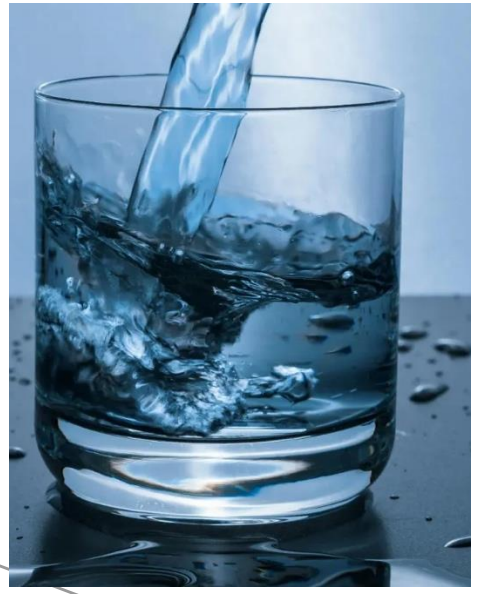
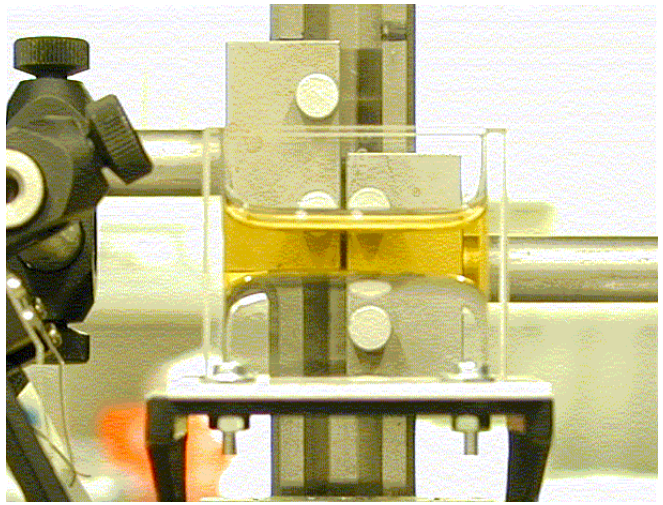
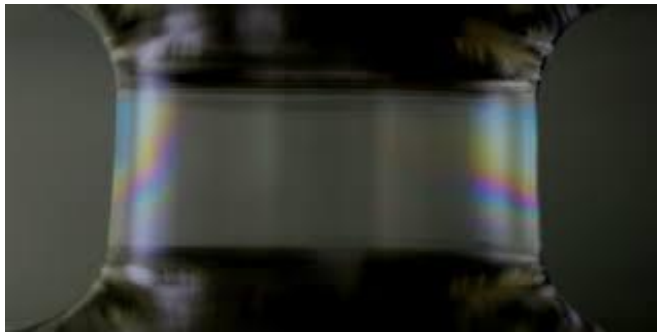
Sonder l'organisation des liquides par generation de second harmonique

Emmanuel Benichou *emmanuel.benichou@univ-lyon1.fr*

Institut Lumière Matière, Equipe Liquides et Interfaces, Université Lyon 1







[Bonhomme, PRL (2013)]

Quantique ???

Réunion Initiative Quantique, Villeurbanne 2025

Sonder les propriétés des liquides: du volume et aux interfaces

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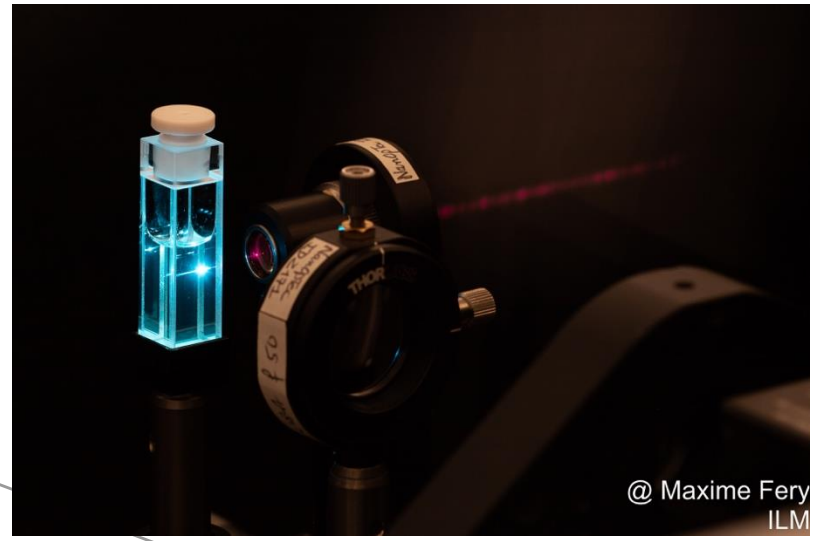
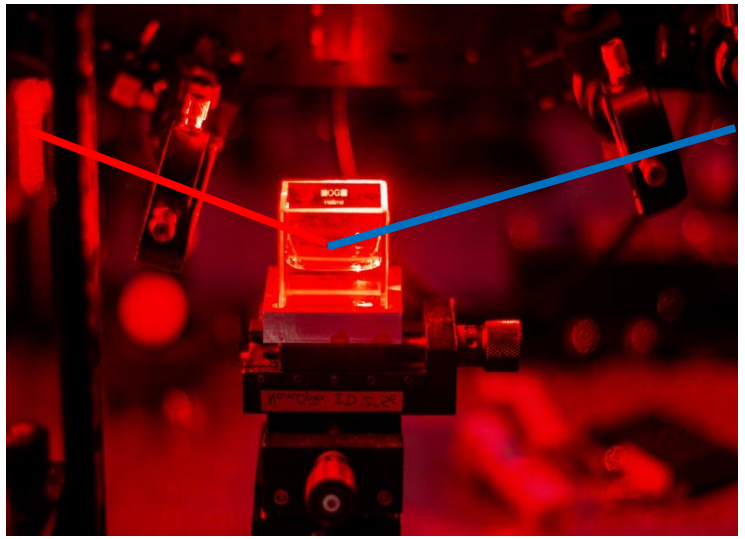
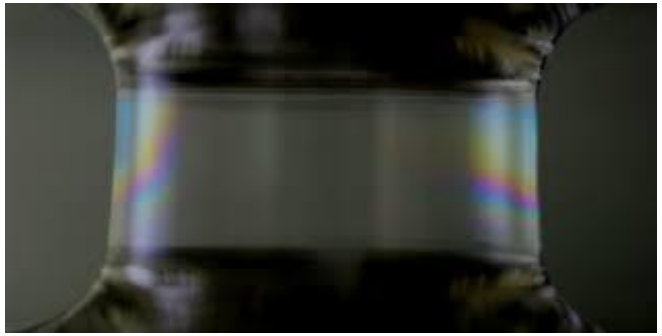




