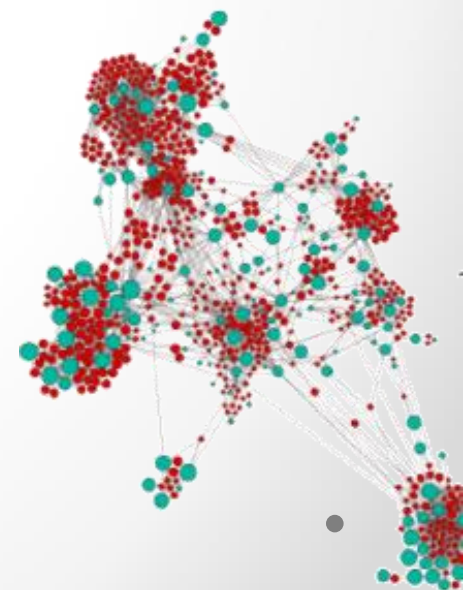


## OTU 06: Basic Structural Elucidation

*Overview of spectroscopic and spectrometric techniques*

*(Directly linked to the tutorials of TU 09)*

**Mehdi BENIDDIR**  
Professor of natural products chemistry  
BioCIS UMR CNRS 8076  
[mehdi.beniddir@universite-paris-saclay.fr](mailto:mehdi.beniddir@universite-paris-saclay.fr)



# Electromagnetic spectrum

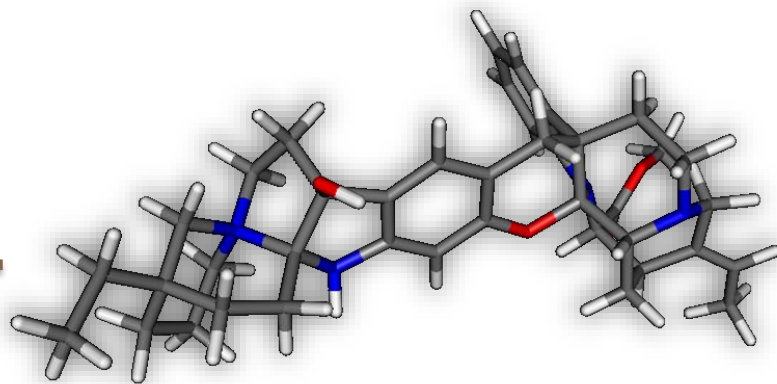
✓ Four techniques are used routinely by organic chemists

# Spectroscopic and spectrometric techniques

✓ Four techniques are used routinely by organic chemists



NMR  
1940



UV  
1930

MS 1960



IR  
1930



# Electromagnetic spectrum

- ✓ Four techniques are used routinely by organic chemists
  - ✓ Spectrometry
    - ✓ Mass Spectrometry
  - ✓ Absorption spectroscopy
    - ✓ UV
    - ✓ IR
    - ✓ NMR

Absorption of specific energies of electromagnetic radiation, that can be used to infer structural features

Planck-Einstein relation

$$E = h\nu = \frac{hc}{\lambda}$$

# Electromagnetic spectrum

Molecular effect

Vibrational transitions

Nuclear spin transitions

Electronic transitions

Wavelength (m)

$10^{-16}$   $10^{-14}$   $10^{-12}$   $10^{-10}$   $10^{-8}$   $10^{-6}$   $10^{-4}$   $10^{-2}$  1  $10^2$   $10^4$   $10^6$   $10^8$

