Diffusion of Small Molecules in Edible Films:

Effect of Water and

Interactions between Diffusant and Polymer

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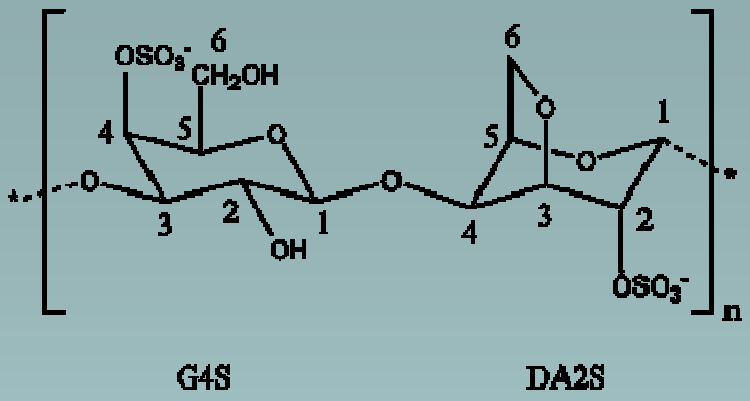
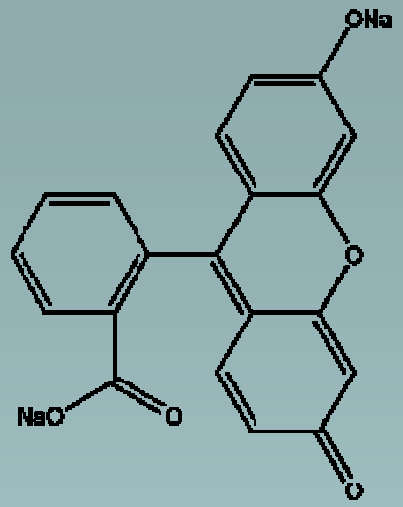
Material



Iota-carrageenan

(linear polymer ~25000 galactose units, double helices association)



Fluorescein

$C_{20}H_{12}O_5Na_2$ (376 g.mol^{-1})

Solvent (Water)
+ Carrageenan : 3 %
+ Fluorescein : 3µM

→ **Film-forming solution** (pH~7) → Casting

↓

Drying
(solvent evaporation / polymerization)

↓

Film (dried carrageenan gel)

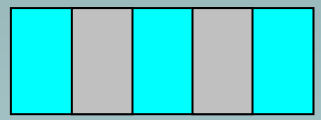
FRAP: Fluorescence Recovery After Photobleaching

- ✓ Principle

Bleachable fluorescent dye

Before bleaching: uniform concentration

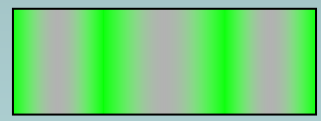
Interference fringe pattern



Bleach (t~500ms)