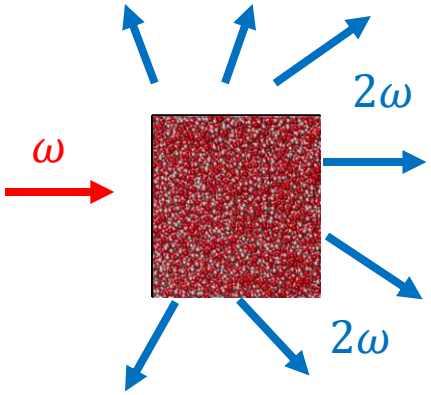


[Bonhomme, PRL (2013)]

Objectif : sonder l'organisation des liquides et des interfaces à l'échelle moléculaire

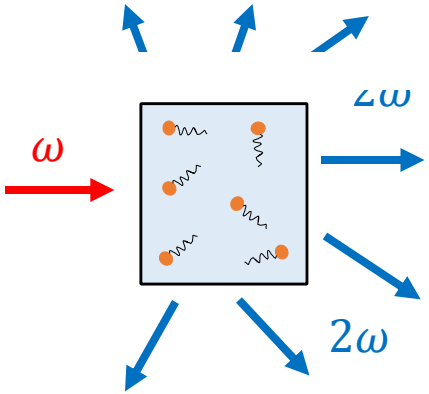
Objets d'étude

Liquides purs



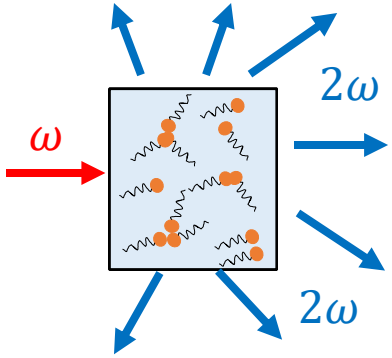
Solutions aqueuses

Surfactants, electrolytes, …

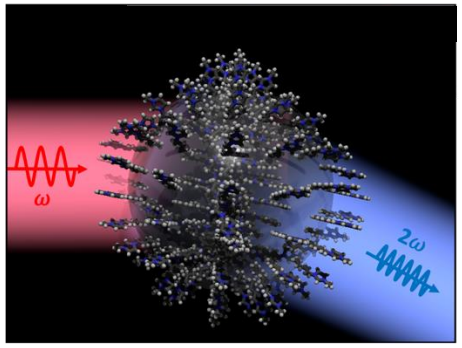


Systèmes moléculaires en interaction

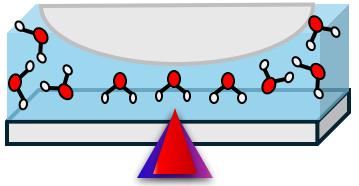
Micelles, electrolytes concentrés , …



Liquides ioniques

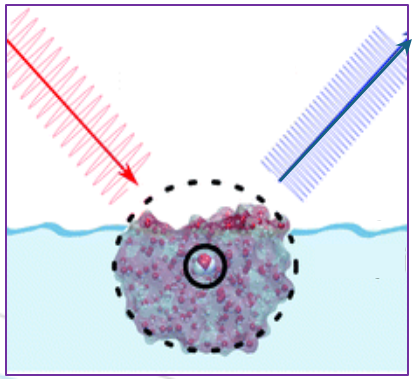


Liquides confinés



interfaces

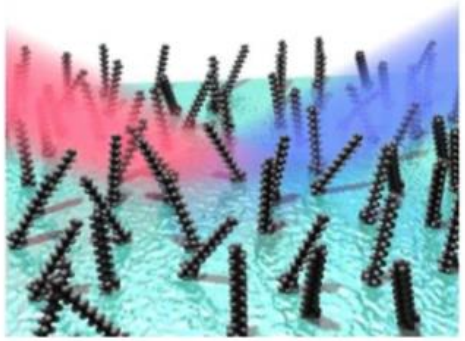
S-SHG à l'interface air/eau



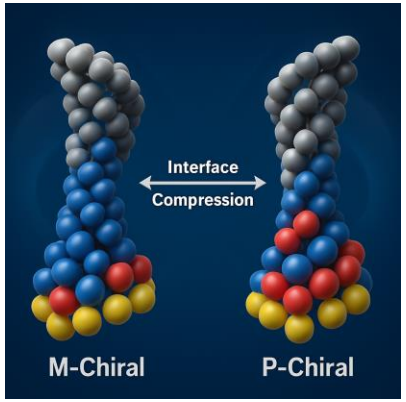
Films moléculaires

Films à l'interface air/eau

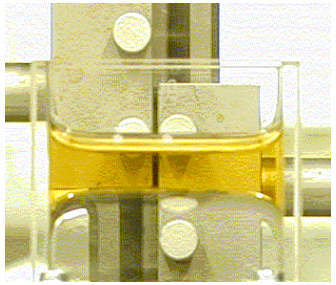
Interfaces savonnées,



Chiralité supramoléculaire

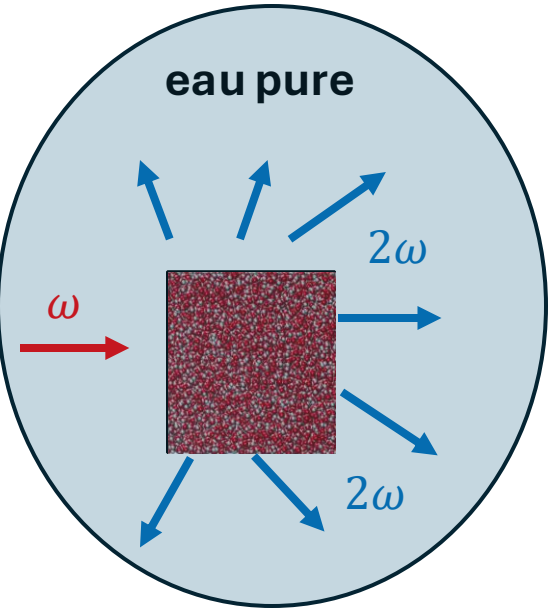


Interfaces liquide/liquide