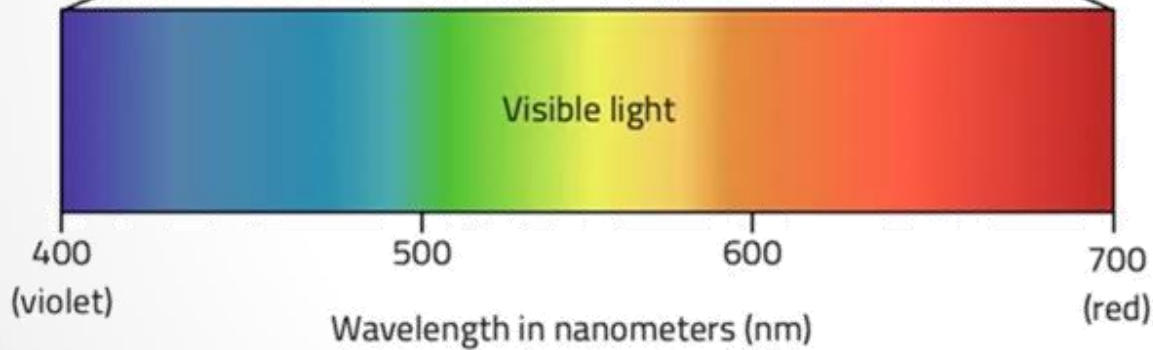
Gamma rays

X rays

UV

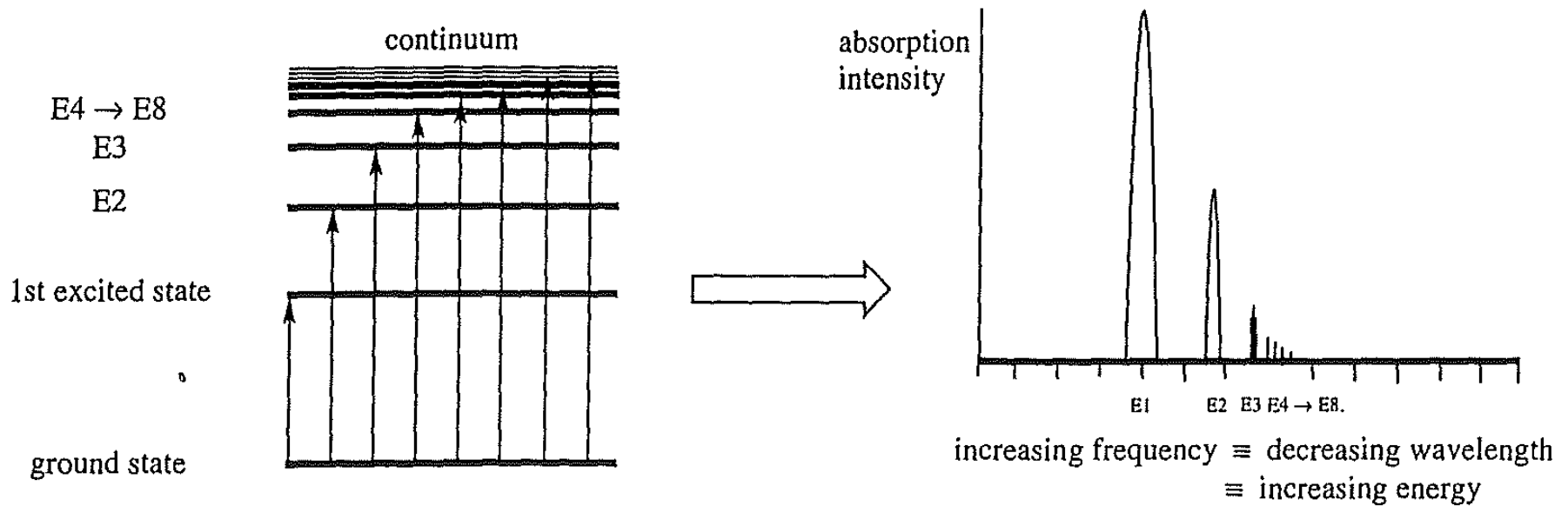
IR

Radio waves



NMR

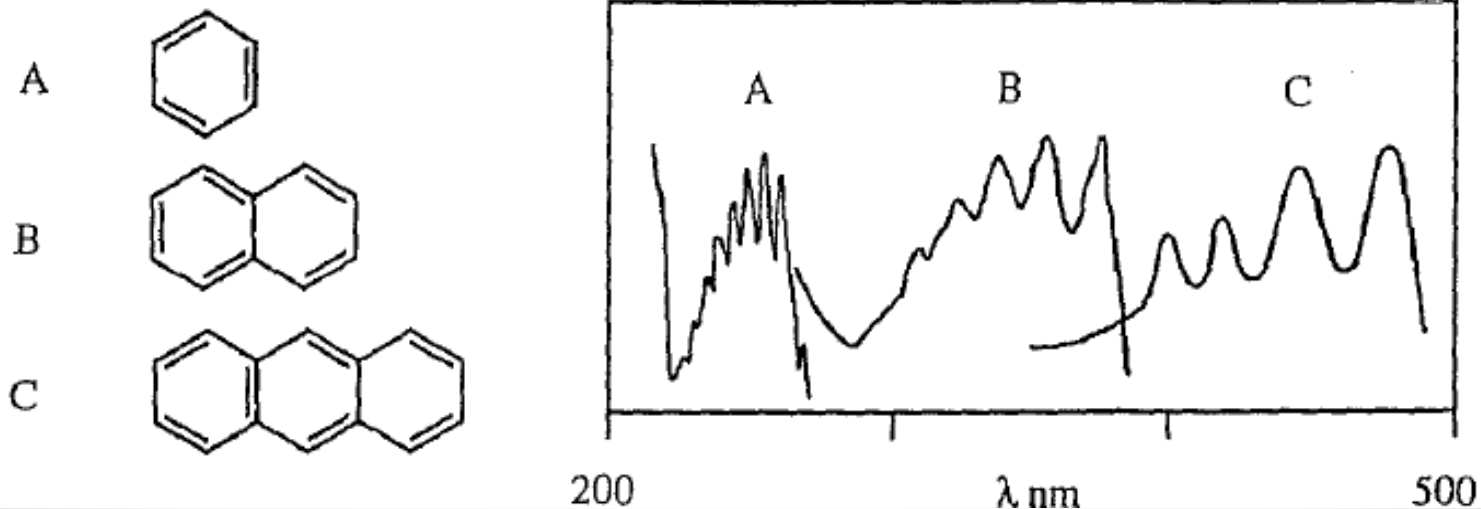
# Electromagnetic spectrum



- ✓ Absorption spectra provide two kinds of data:
  - ✓ Absorption wavelength/frequency that can be related to a functional group responsible for absorption
  - ✓ Absorption intensity: reflects the concentration of the absorbing species

# UV

- ✓ Introduced in the 1930s
- ✓ Non-destructive analytical technique
- ✓ Even if this technique is powerful, this technique is rarely used as a first means of analysis nowadays
- ✓ It requires the presence of chromophores
- ✓ Increasing conjugation results in an increase in the wavelength

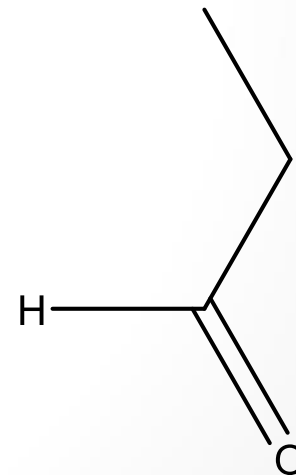
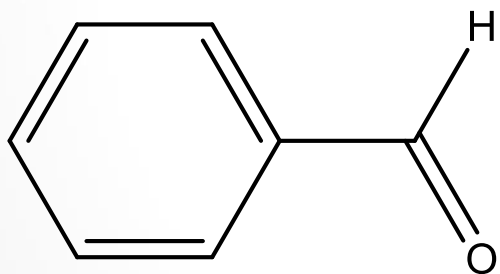
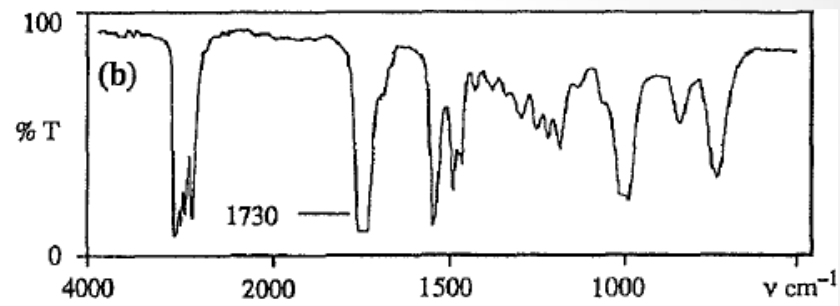
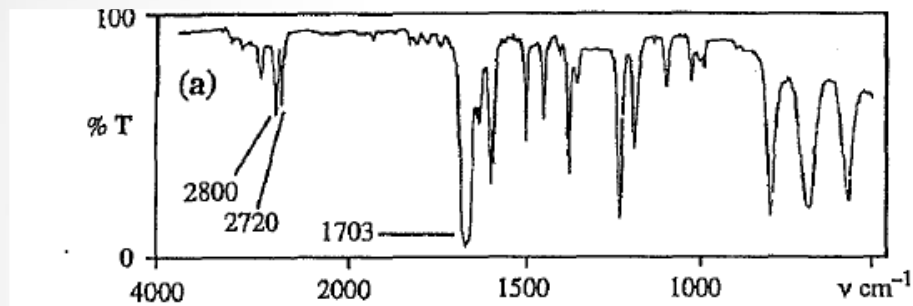


# UV

- ✓ **Typical UV transitions**
- ✓ Diagnostic absorptions results from  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions
- ✓ Aromatics and heteroatomic systems
  
- ✓ **UV spectrum data**
  - ✓  $\lambda_{\max}$  (nm)
  - ✓  $\epsilon$  molar absorptivity (also known as molar extinction coefficient) (this value increases when the molecule will strongly absorb the light)
  - ✓ **Beer-Lambert law:**  $A = \epsilon l c$  ( $c = \text{concentration mol/L}$ ,  $l = \text{path length of absorbing solution in cm}$ ,  $A = \text{absorbance}$ )
  
- ✓ **Interpreting UV data**
  - ✓ **Allowed transitions:**  $\pi \rightarrow \pi^*$ ,  $\sigma \rightarrow \sigma^*$ ,  $\epsilon > 10^3$
  - ✓ **Forbidden transitions (strongly disfavoured):**  $n \rightarrow \pi^*$ ,  $\epsilon < 100$



