台灣大學開放式課程

有機化學乙

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Chapter 13
UV-Visible Spectroscopy

紫外線可見光光譜

跳躍的電子

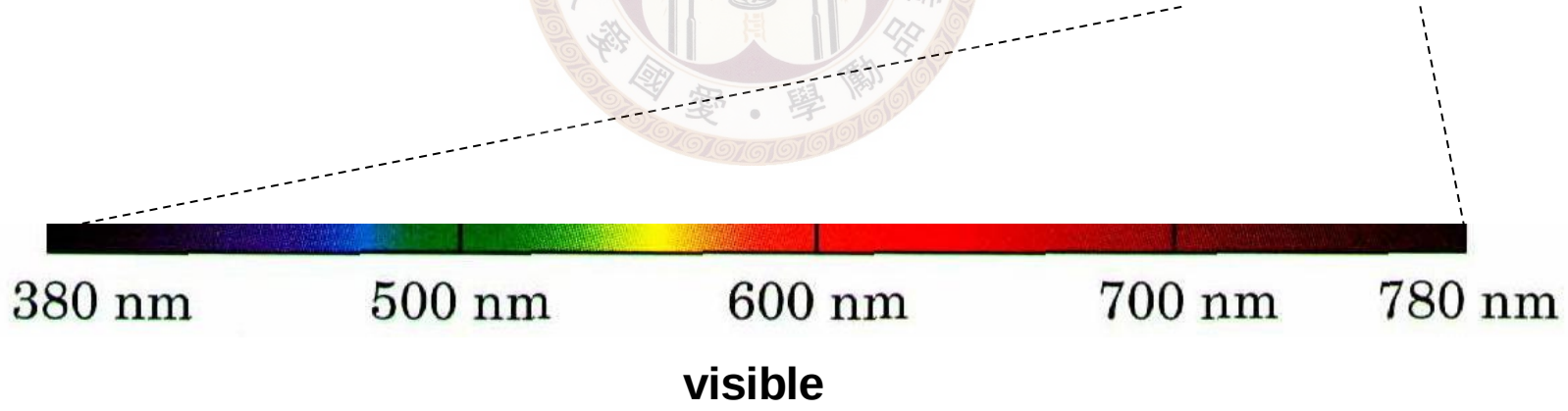
範圍

Vacuum UV　　UV　　Visible

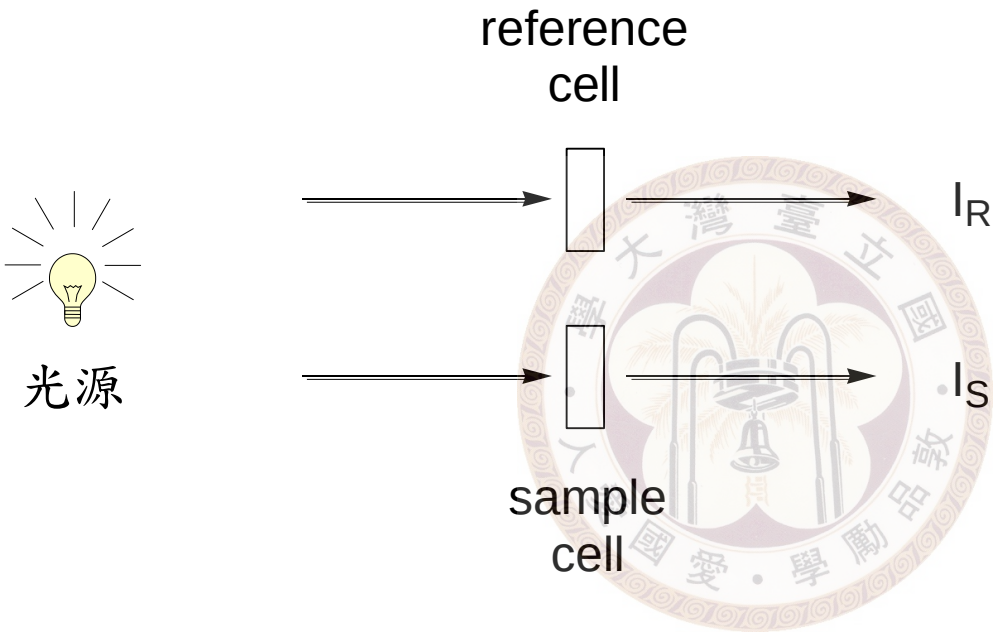
200-400 nm　　400-800 nm

high E　　low E

UV: ultraviolet wave



※ Instrumentation



