Microwave Assisted Organic Synthesis (MAOS):

An Introduction

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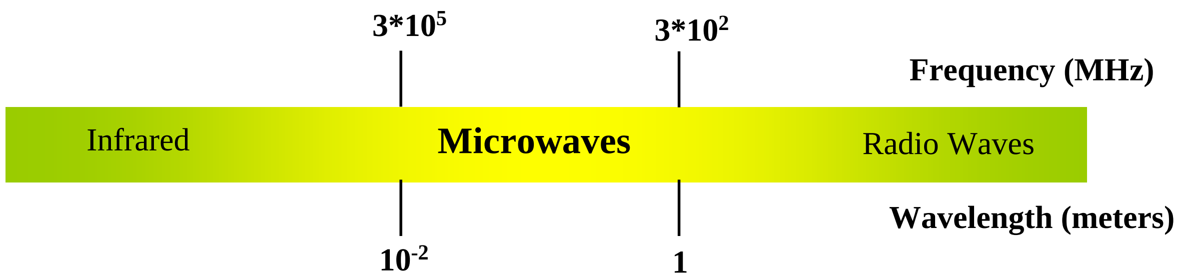
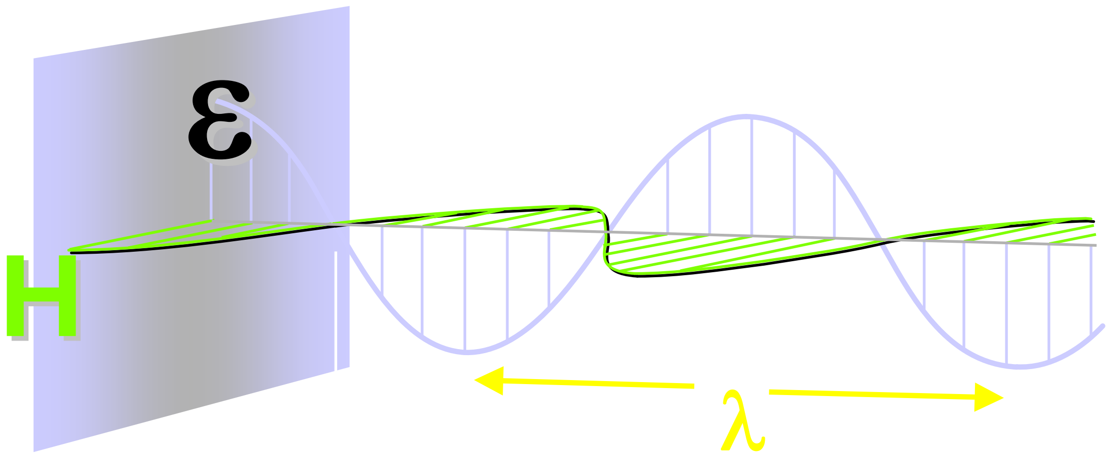
What are Microwaves?