Objets d'étude

eau pure



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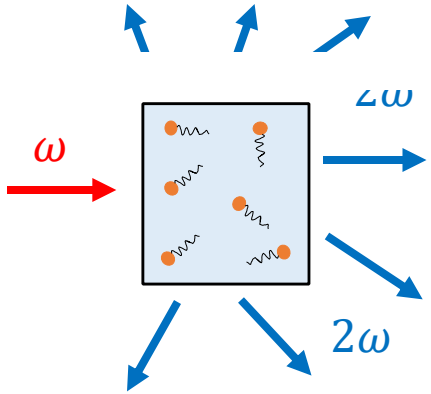

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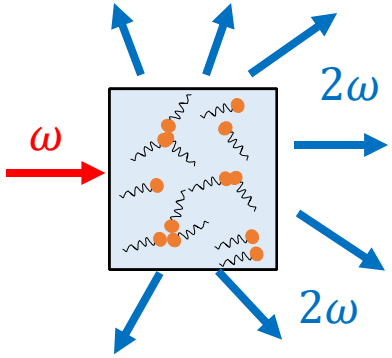
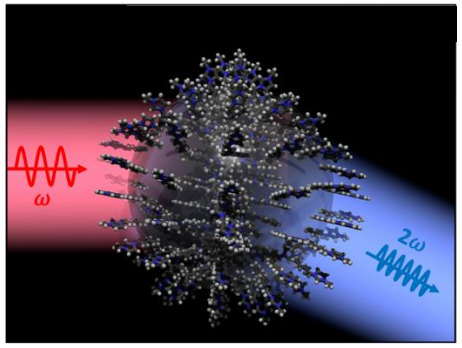


Liquides ioniques



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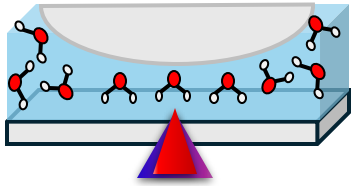

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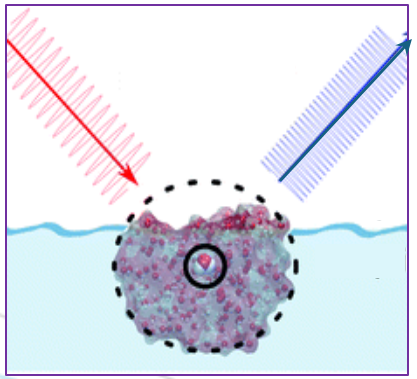

Films moléculaires

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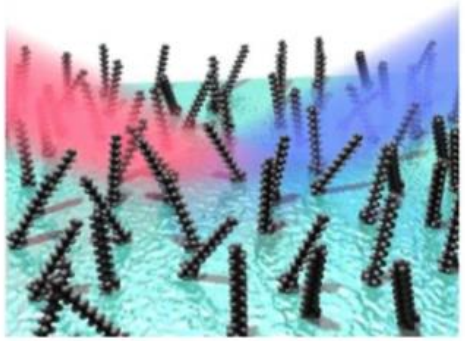

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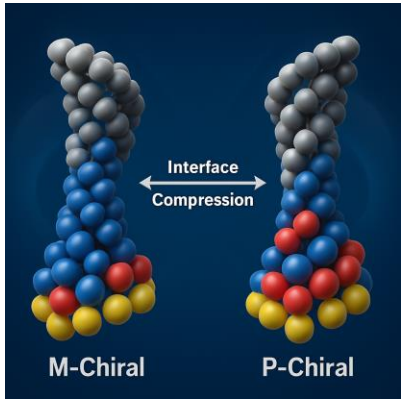
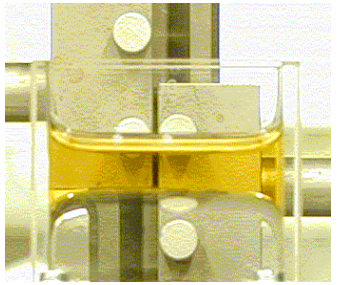
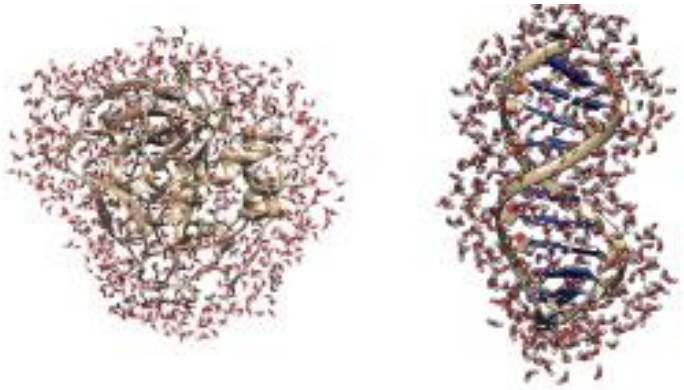


Interfaces liquide/liquide



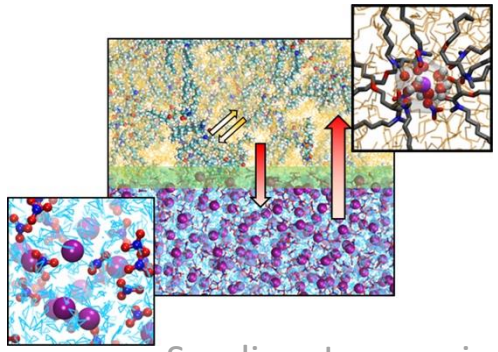
Pourquoi sonder sonder l'organisation des liquides?