$$\text{absorbance } A = \log \frac{I_R}{I_S}$$

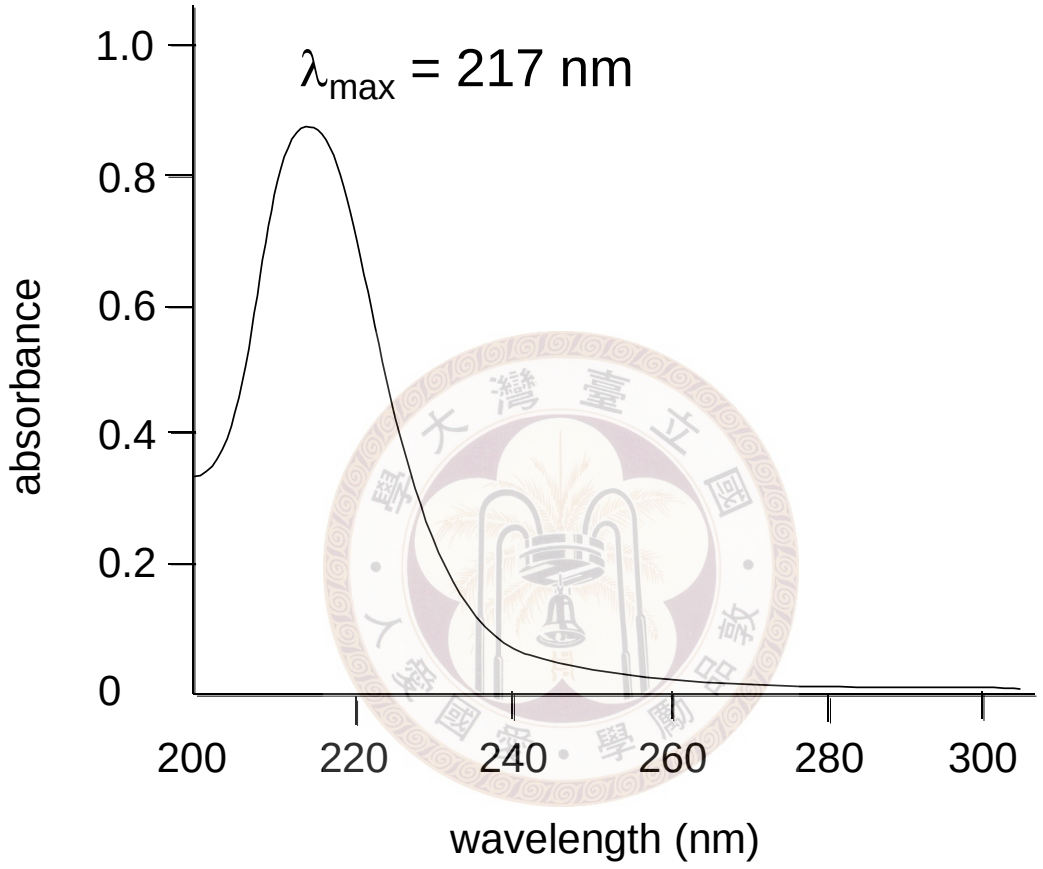
When $I_R = I_S$, $A = 0$

※ Beer-Lambert Law

$A = \varepsilon \times c \times l$

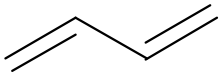
- ε: molar extinct coefficient or molar absorptivity
- c: concentration in M
- l: cell length in cm