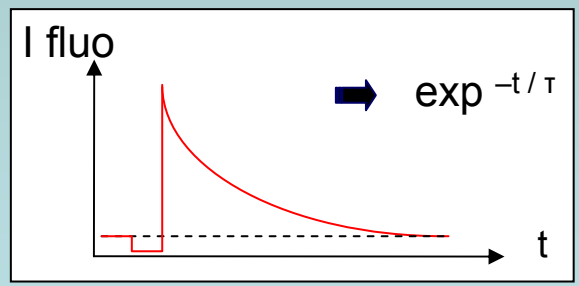
Concentration profile

t=0



t

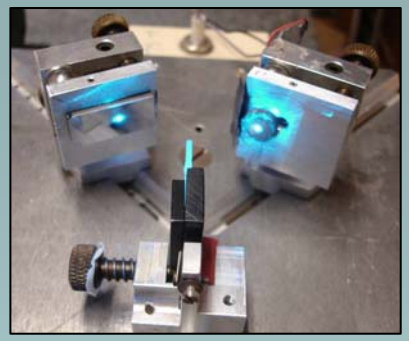
Inversed I_F recovery signal



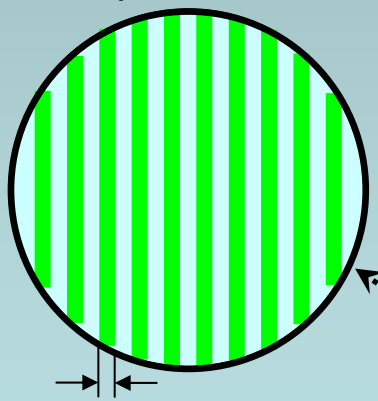
- ✓ Application: Measurement of the diffusion coefficient of fluorescein introduced in a carrageenan-based film

M : mirrors
MPZ : mobile mirror, piezoelectric controlled
Fi : band pass filter (centered at 520 nm)
PMT = photomultiplier tube

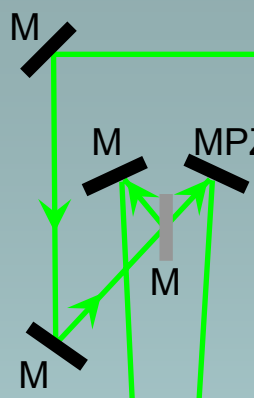
Experimental setup



Interference pattern

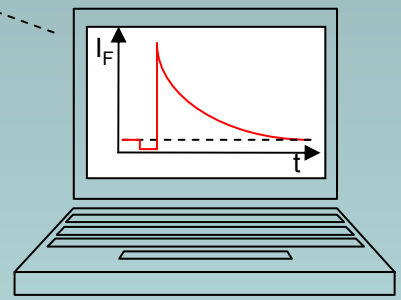


i = fringe spacing
(2-100µm)



Modulation (MPZ):
fringes ± i/2
at frequency f_0

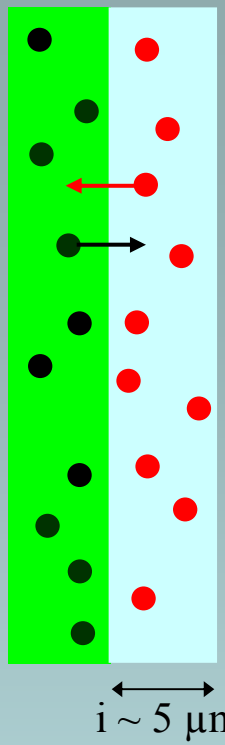
Argon Laser
(λ = 488 nm)



I_F = Fluorescence Intensity

I_F signal
at frequency 2 f_0

Fi
PMT
Lock-in amplifier
Sample



Mesurement of $D_{fluorescein}$

- Mesoscopic scale (>µm)
- Translational diffusion
- Dye molecular weight close to sucrose

$$\frac{\delta C}{\delta t} = D\frac{\delta^2 C}{\delta x^2}$$

Translational Diffusion
Fick's 2nd law

Solution of Fick's equation in this system
with a sinusoidal fringe interference modulation:

$$C = C_0 \cdot \exp^{-Dq^2 t}$$

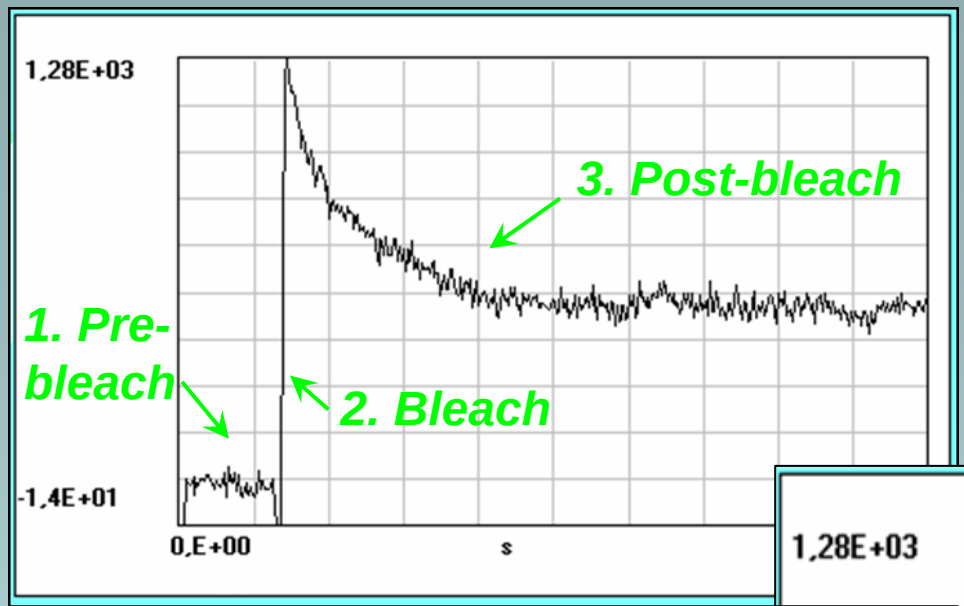
C_0 = Fluorescein initial concentration (immediately after photobleaching)

D = translational diffusion coefficient ($m^2.s^{-1}$)

q = wave vector (m^{-1})

t = time (s)

Experimental FRAP data analysis

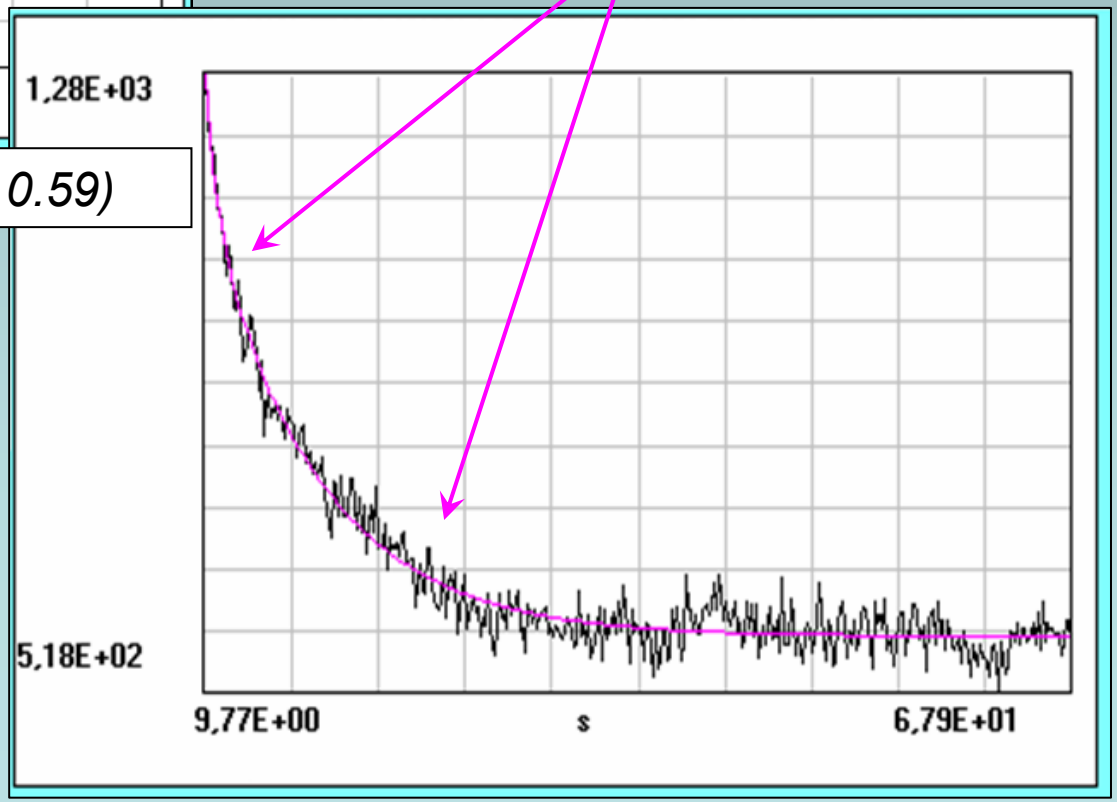


Example: carrageenan film (aw = 0.59)