Solvatation des molécules



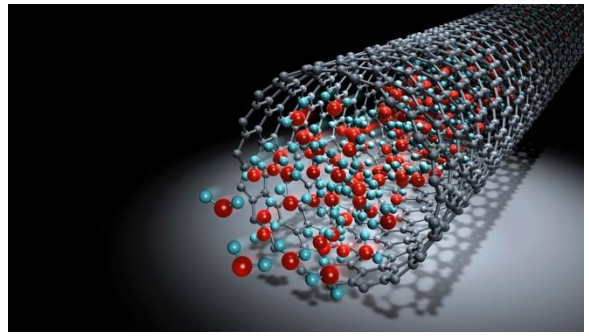
Laage, Chem. Rev., 2017

Extraction liquide/liquide

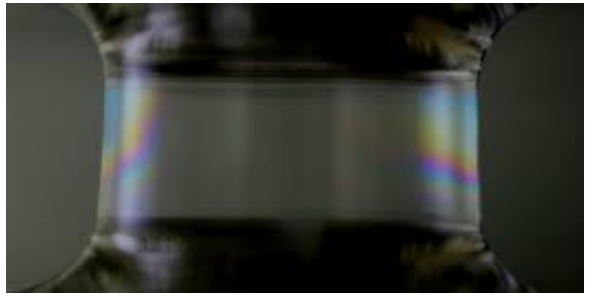


Spadina, Langmuir, 2021

Nanofluidique

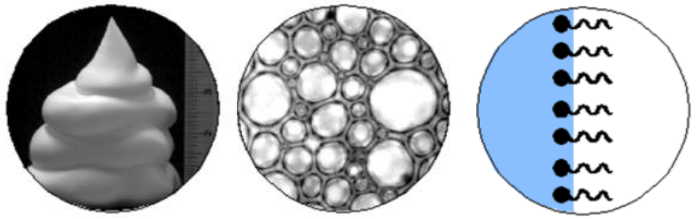


Bocquet, Pour la science, 2022



[Bonhomme, PRL (2013)]

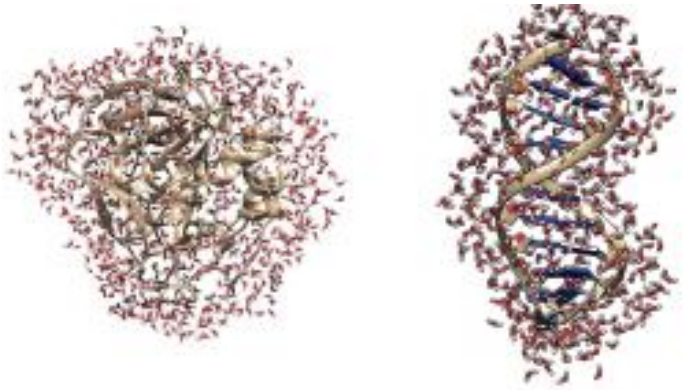
Mousses et interfaces savonnées



Les mousses: Structure et dynamique

Pourquoi sonder sonder l'organisation des liquides?

Solvatation des molécules



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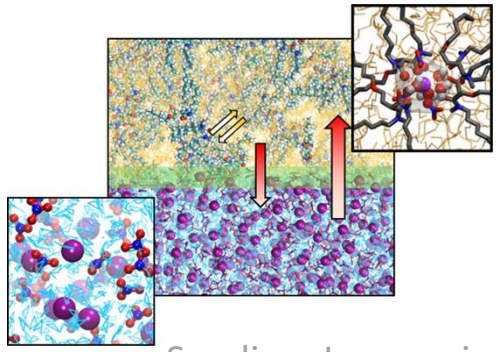
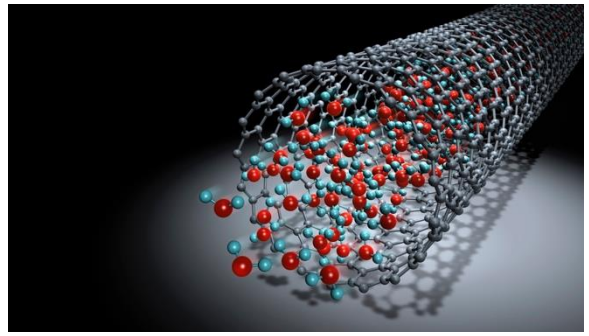


Spadina, Langmuir, 2021

Nanofluidique



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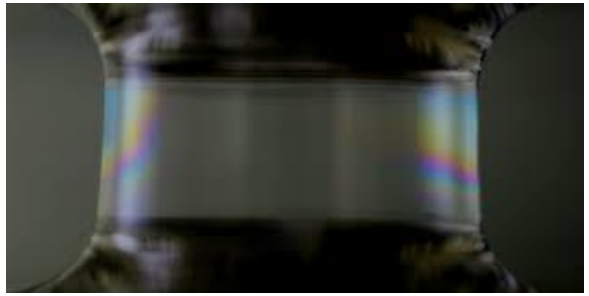