◎ A typical spectrum



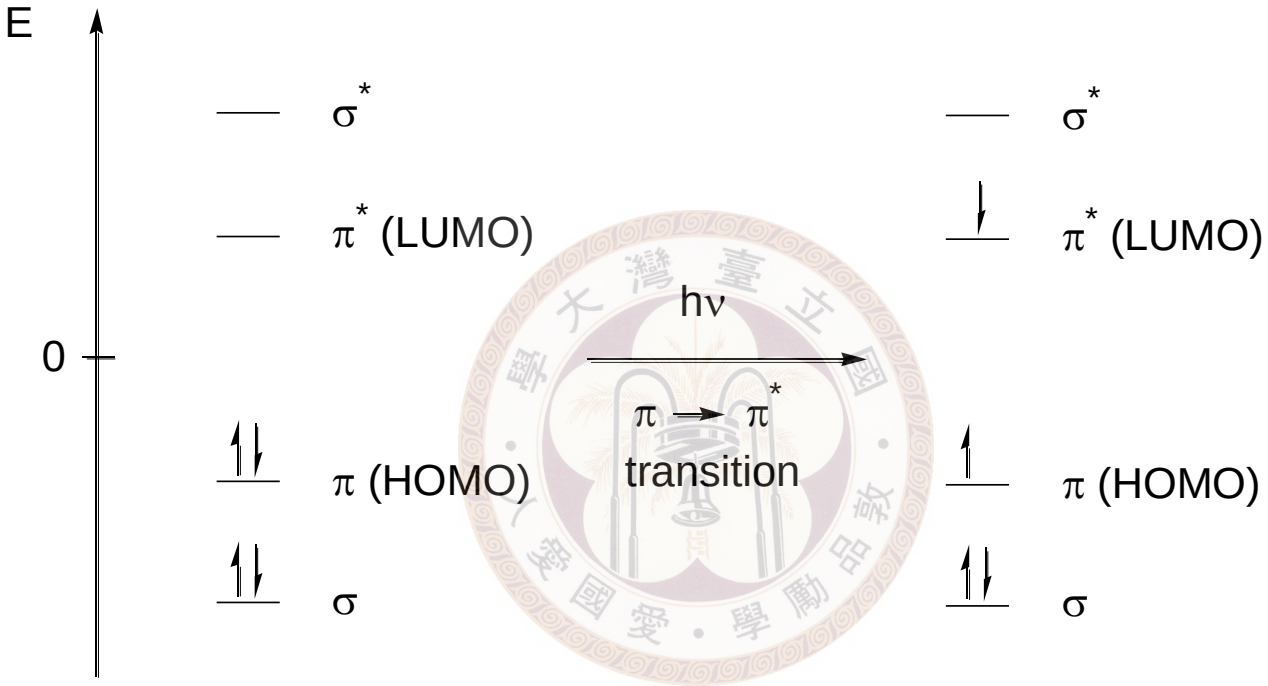
Ultraviolet spectrum of buta-1, 3-diene.

ε = 21,000



◎ The absorption corresponds to electronic transition

MO of ethene



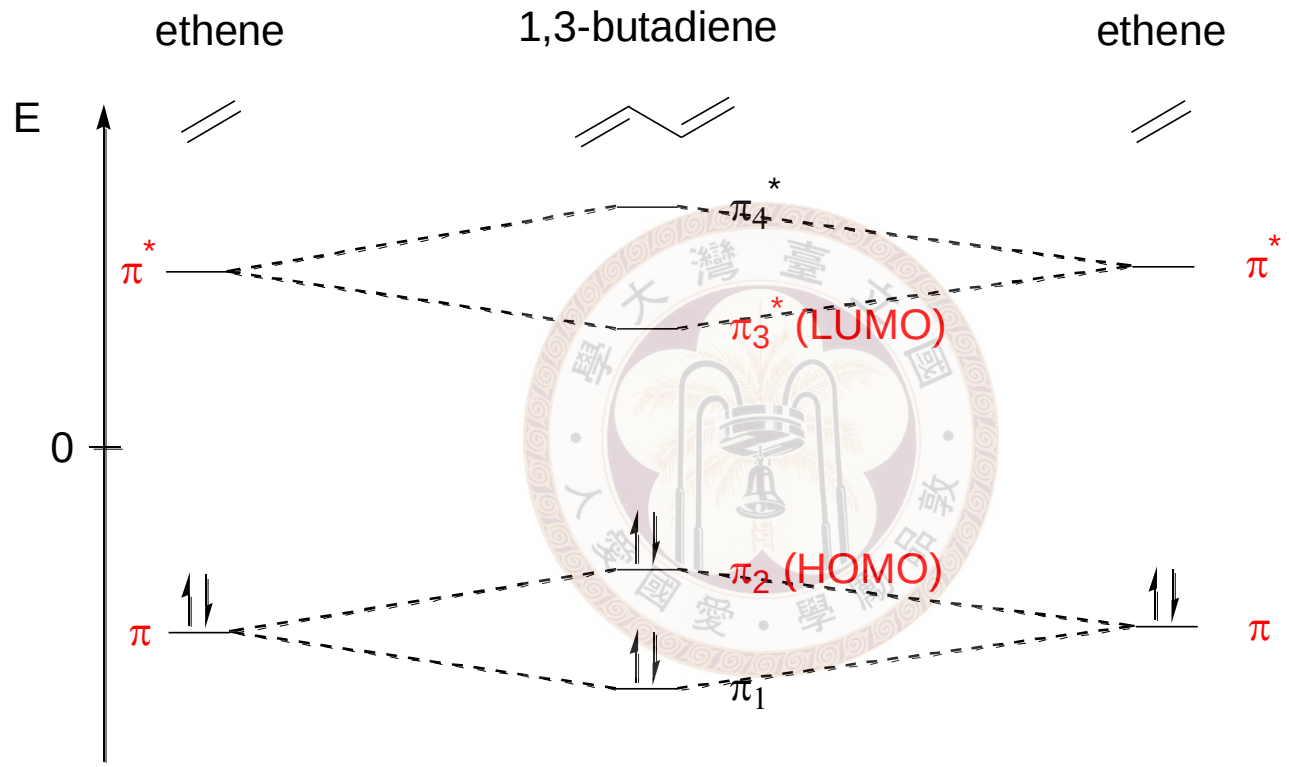
Broad signal due to vibrational and rotational states