Fit:

$$I(t) = A1 \cdot \exp^{-t/\tau 1} + A2 \cdot \exp^{-t/\tau 2} + B$$

Bi-exponential



I = Fluorescence intensity

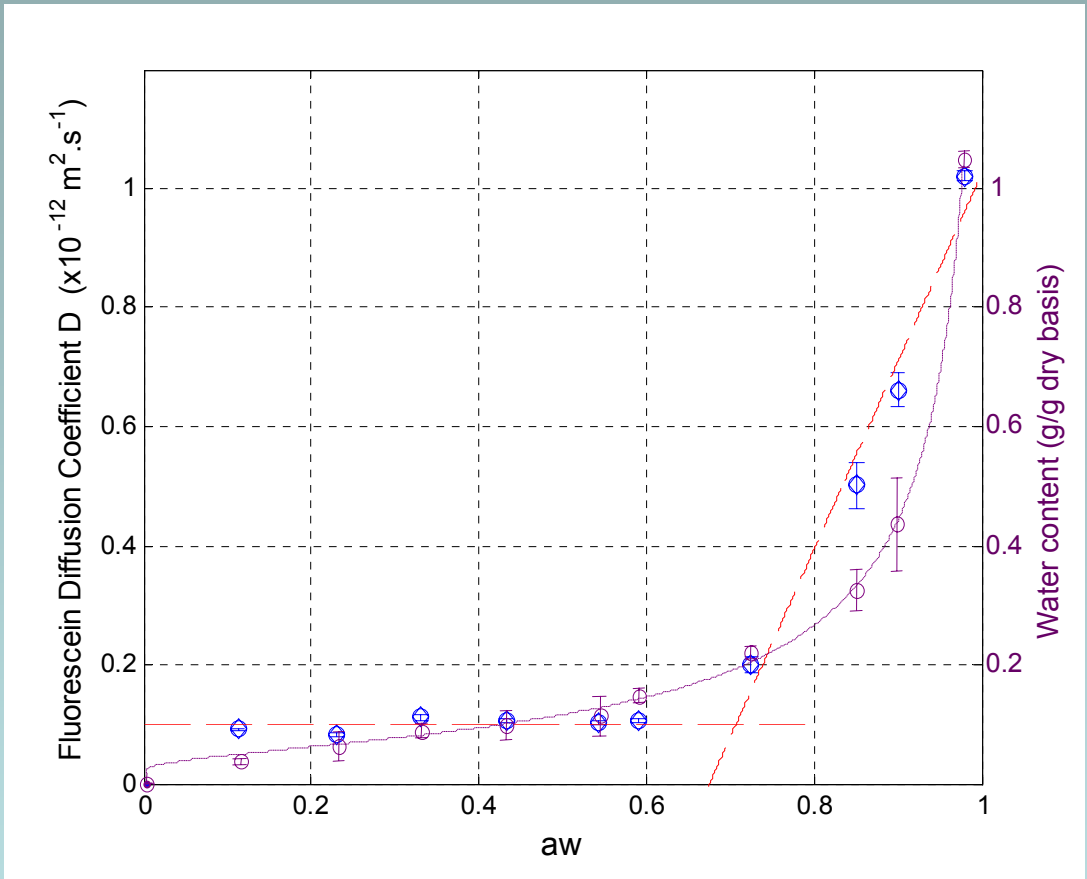
5 unknown parameters:

A1 & A2 = amplitude

$\tau 1$ & $\tau 2$ = time constant of D

B = I_F basis

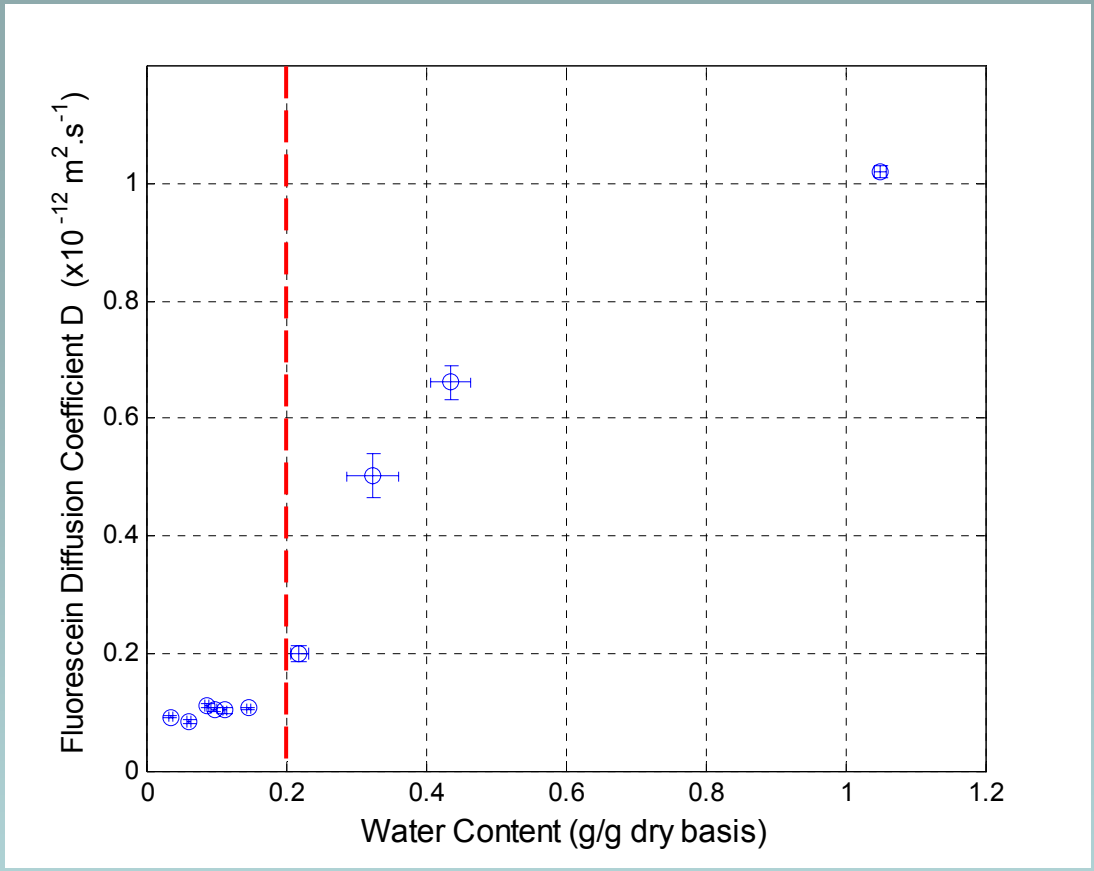
How does D vary with the film hydration level ?



Carrageenan films
0.11 < aw <0.98

Estimation of D on t~60s

Sorption isotherm of iota-carrageenan film (fitted with Ferro-Fontan model)