# IR



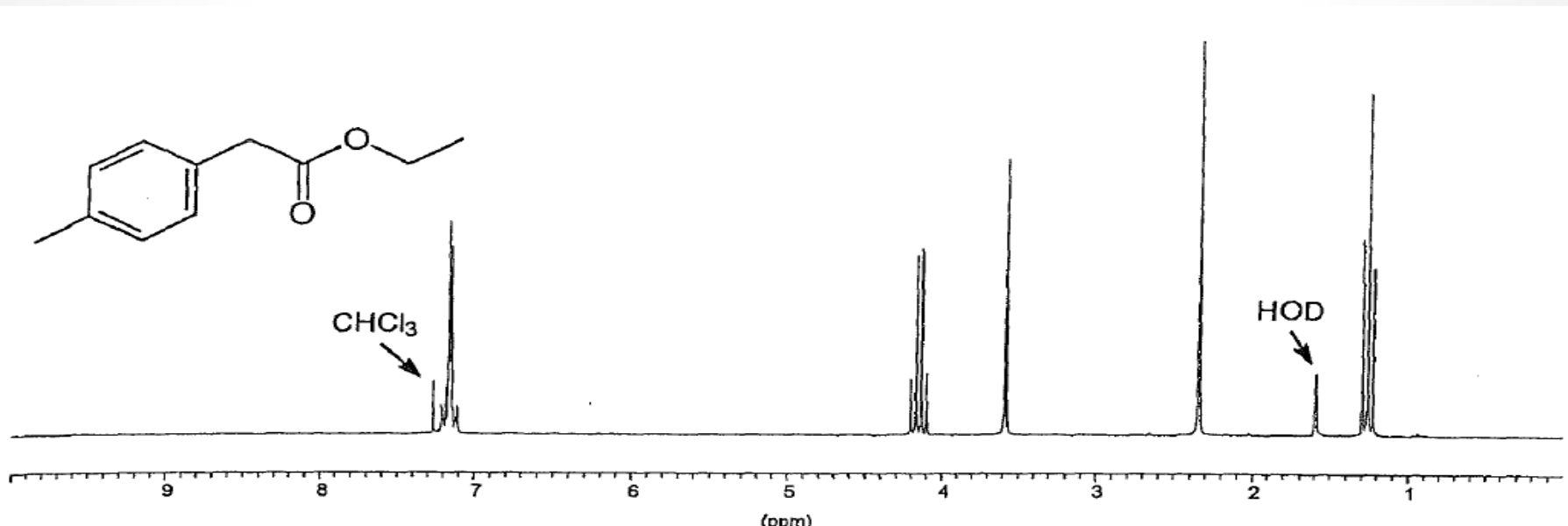
# NMR

- ✓ The most powerful and versatile of all structure elucidation techniques
- ✓ Detailed structural information that correlate with individual atoms (rather than groups as in UV and/or IR)
- ✓ Nuclei with zero spin ( $I = 0$ ) are not amenable to NMR observation
- ✓ In Org. Chem.,  $^1\text{H}$  and  $^{13}\text{C}$  are the most studied nuclei
- ✓  $^1\text{H}$  has almost 100% natural abundance, the most sensitive nuclei to observe in NMR
- ✓ Note that as we are forced to observe the low natural abundance  $^{13}\text{C}$  (1.1 %) => facing one of the major limitations in NMR: sensitivity

# NMR

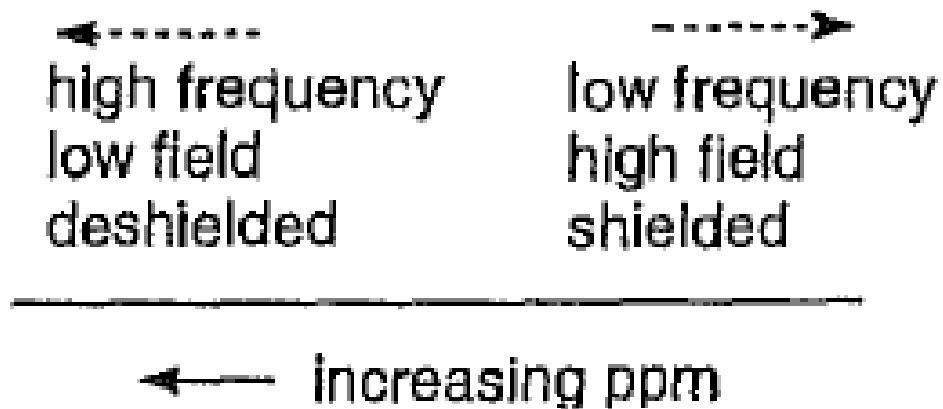
✓ Features of NMR spectra:

- ✓ Each proton resonances sits in a distinct chemical environment, characterized by its **chemical shift  $\delta$  (ppm)**
- ✓ The shape of the peaks is related to the proton neighbouring atoms: the degree of coupling is defined by a **coupling constant,  $J$  (Hz)**
- ✓ Each peaks can feature different intensities, which relates to the number of protons (**integration**)



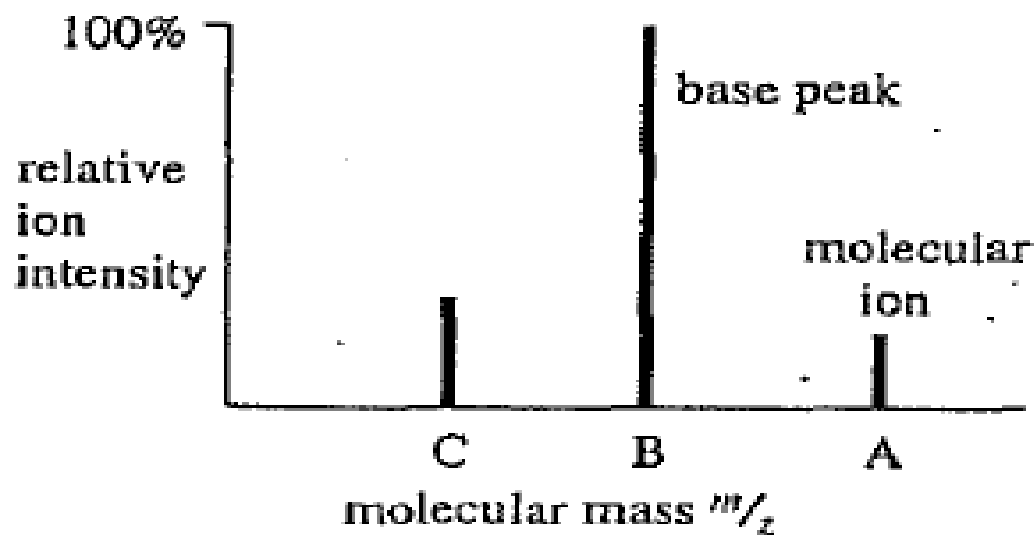
# NMR

✓ Nomenclature used:



# MS: Mass Spectrometry

- ✓ Compounds are ionized (**ionization method**) and the resulted ions are separated according to their mass/charge ratio ( $m/z$ )
- ✓ EI: Electron Impact (EI): the sample is bombarded with a beam of high energy (70 eV)
- ✓ ES: Electrospray: (well suited for HPLC), polar compounds, soft ionization  $[M+H]^+$ ,  $[M+Na]^+$



# MS

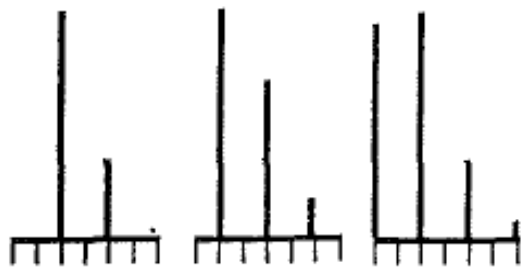
✓ It measures individual atoms and enables the isotopic constitution to be determined

✓ **The number of carbons in a molecule:**

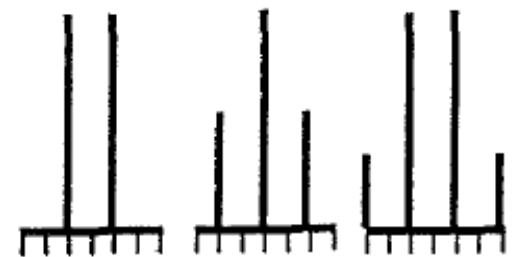
carbon is roughly 98.9%  $^{12}\text{C}$  and 1.1%  $^{13}\text{C}$ , then in a molecule containing 10 carbon atoms, the  $\text{M}^+$  peak will be accompanied by a peak at  $\text{M}+1$  having 10% intensity (containing molecules having one  $^{13}\text{C}$  atom).

$$n\text{C} = (\text{intensity of M}+1/\text{M}) \times 100$$

✓ **Halogene-containing molecules:**



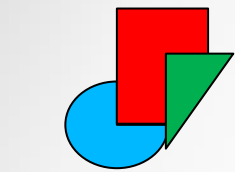
**Fig. 6.19** Isotope patterns of Cl, Cl<sub>2</sub>, Cl<sub>3</sub> species.