λ_{max} = 171 nm

(HOMO: highest occupied molecular orbital

LUMO: lowest unoccupied molecular orbital)

※ The effect of conjugation



HOMO-LUMO gap decreases due to conjugation：
λ_{max} shifts to longer wavelength

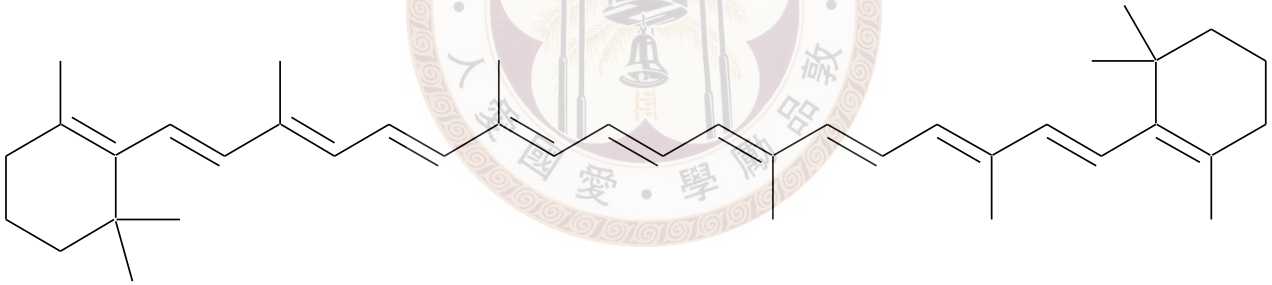
λ_{max} 171 217 274

Longer conjugation, longer wavelength

in the vac. UV region, not useful

cf.

