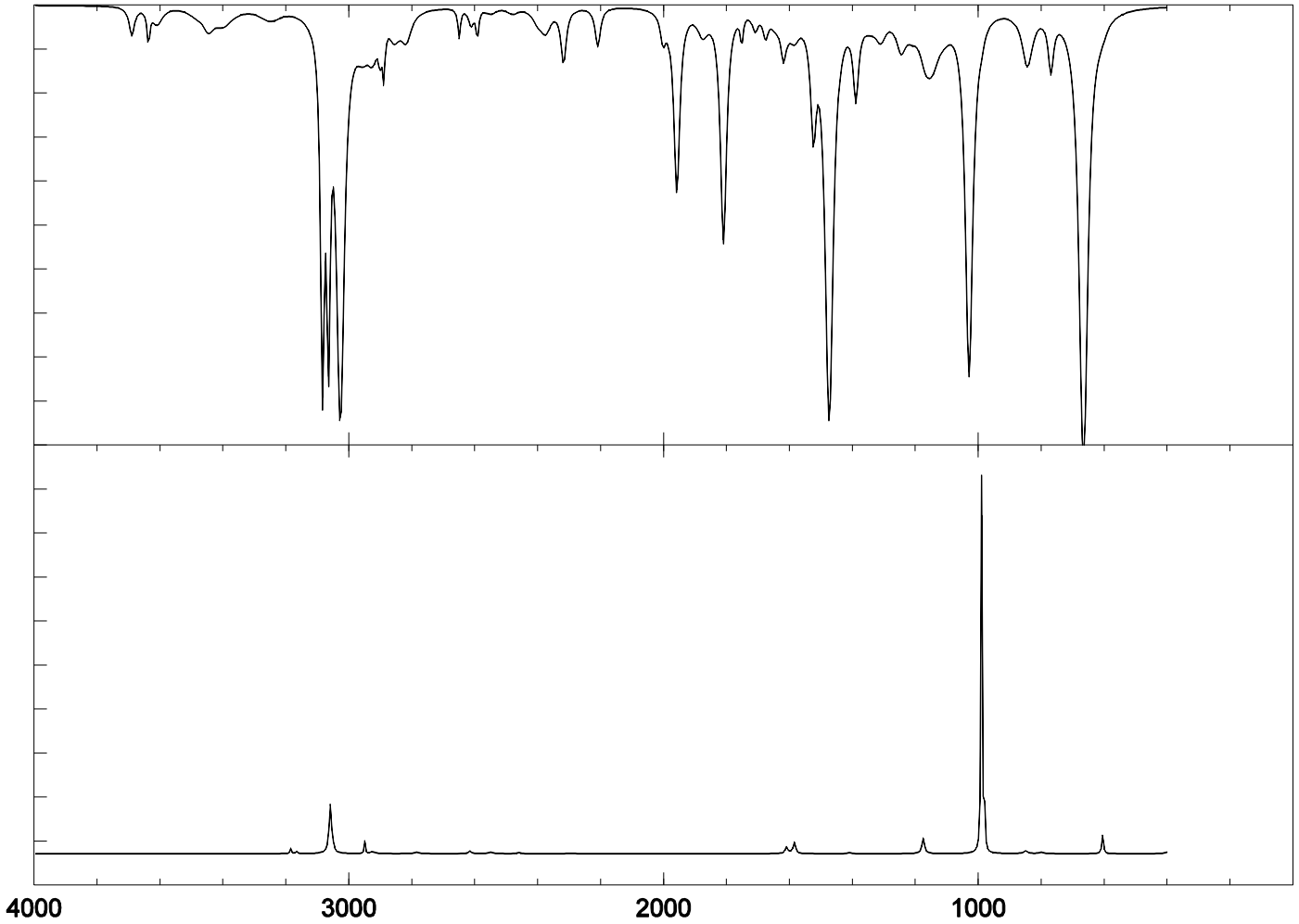
Samma vibrationsrörelser men ...

Molecule	Band position cm^{-1}	Intensity Raman	IR
Naphtalene	1630 - 1595	w	m
	1580 - 1570	vs	vw
	1510 - 1500	vw	m
	1390 - 1350	vs	ms
Anthracene	1630 - 1620	ms	ms
	1560 - 1550	vs	s
	1400 - 1390	vs	vw
Fenantrene	1620 - 1600	m	m
	1520 - 1500	m	s
	1460 - 1440	s	m
	1350 - 1300	vs	w



Enkla spektra

Benzene



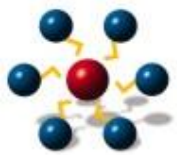
Bensen

$\Gamma_{vib} = 2A_{1g} + A_{2g} + A_{2u} + 2B_{1u} + 2B_{2g} + 2B_{2u} + E_{1g} + 3E_{1u} + 4E_{2g} + 2E_{2u}$