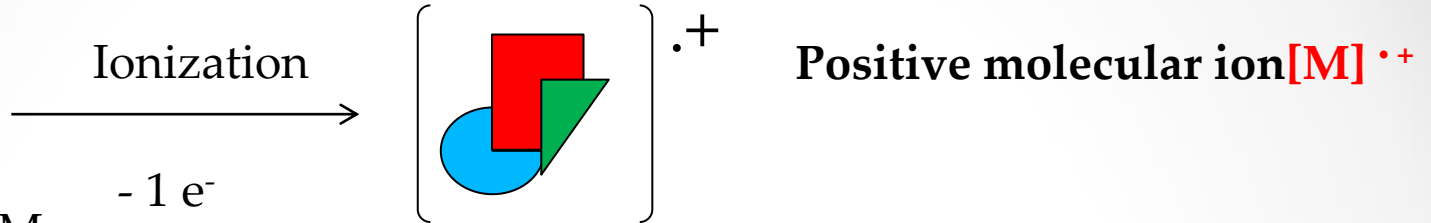
**Fig. 6.18** Isotope patterns of Br, Br<sub>2</sub>, Br<sub>3</sub> species.

# MS

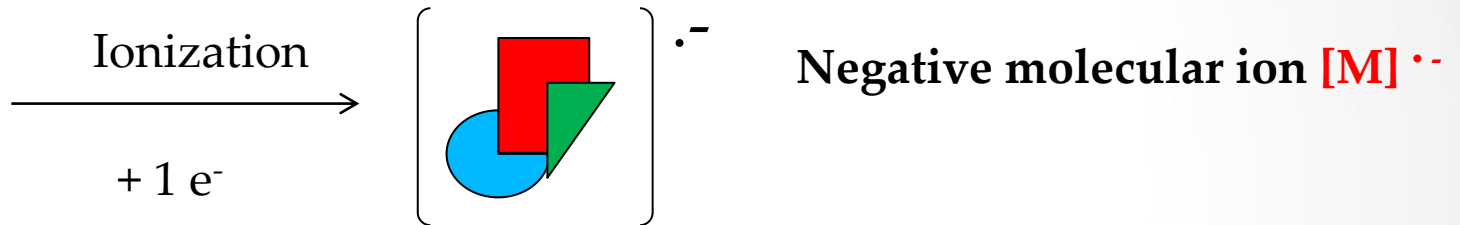
## Terminology



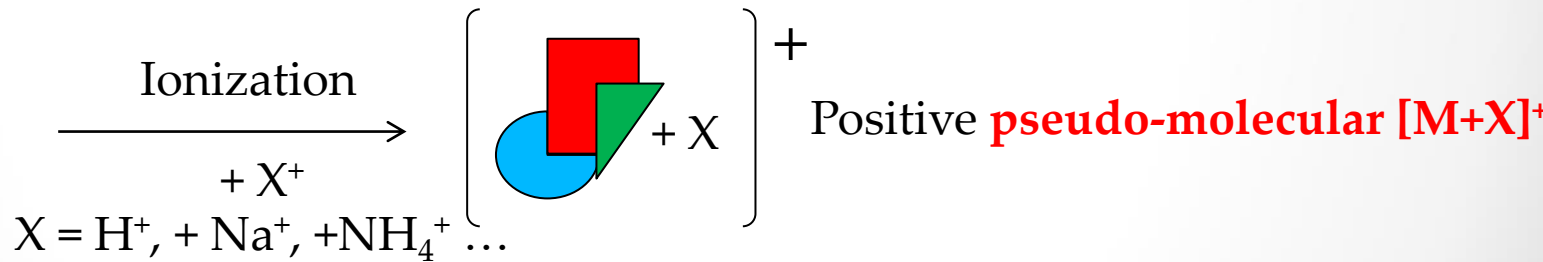
Neutral molecule M



Positive molecular ion **[M]•+**

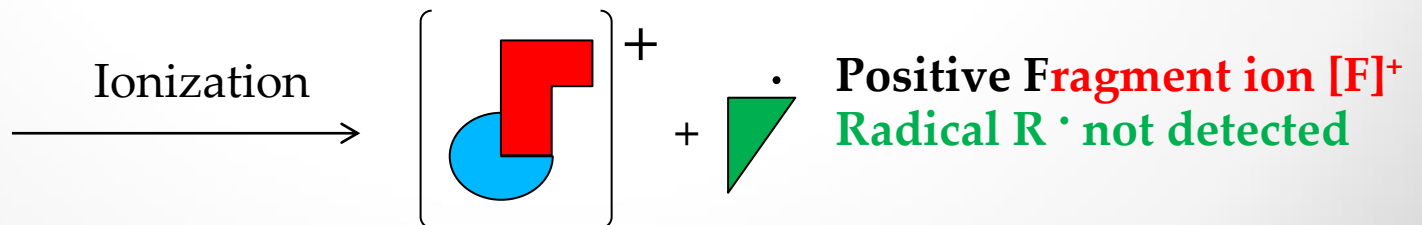


Negative molecular ion **[M]•-**



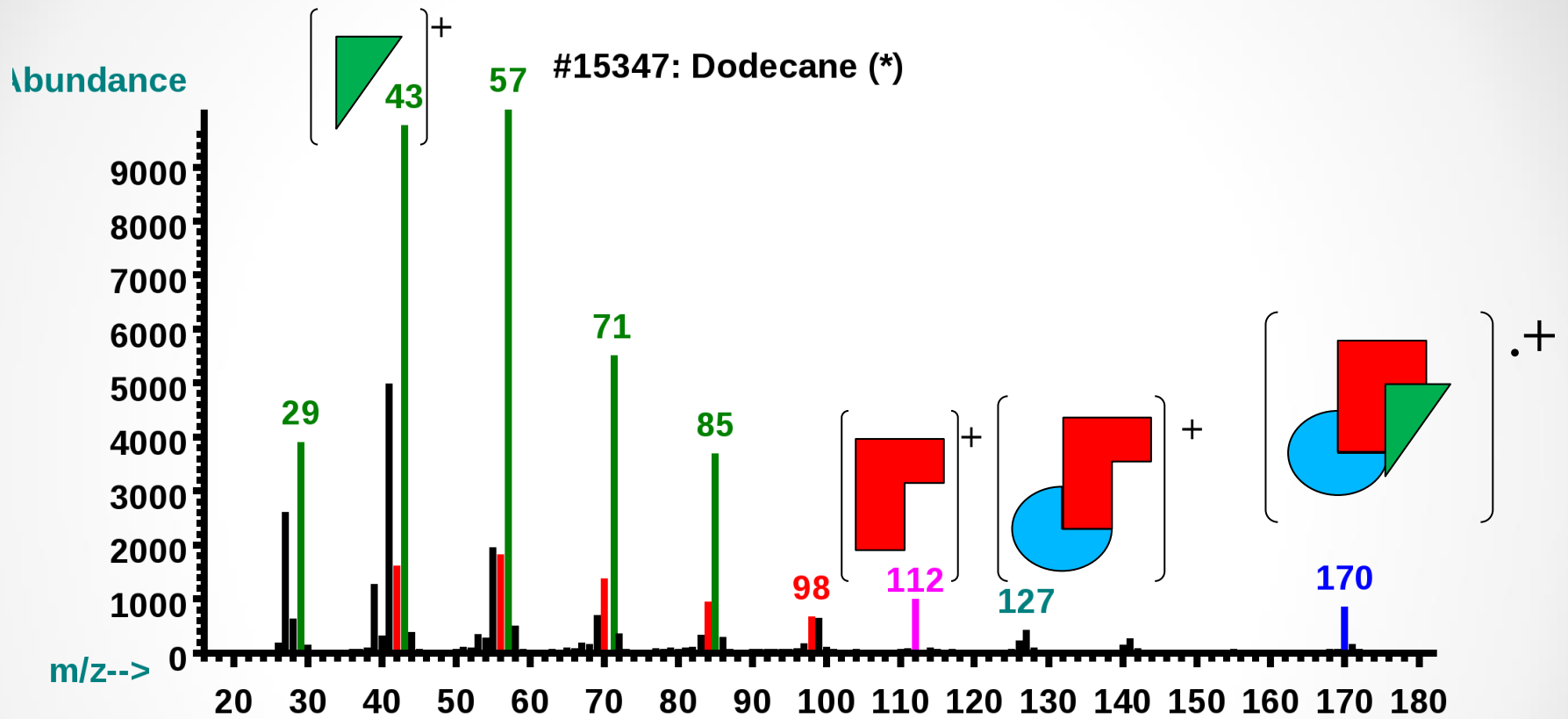
Positive **pseudo-molecular [M+X]<sup>+</sup>**

X = H<sup>+</sup>, + Na<sup>+</sup>, + NH<sub>4</sub><sup>+</sup> ...



Positive **Fragment ion [F]<sup>+</sup>**  