λ_{max} = 178 nm

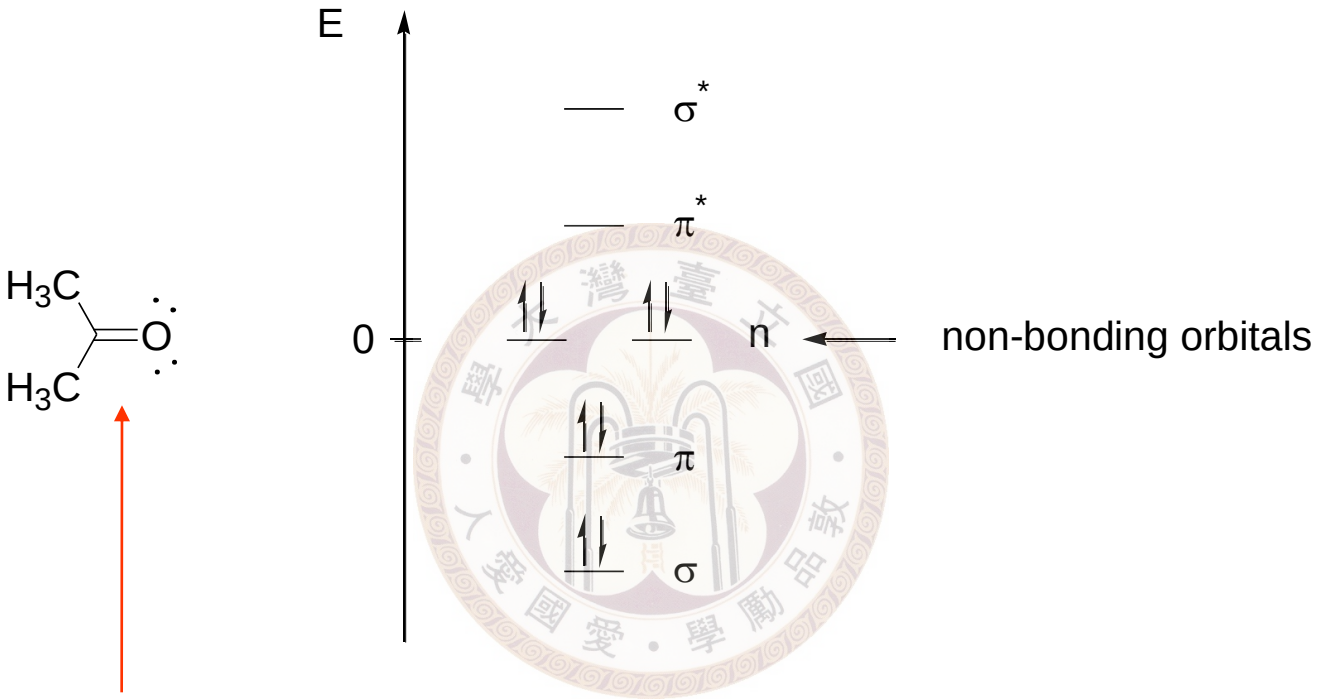


β-carotene

λ_{max} = 497 nm

blue-green

※ Carbonyl group



Strong π bond

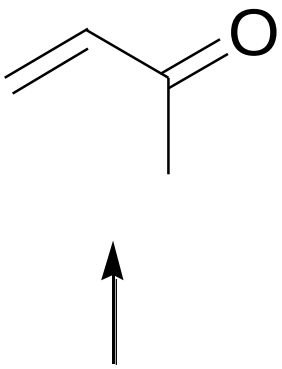
π → π* energy too high

⇨ not useful

n → π* in the UV region but with small ε

⇨ not allowed transition

For acetone: λ_{max} = 280 nm (ε = 15)

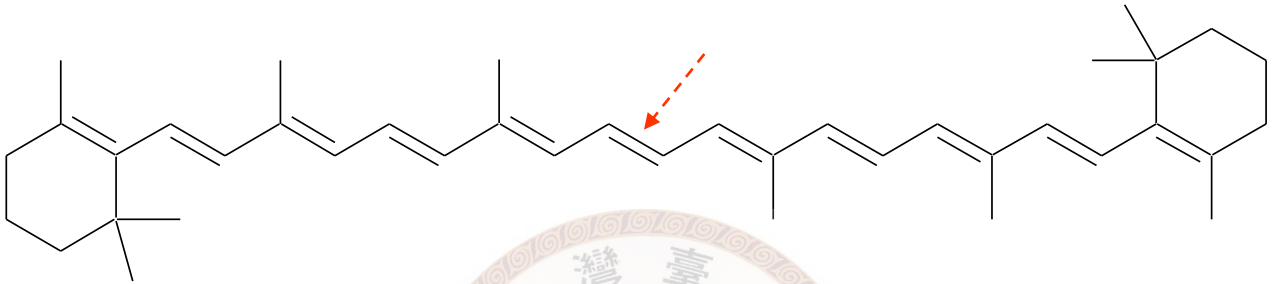


A conjugated enone

$n \rightarrow \pi^* \lambda_{max} = 324$ nm ($\varepsilon = 24$)