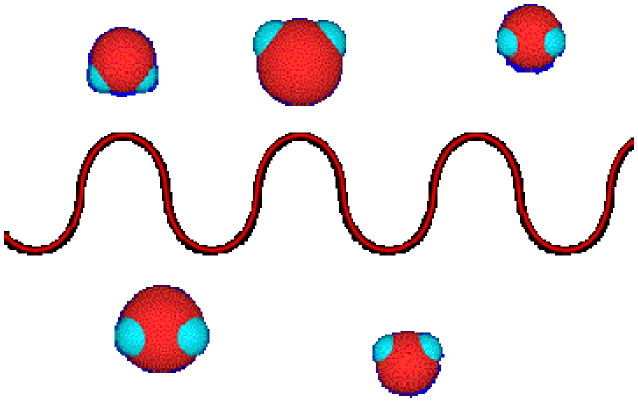
ε :Electric field

H : Magnetic field

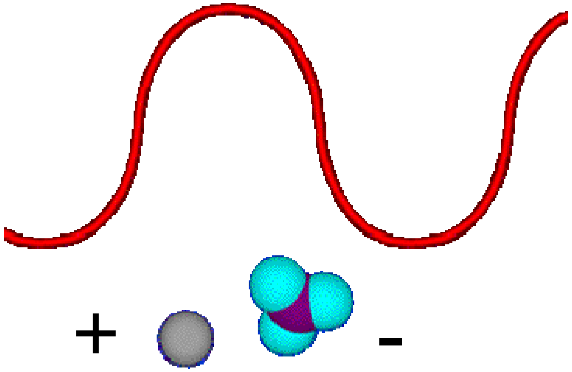
λ : Wavelength (12,2 cm for 2450 MHz)

How do Microwaves interact with materials ?

Dipole Rotation



Ionic Conduction



Alignment with the oscillating electric field

Loss of energy in the form of heat

Mingos, D. M. P. and coworkers, Chem. Soc. Rev. **1991**, 20, 1 and **1998**, 27, 213

$$\tan\delta = \varepsilon'' / \varepsilon'$$

Loss Factor → $\tan\delta$

Dielectric Loss → ε''

Dielectric Constant → ε'

Solvent	tanδ	Solvent	tanδ
ethylene glycol	1.350	DMF	0.161
ethanol	0.941	1,2-dichloroethane	0.127
DMSO	0.825	water	0.123
2-propanol	0.799	chlorobenzene	0.101
formic acid	0.722	chloroform	0.091
methanol	0.659	acetonitrile	0.062
nitrobenzene	0.589	ethyl acetate	0.059
1-butanol	0.571	acetone	0.054
2-butanol	0.447	tetrahydrofuran	0.047
1,2-dichlorobenzene	0.280	dichloromethane	0.042
NMP	0.275	toluene	0.040
acetic acid	0.174	hexane	0.020

B. L. Hayes, Microwave Synthesis: Chemistry at the Speed of Light, CEM Publishing, Matthews NC, **2002**.

MAOS Advantages

- Reduced reaction times
- Reduced side reactions
- Increased yields
- Improved reproducibility

Microwave Effects

Purely Thermal Effects

- **High reaction temperature**
- **High heating rate**

$$k = Ae^{\left(\frac{-Ea}{RT}\right)}$$

Arrhenius Law

Microwaves Effects

Non Thermal : “Specific MW Effects”

- **Polar reaction mechanisms, where the polarity is increased going from the ground state to the transition state**

$$k = Ae^{\left(\frac{-Ea}{RT}\right)}$$

Arrhenius Law

L. Perreux, A. Loupy, Tetrahedron **2001**, 57, 9199 – 9223.

Microwaves Effects

Non Thermal : "Specific MW Effects"

- **Direct interaction of E with specific molecules (strong MW absorbers) in the reaction medium**

$$k = Ae^{\left(\frac{-Ea}{RT}\right)}$$

Arrhenius Law

L. Perreux, A. Loupy, Tetrahedron **2001**, 57, 9199 – 9223.

Processing Techniques

Sealed vessel

- High pressure (up to 20 bar)
- Superheating of reaction medium
- High reproducibility with on-line temperature and pressure measurements

Processing Techniques

Open system

- Temperature limited to the boiling point of the solvent
- Strong reaction enhancement by using low MW absorber solvents
- Possibility to use the same experimental set-up used in normal conditions

Processing Techniques

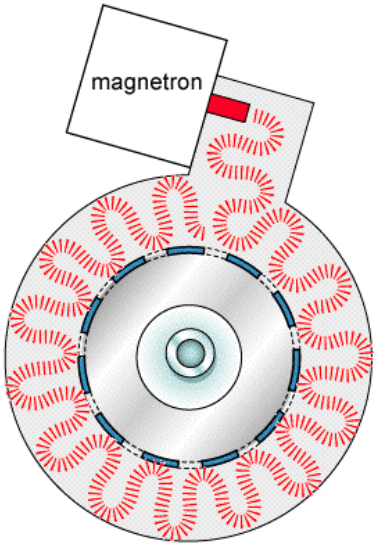
"Dry Media"