**Radical R• not detected**

# MS





# MS: Fragmentation pathways

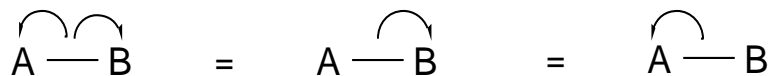
## One-Bond cleavages

### - Homolytic cleavage

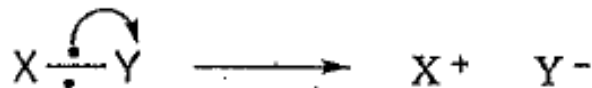


*Homolytic cleavage involves movement of single electrons.*

Notation:

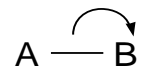


### - Heterolytic cleavage

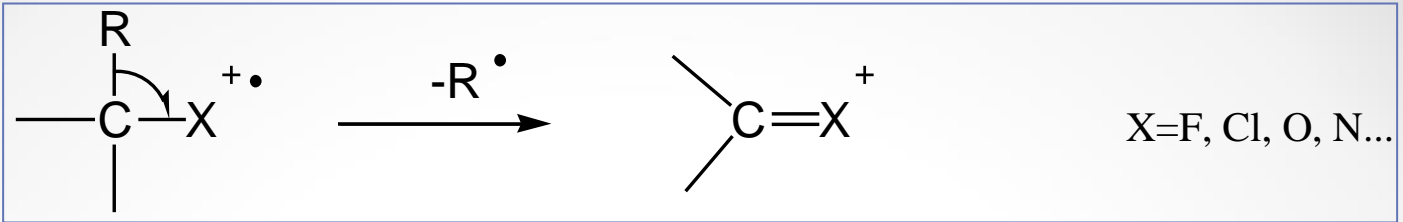


*Heterolytic bond cleavage involves movement of a pair of electrons.*

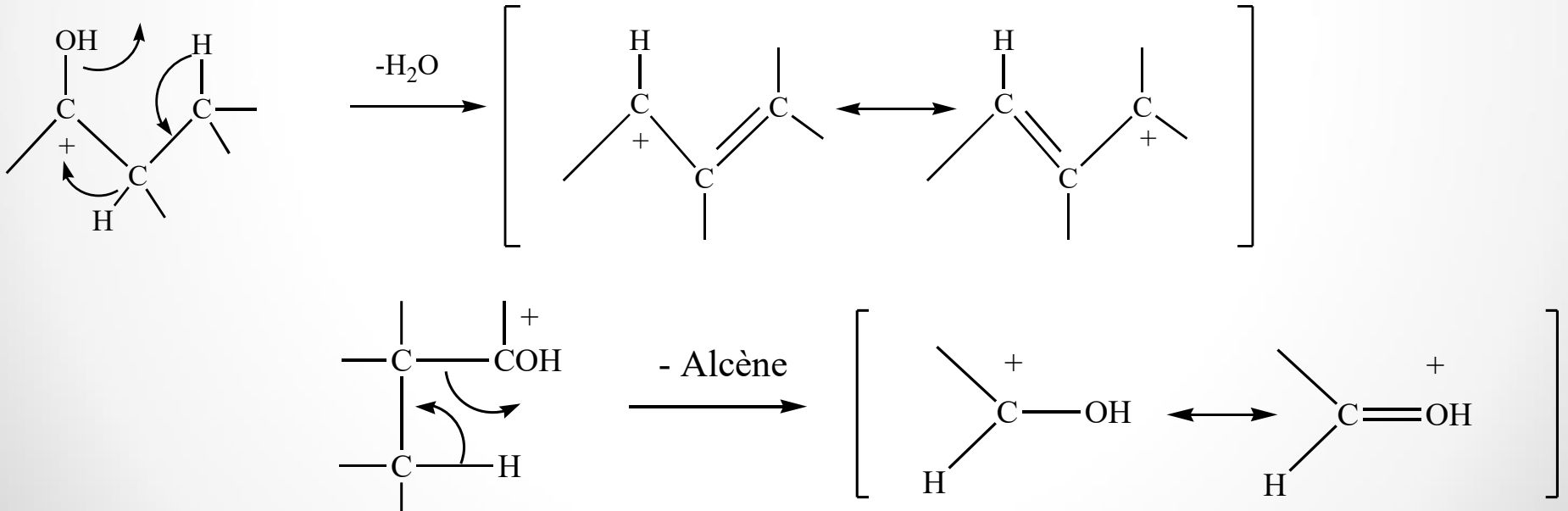
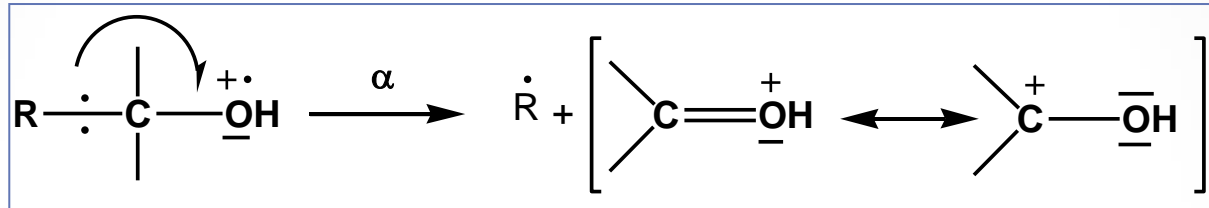
Notation:



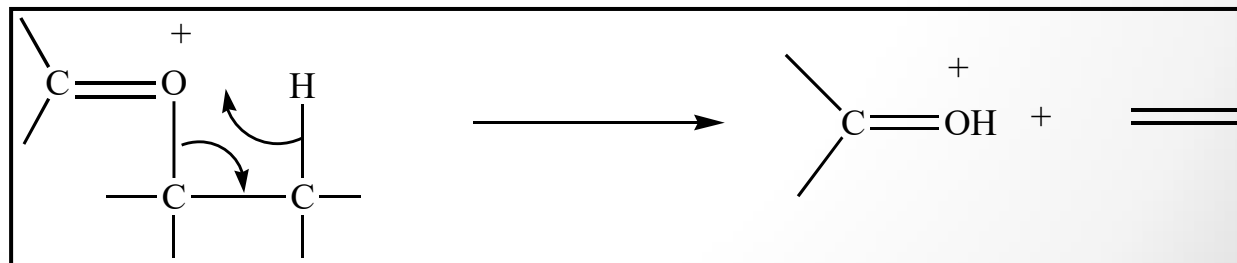
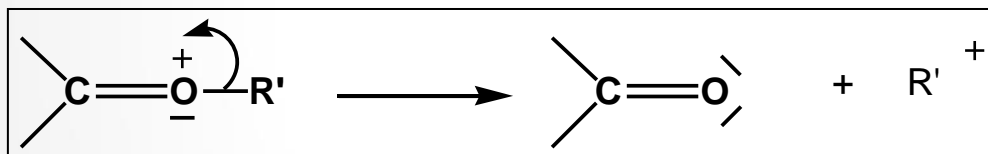
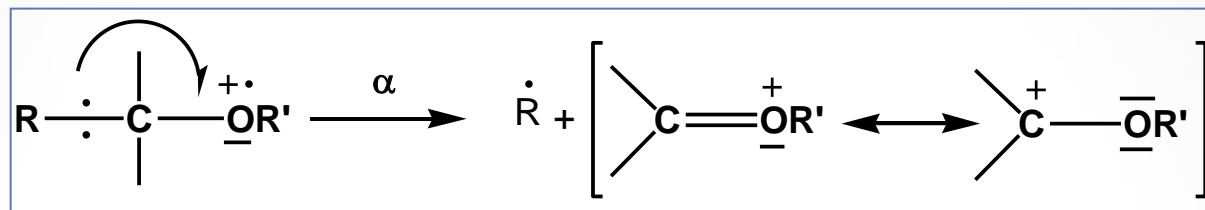
MS

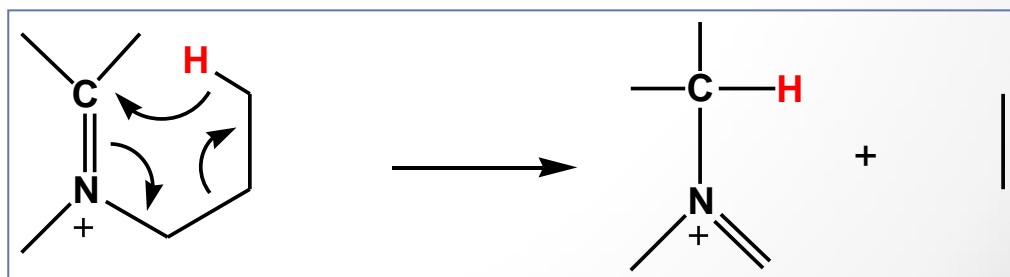
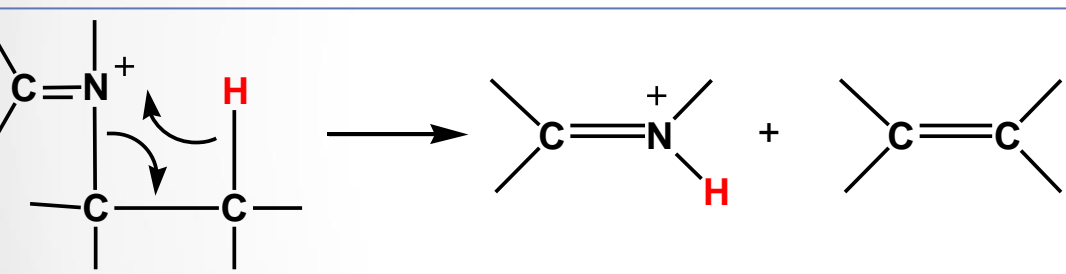
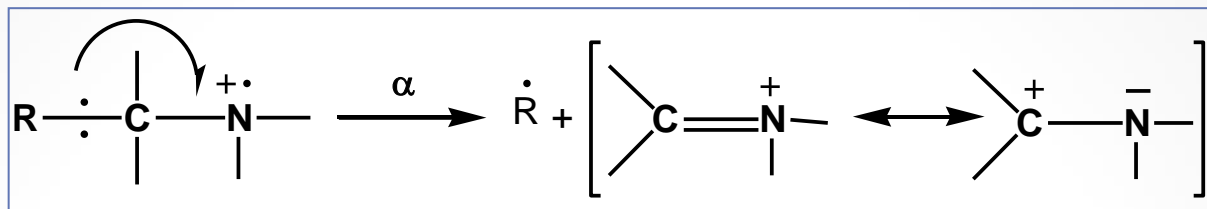


## Alcohol

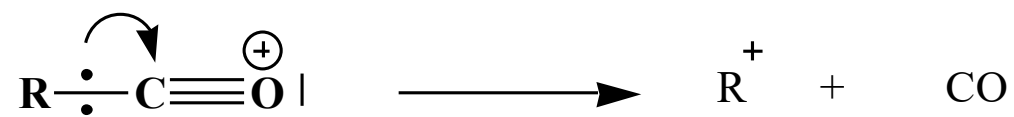
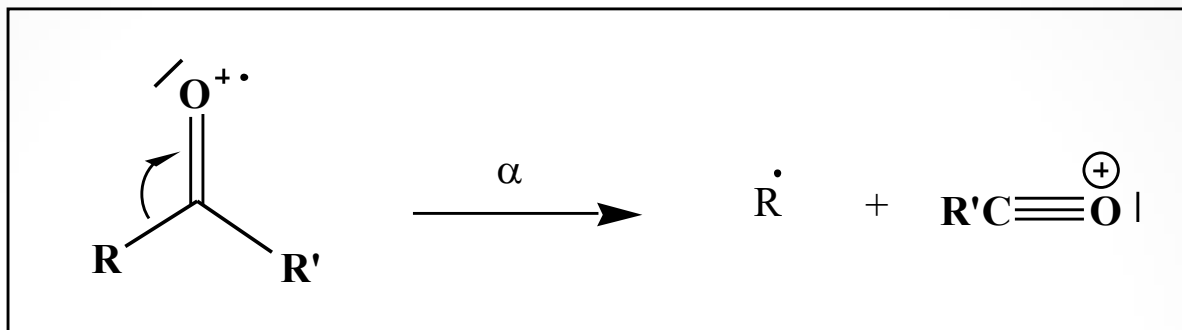