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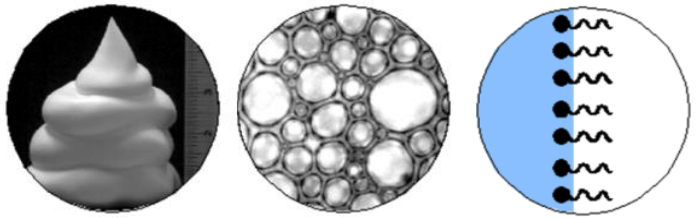
Mousses et interfaces savonnées



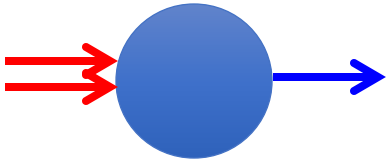
Les mousses: Structure et dynamique

Outils non-invasifs pour sonder cette organisation

→ Génération de second harmonique (SHG)

Génération de second harmonique

Processus de doublage de fréquence

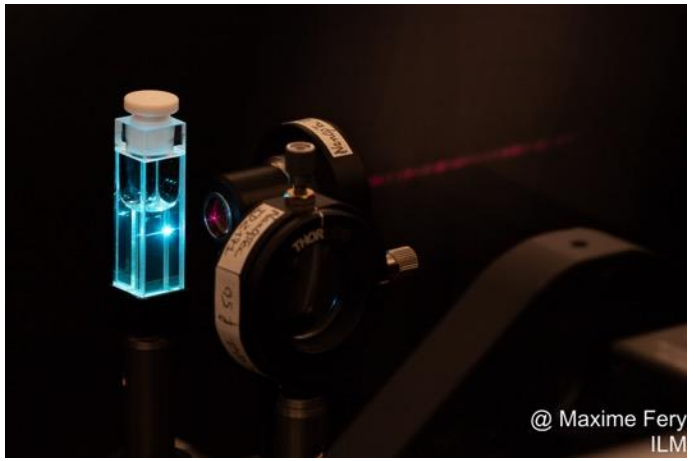


$$\omega + \omega \rightarrow 2\omega$$

$$\vec{P}_{NL}(\omega) = \varepsilon_0 \vec{\chi}^{(2)}(2\omega\ ;\omega\ ,\omega\ ) : \vec{E}_1(\omega)\vec{E}_2(\omega) + ...$$

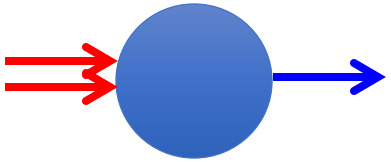
$$\chi^{(2)} \neq 0$$

Seulement dans les milieux non-centrosymétriques
(aux interfaces et dans le volume!)



Génération de second harmonique

Processus de doublage de fréquence



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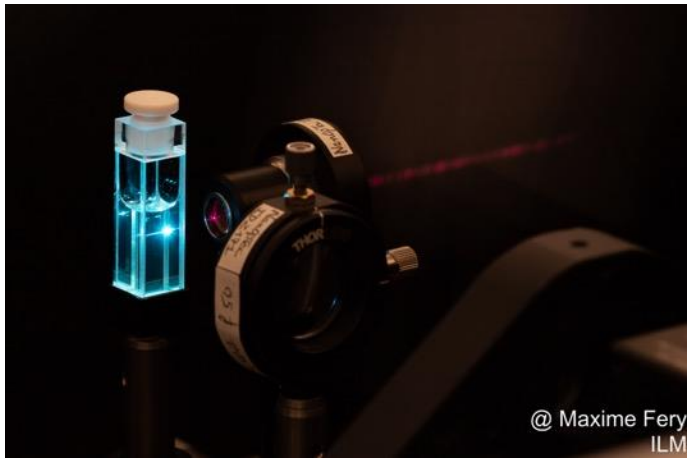


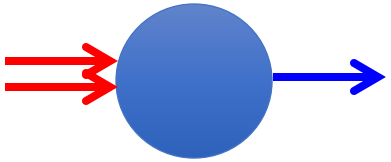
Surface Second Harmonic Generation (S-SHG)

Processus cohérent à l'interface

$\chi^{(2)}$

Génération de second harmonique

Processus de doublage de fréquence

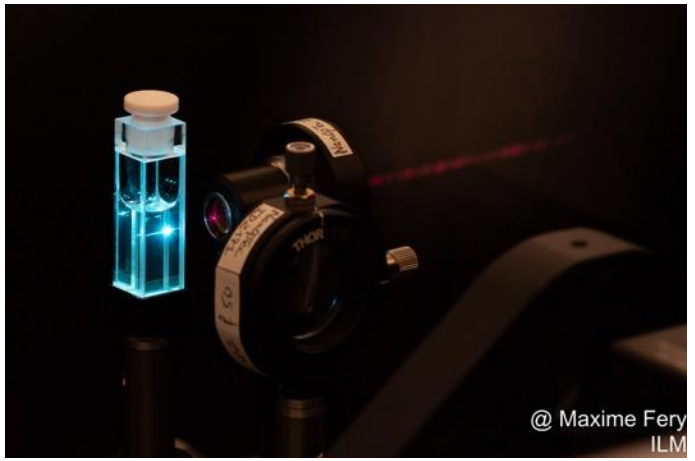


$$\omega + \omega \rightarrow 2\omega$$

$$\vec{P}_{NL}(\omega) = \varepsilon_0 \vec{\chi}^{(2)}(2\omega\ ;\omega\ ,\omega\ ) : \vec{E}_1(\omega)\vec{E}_2(\omega) + ...$$

$$\chi^{(2)} \neq 0$$

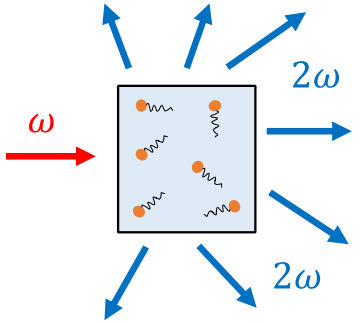
Seulement dans les milieux non-centrosymétriques (aux interfaces et dans le volume!)