IR active: A_{2u}, E_{1u}
Raman active: A_{1g}, E_{1g}, E_{2g}

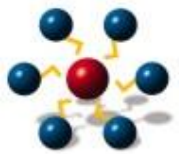
IR		
C-H out-of-plane	671	A_2u
CH stretch	3099	E_{1u}
C—C stretch	1485	E_{1u}
C-H bend	1037	E_{1u}

Raman		
C-H stretch	3062	A1g
C-H stretch	3047	E2g
C-C stretch	1585	E2g
C-H bend	1178	E2g
C-C stretch	992	A1g
C-H out-of-plane	849	E1g
C-C-C bend	605	E2g

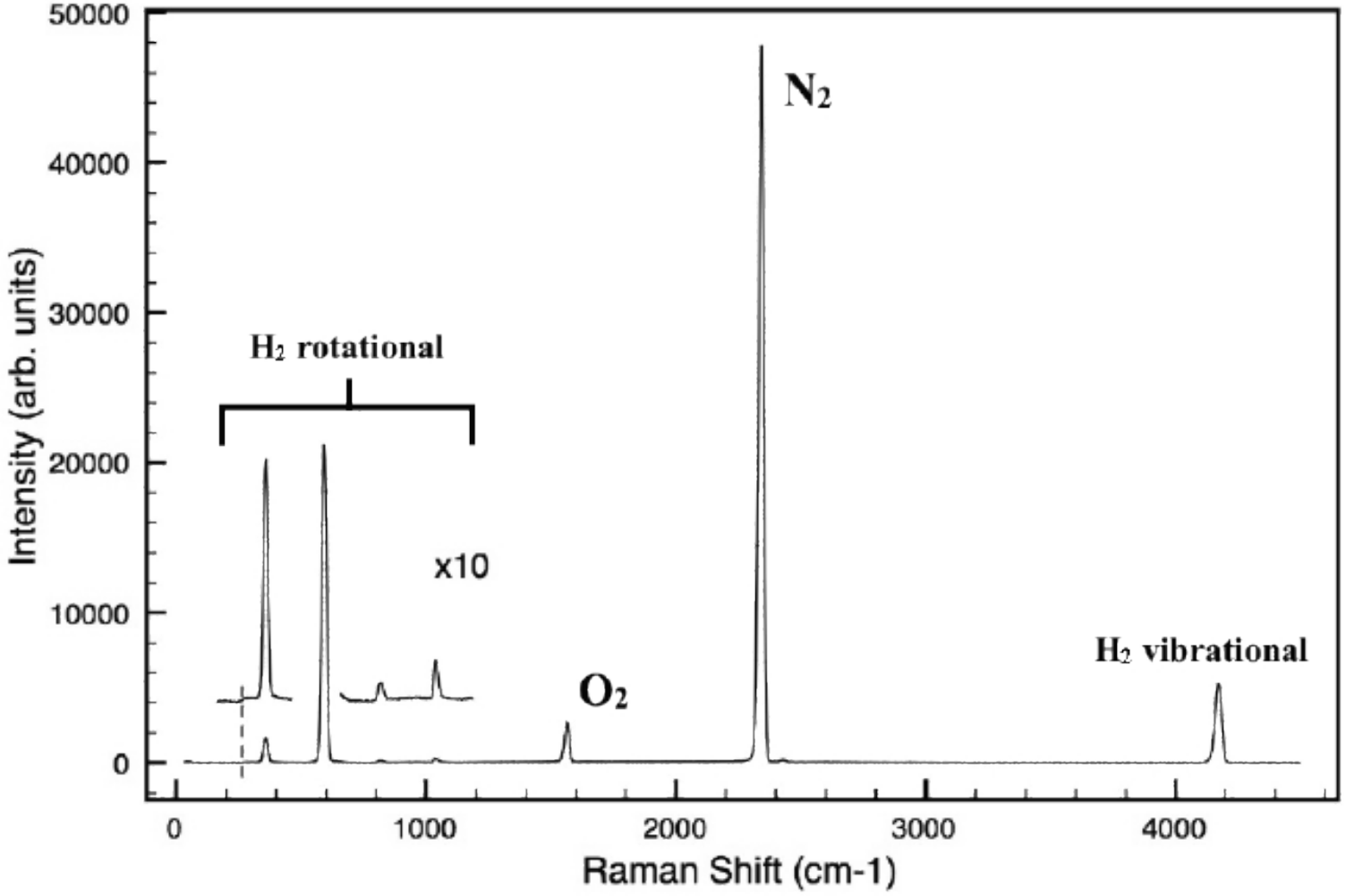


Symmetriska vibrationer

- ⇨Symmetrin bestämmer urvalsreglerna
- ⇨Tumregel
  - ➢Symmetriska vibrationer observeras i Raman men inte i ir
  - ➢Detta har vi redan sett för CO_2
  - ➢Effekten är mycket tydlig i tvåatomiga molekyler



Symmetriska vibrationer



Fördelar

- ⇨Vatten sprider dåligt
  - ➢Bra lösningsmedel t.ex. i biosammanhang