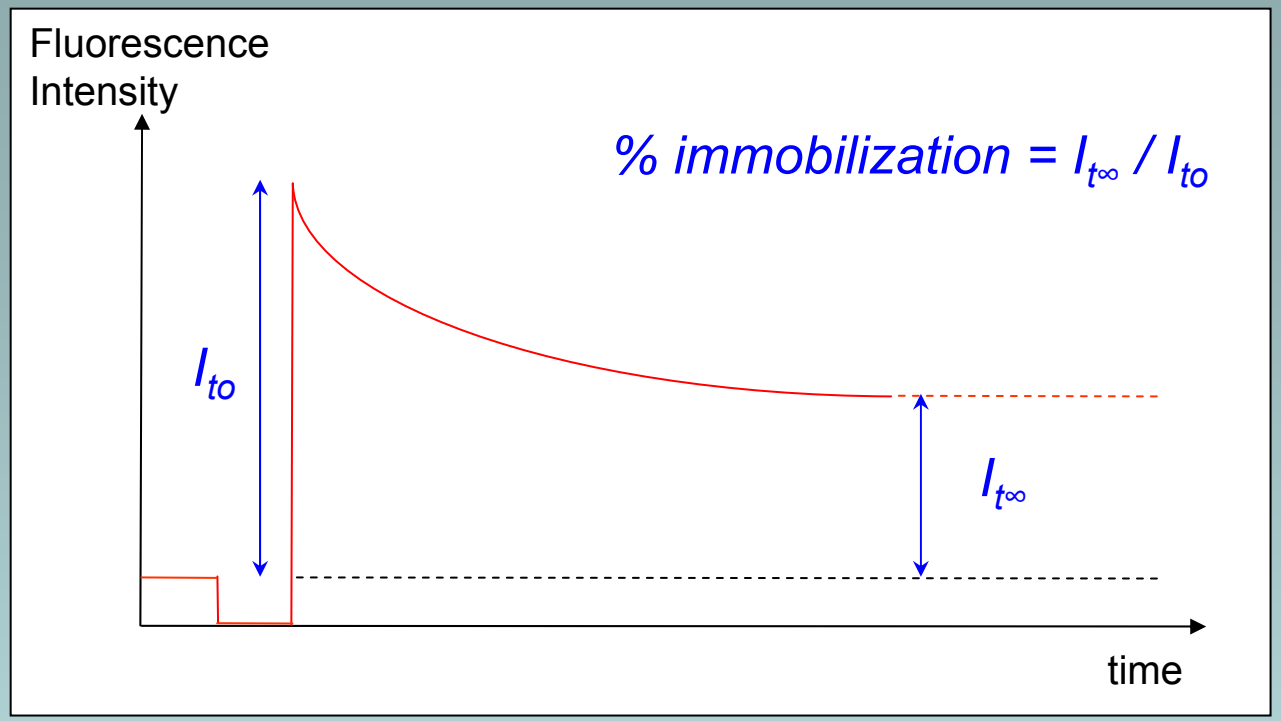
- ✓ Water content threshold effect on diffusion:

  < 0.2 (aw = 0.1 to 0.6) : D ~ constant ~ 10^{-13} $m^2.s^{-1}$

  > 0.2 (aw > 0.7) : D increases up to 10^{-12} $m^2.s^{-1}$

- ✓ The polymeric network becomes more and more permeable

Matrix effect on molecular mobility ?