Surface Second Harmonic Generation (S-SHG)

Processus cohérent à l'interface

Hyper-Rayleigh Scattering (HRS)
Second Harmonic Scattering (SHS)

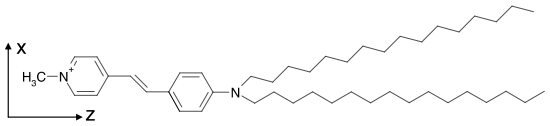


Processus incohérent: les molécules sont distribuées aléatoirement dans le volume (positions et orientations).

$$\chi^{(2)} \propto N\beta^{(2)}\langle T \rangle$$

$\chi^{(2)}$ $\beta^{(2)}$

D'une réponse purement incohérente …



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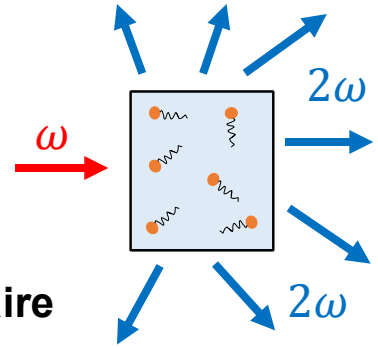
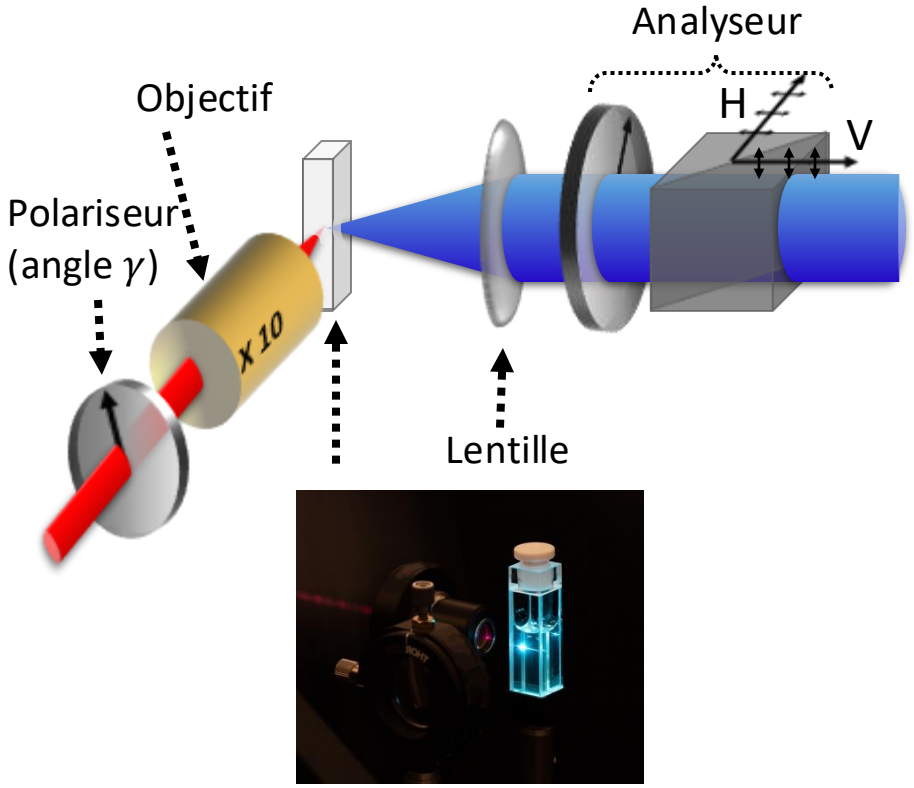
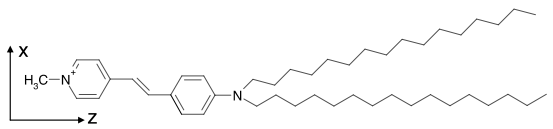


4 -(4-dihexadecylaminostyryl)-N-methylpyridinium iodide = DiA

Molécules « push-pull » → forte réponse non-linéaire



D'une réponse purement incohérente …



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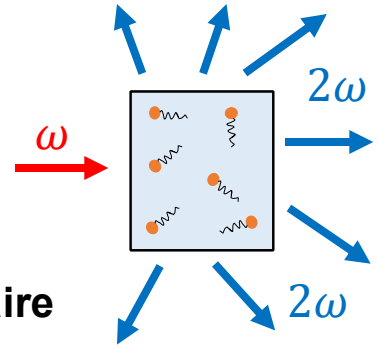