- **Eco-friendly reactions (solventless)**
- **Almost MW transparent inorganic supports (silica, alumina)**
- **Improved catalytic activity**
- **Problems with non-uniform heating and temperature control**

Microwave Technologies

Mono-Mode Microwave Reactor

- **High Field Homogeneity**



Optimal Energy Distribution

No Hot Spots

Microwave Technologies

Mono-Mode Microwave Reactor

- **High Energy Density**

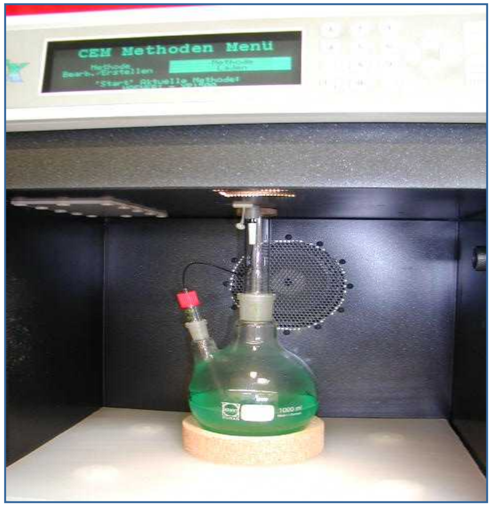
  709 W/l for a 300W Power Applied

- **High Reproducibility of Controlling Parameters**

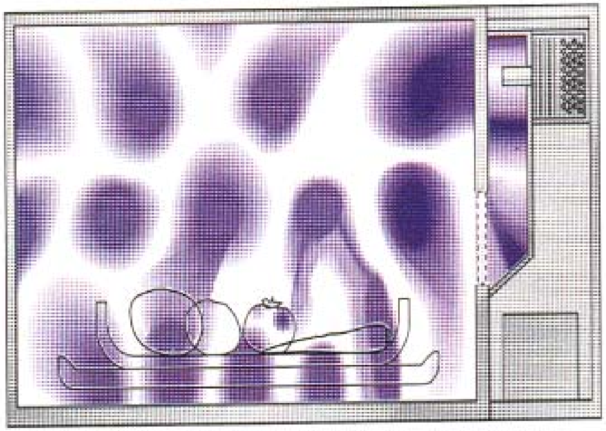
  Highly suitable for Synthetic Applications

Microwave Technologies

Multi-Mode Microwave Reactor



- **Irregular MW Field Distribution**

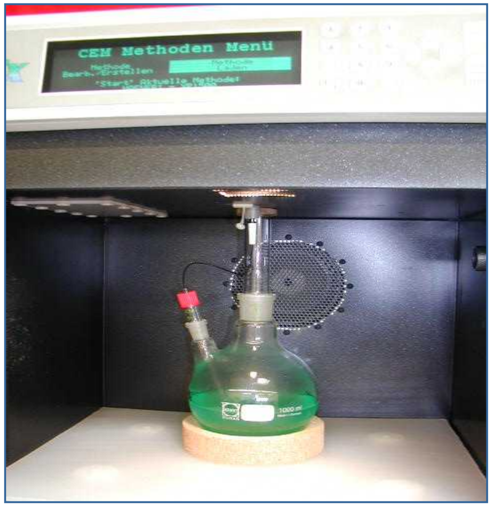


Hot and Cold Spots

Uncontrolled localized Superheating

Microwave Technologies

Multi-Mode Microwave Reactor



- **Low Energy Density**

  About 30 W/l for a 600 W Applied Power

- **Troubles in Controlling and Reproducibility**

  Only suitable for Analytical Purposes