## Ether



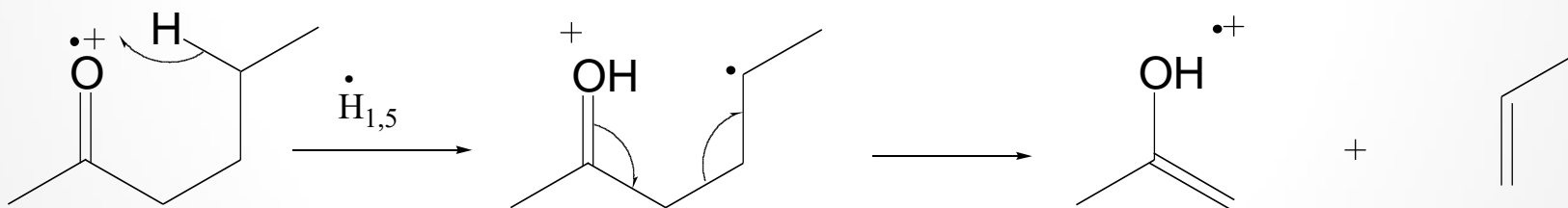
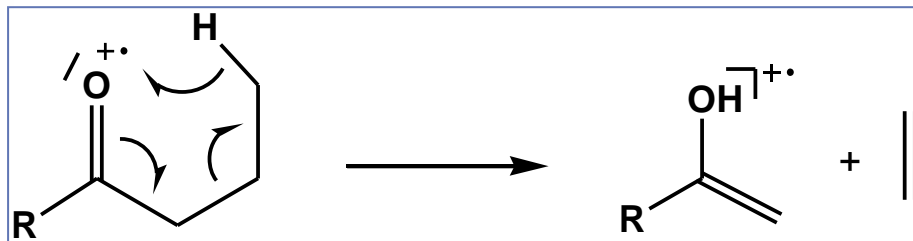


## Ketones and aldehydes



# MS

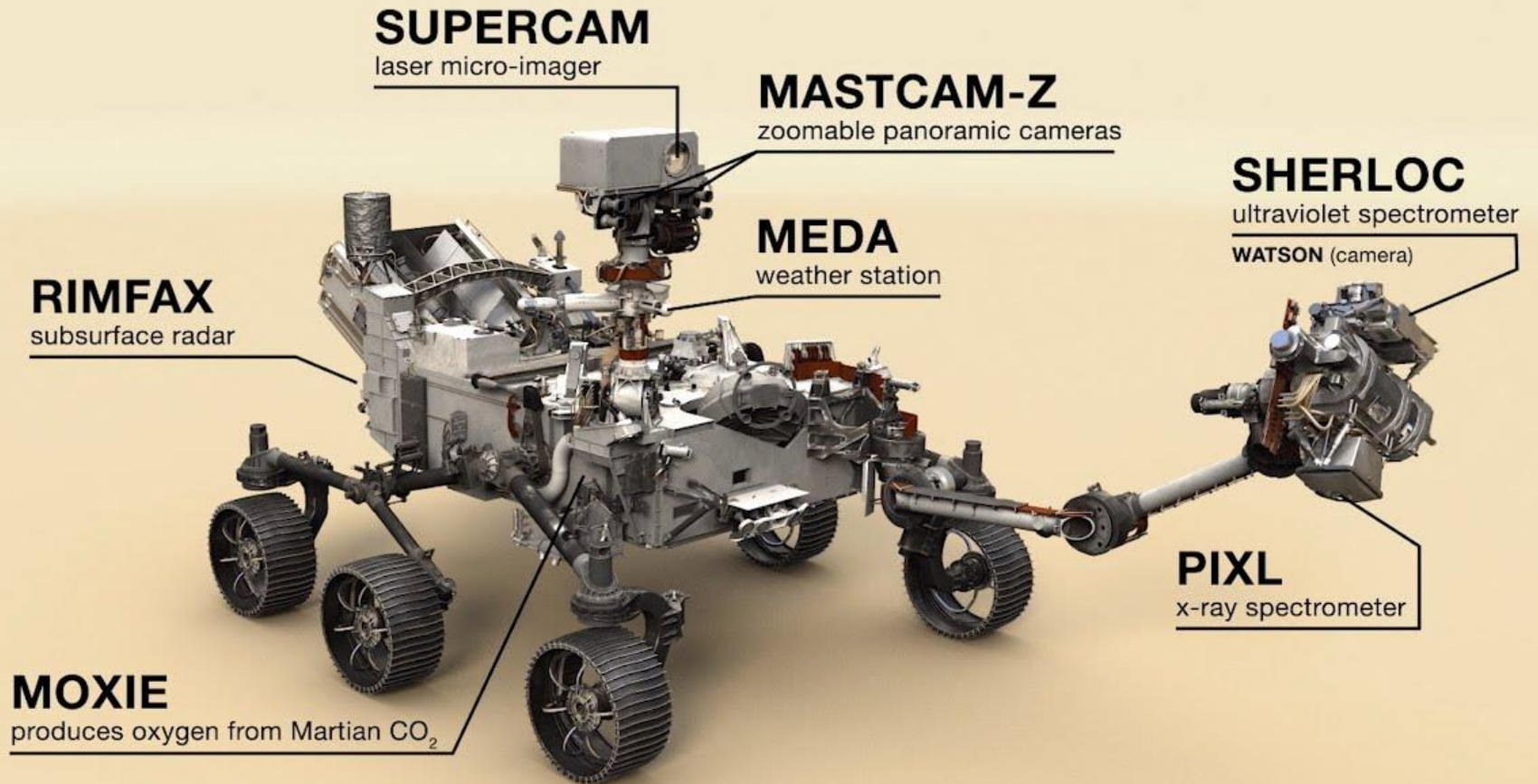
## Ketones and aldehydes: McLafferty rearrangement