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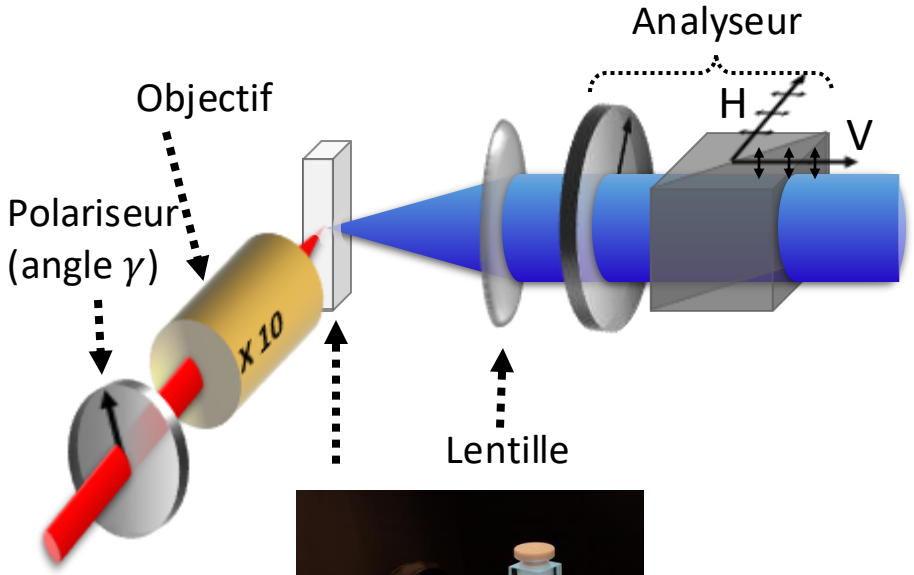
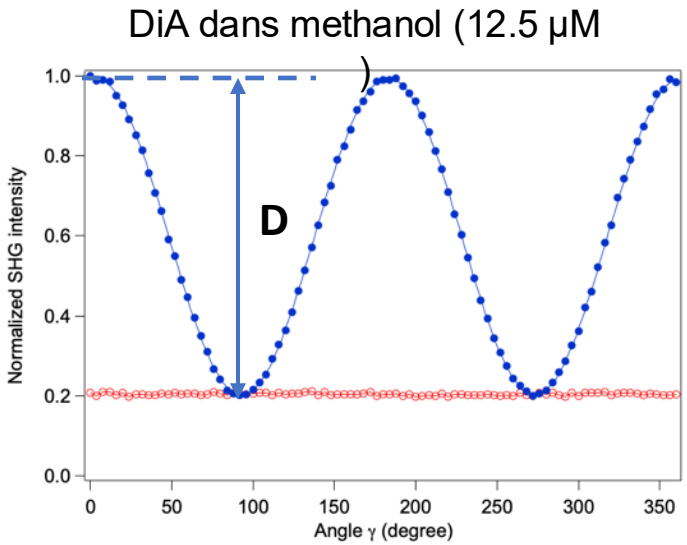
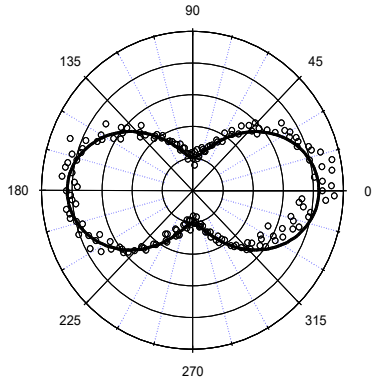


Rapport de dépolarisation

$$D = \frac{c}{a} = 0.203$$

(valeur théorique : 0.2)



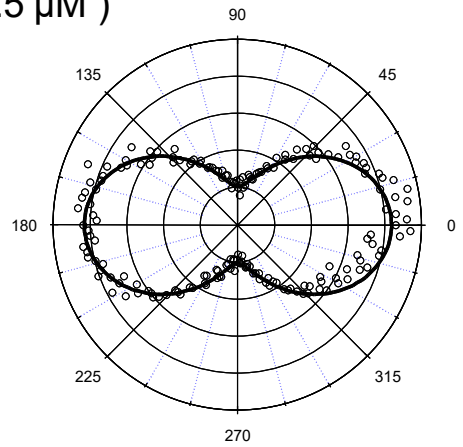


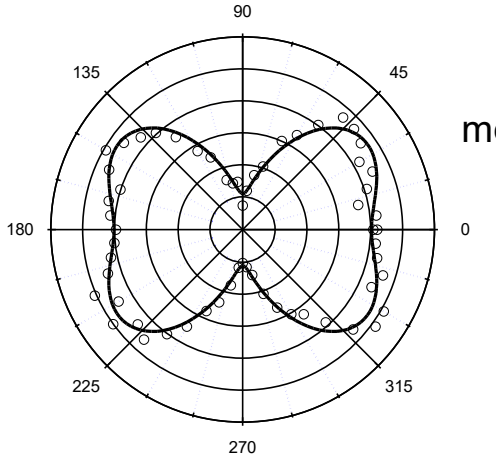
➡ Processus purement incohérent

G. Revillod el al., *J. Phys. Chem. C, 112,* 2716 (2008)

… à une réponse partiellement cohérente

DiA in methanol
(12.5 µM)

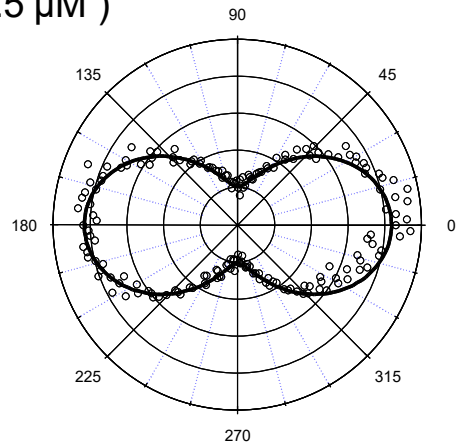




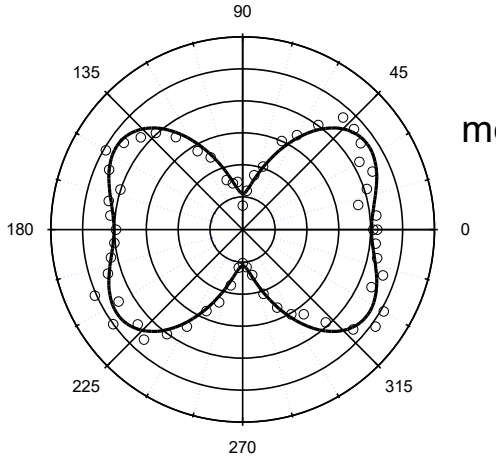
DiA in water-methanol (5:1) v/v
(12.5 µM)

… à une réponse partiellement cohérente

DiA in methanol
(12.5 µM)