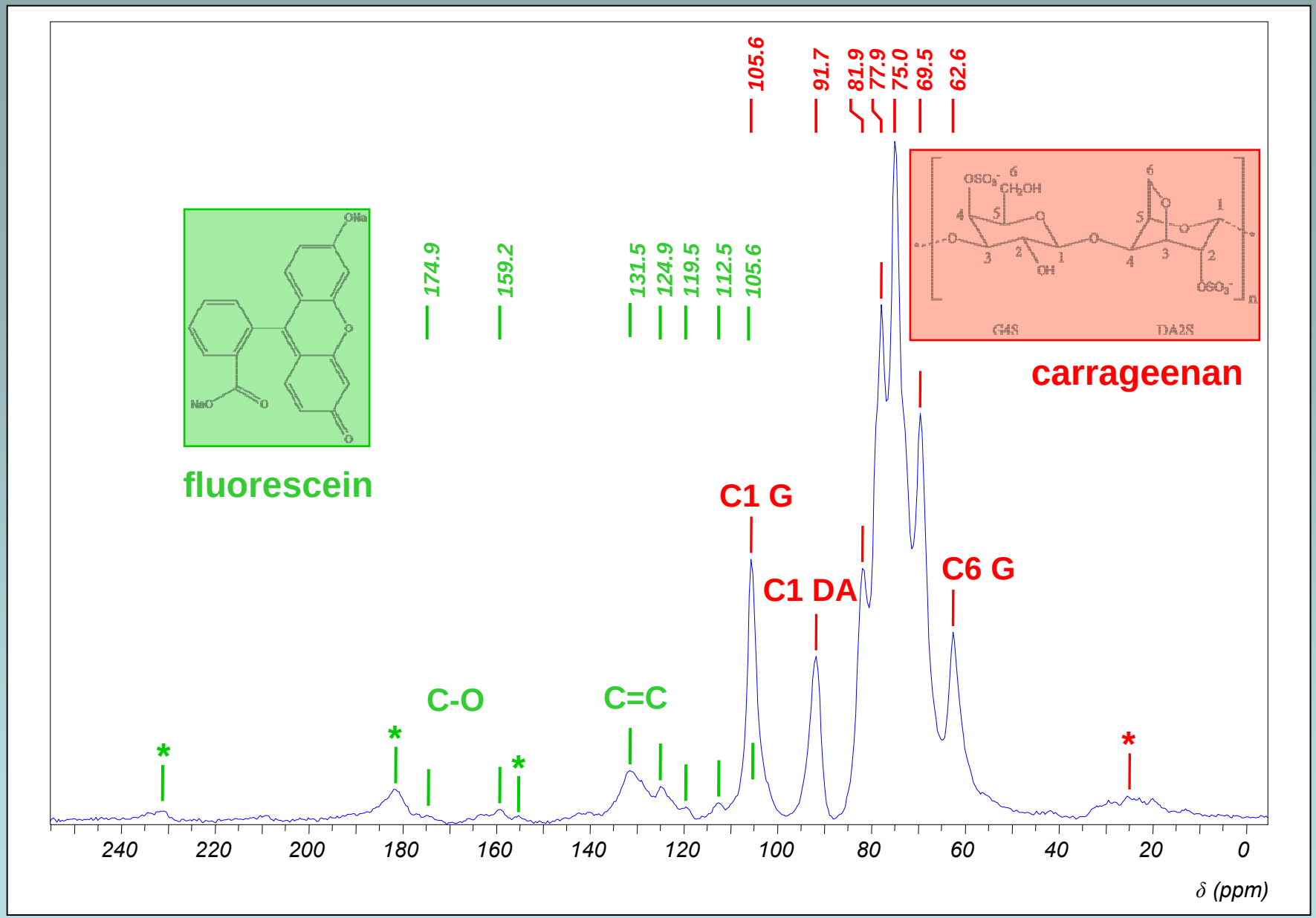
- ✓ Estimation of a fluorescein fraction immobilized within the matrix = $I_{t\infty}$ / I_{to}
- ✓ 50 to 60% immobilized for aw = 0.1 to 0.7
- ✓ Then 40% for aw=0.8, 30% for aw=0.9 and 0% for aw=0.98 : total mobility