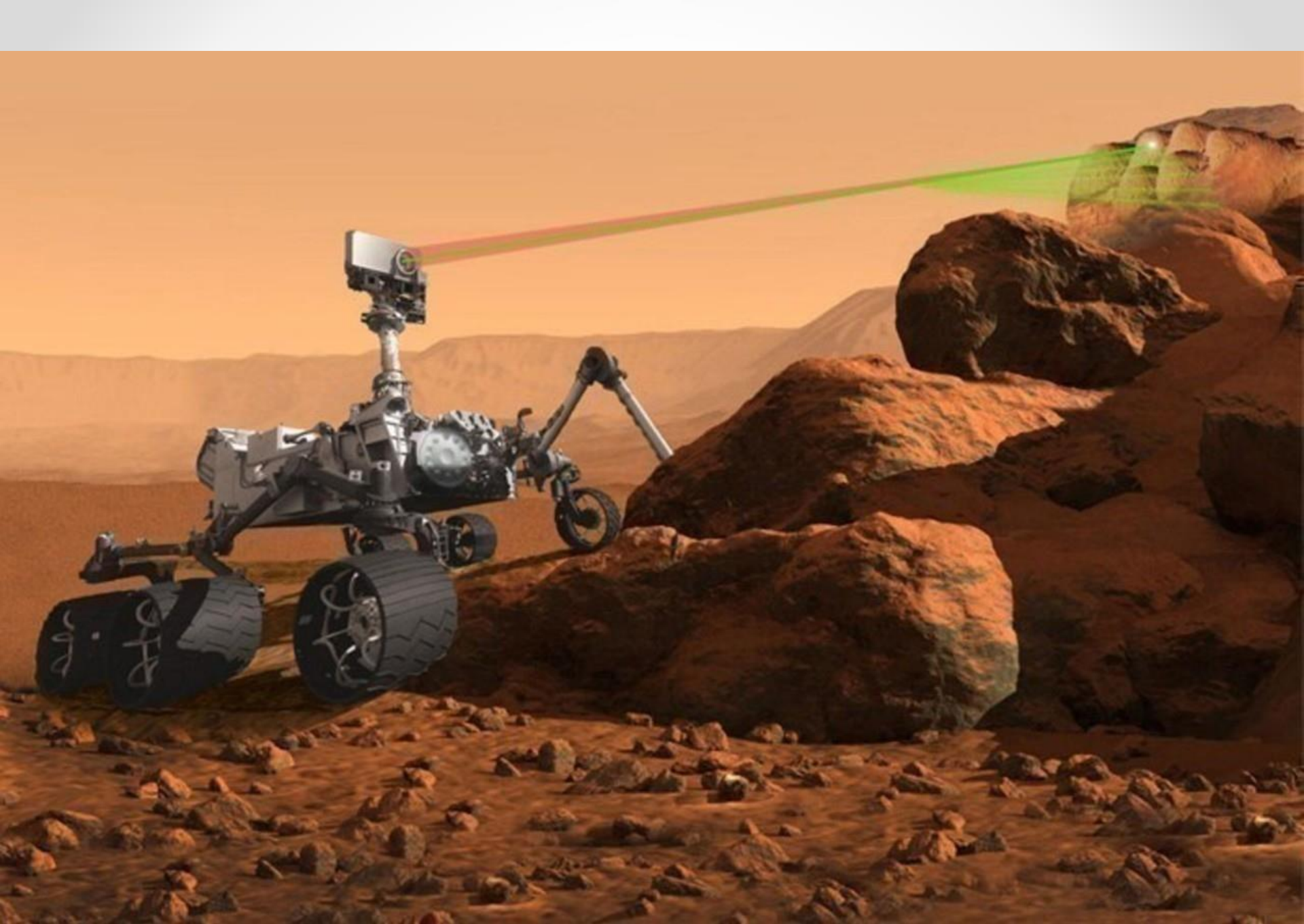
# MS

- ✓ The « nitrogen rule »
- ✓ Any compound containing one or an odd number of nitrogen atoms will have an odd molecular weight, conversely, compounds lacking nitrogen or containing even numbers of nitrogens have an even molecular weight. Of course, the inverse applies to spectra obtained under electrospray ionization (considering  $[M+H]^+$ )

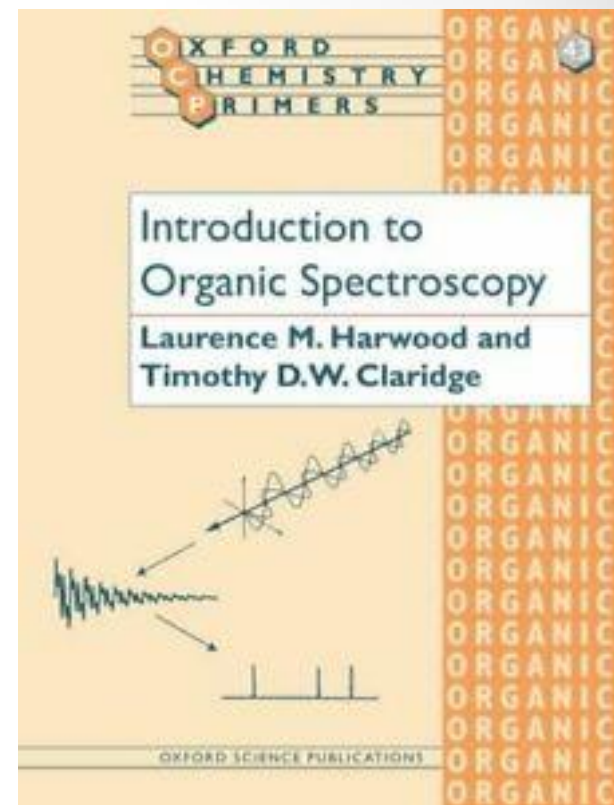
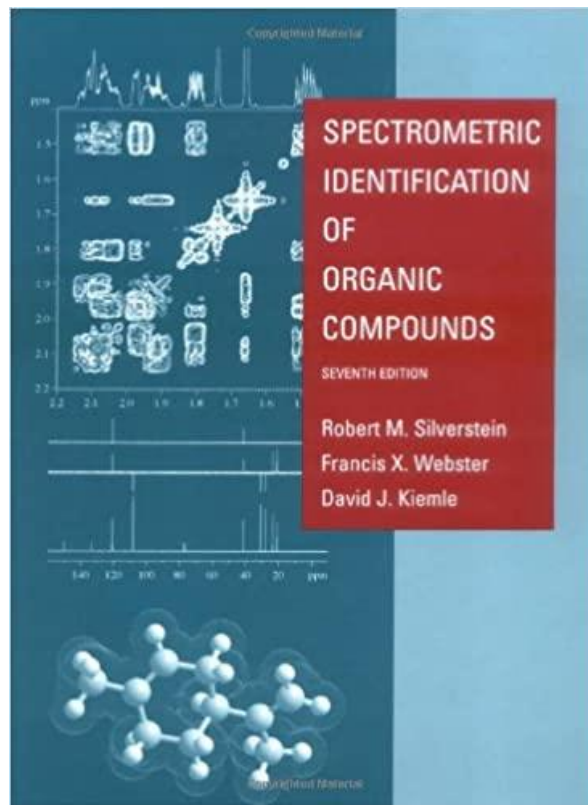
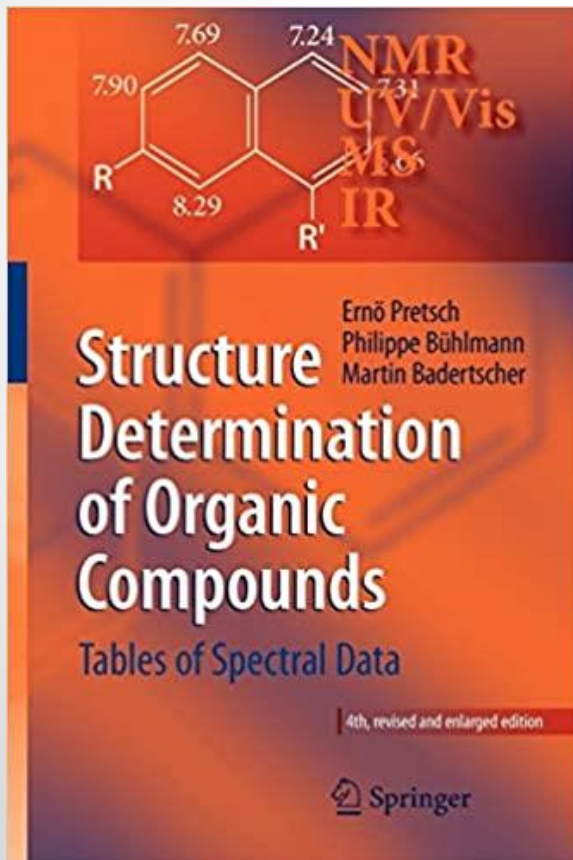
# PERSEVERANCE landing on Mars







# If you want to know more



Thank you for your  
attention