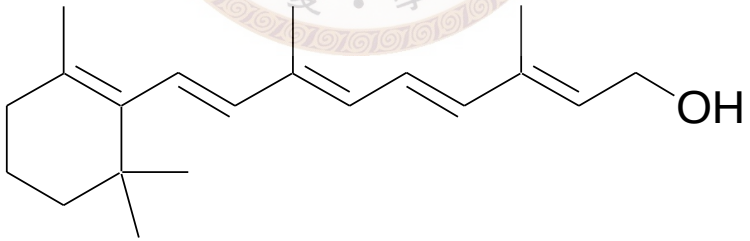
$\pi \rightarrow \pi^* \lambda_{max} = 219$ nm ($\varepsilon = 3600$)

※ Visual connection



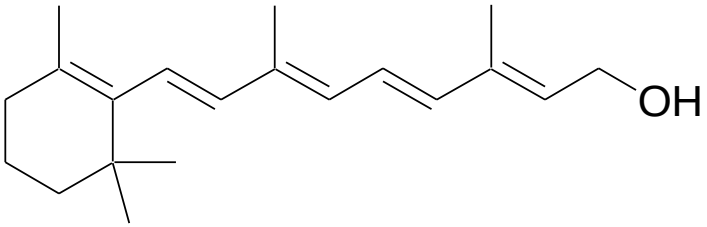
β-carotene

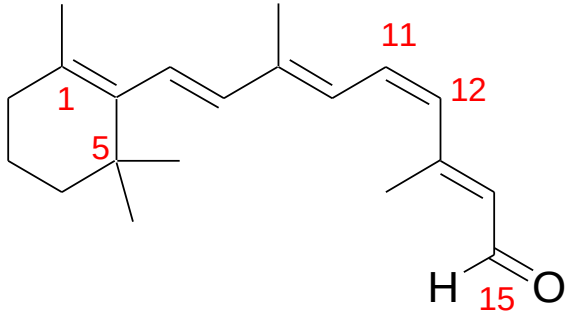
enzyme-catalyzed cleavage and reduction in the liver



retinol (vitamin A)

λ_{max} = 325 nm (ε = 50,000)

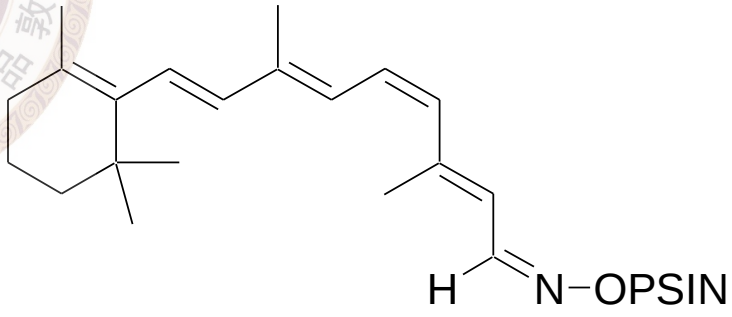




11-*cis*-retinal

(λ_{max} = 380 nm)

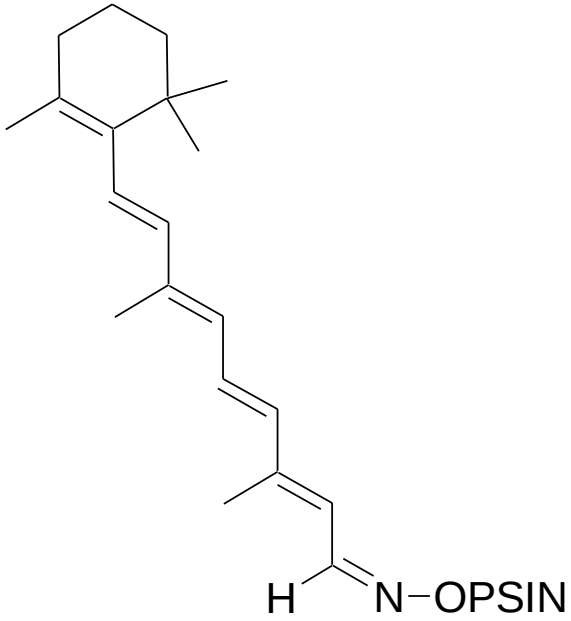
H_2N−OPSIN



rhodopsin
(visual purple)

light

nerve
impulse



metarhodopsin II

Isomerization rate: within 2 x 10^{-13} s