Polymer / diffusing molecule interactions

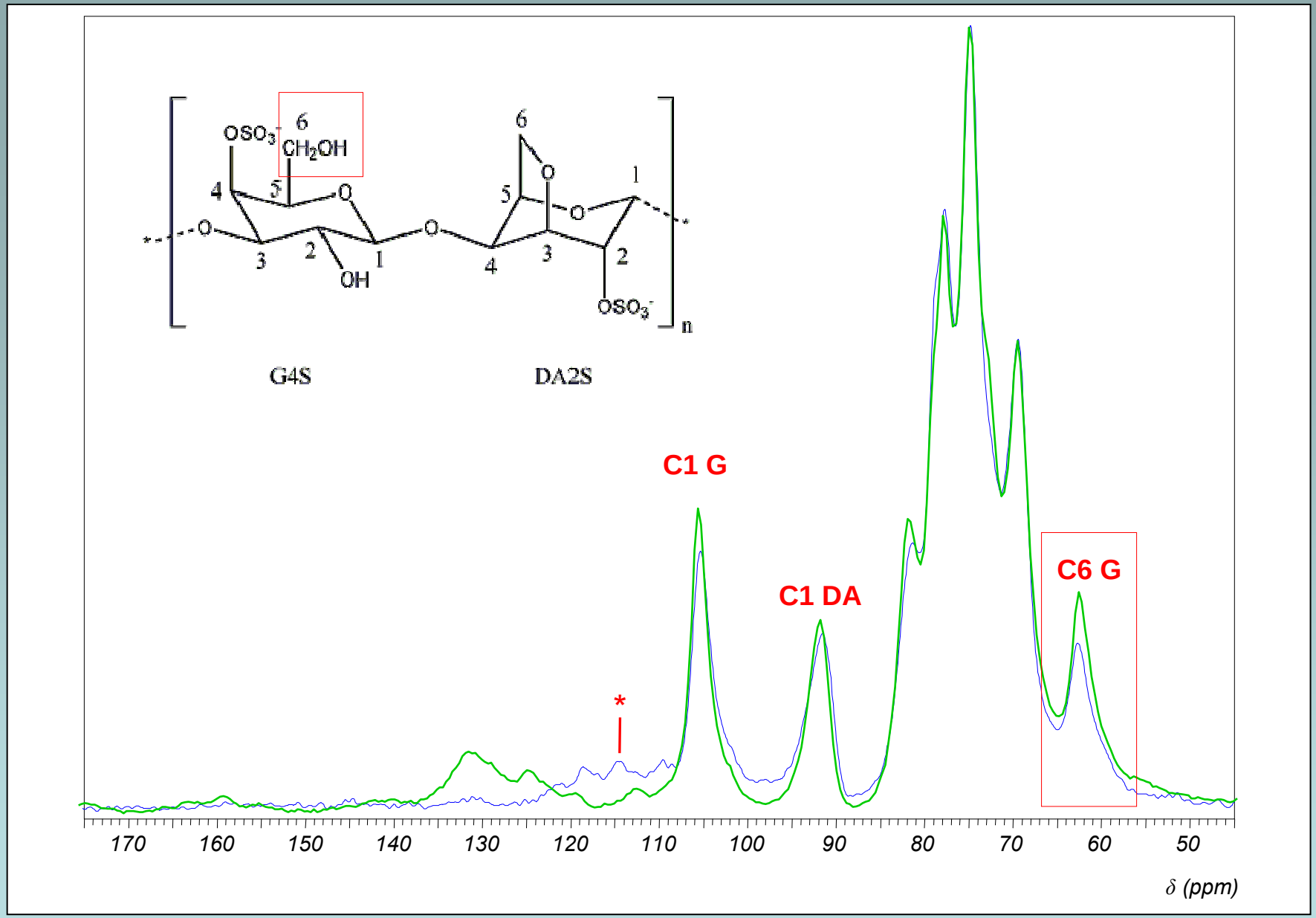
Weak interactions between carrageenan & fluorescein ?
AND / OR steric hindrance
responsible for molecular immobilization ?

Study of interactions carrageenan – fluorescein
by high resolution solid state NMR

Material : Bruker DSX 400 MHz spectrometer



^{13}C CPMAS spectrum of **carrageeanan film with 10% (w/w) fluorescein**
(Spinning side bands are identified by *)



^{13}C CPMAS spectrum of **carrageenan film with 10% (w/w) fluorescein** and **carrageenan film** spectrum

(Spinning side bands are identified by *)

Conclusions :

- ✓ FRAP : Rapid, direct and non destructive measurement of translational D
- ✓ Need of a bleachable fluorescent dye
- ✓ Knowledge of film permeability to small molecules under various environmental conditions (RH, T)
- ✓ Investigation of interactions between polymer and diffusant by NMR
- ✓ Interest for application to controlled release studies

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