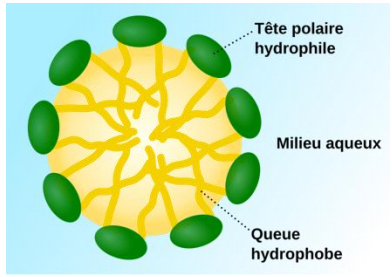


Molécules dispersées

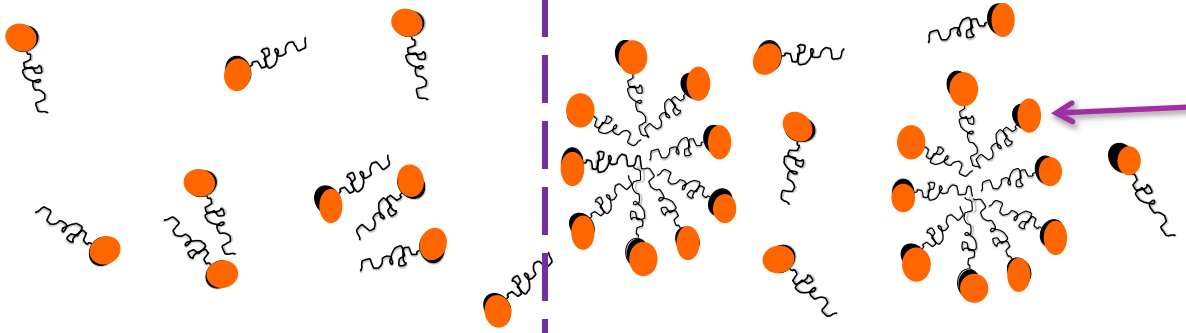


DiA in water-methanol (5:1) v/v
(12.5 µM)

40 % of micelles

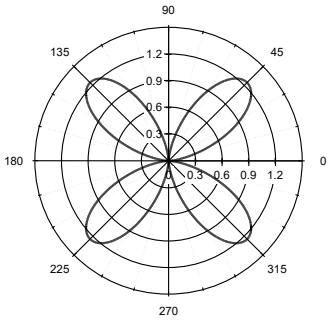


CMC



Concentration

Pure Micelles



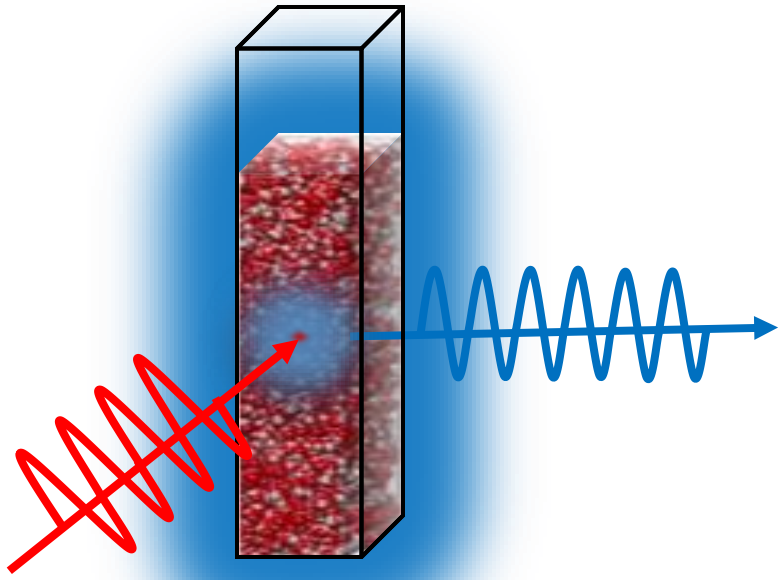
G. Revillod el al., *J. Phys. Chem. C, 112,* 2716 (2008)

Mise en évidence d'agrégats (organisation à l'échelle nanométrique)

Génération de second harmonique de l'eau

Peut-on obtenir une information de l'organisation à l'échelle moléculaire?

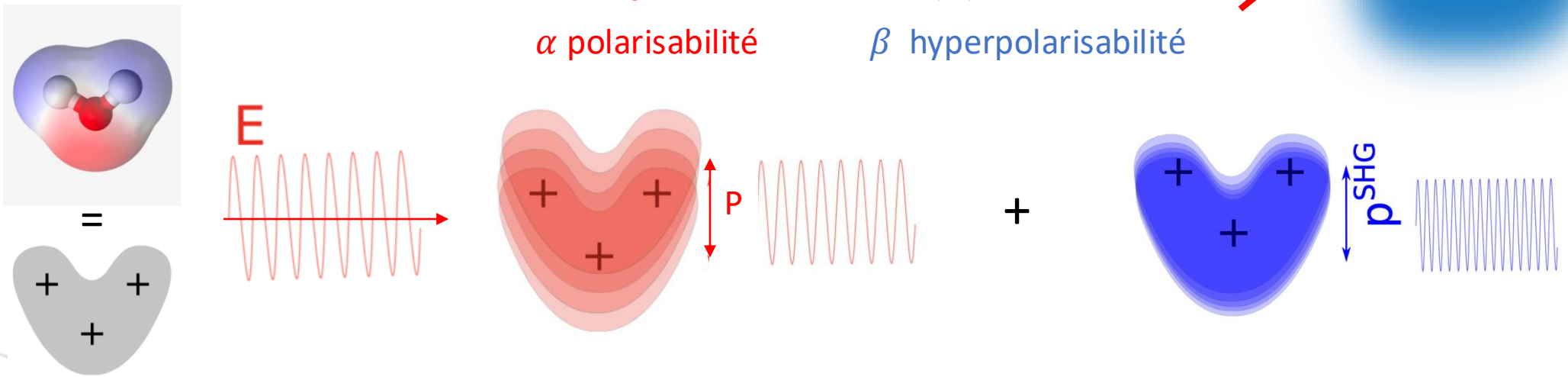
Génération de second harmonique dans un liquide
- Second Harmonic Scattering (SHS) -



A l'échelle moléculaire

$$\vec{p} = \overrightarrow{\mu_0} + \alpha(\omega)\vec{E}(\omega) + \beta(\omega)\vec{E}(\omega)\vec{E}(\omega)$$

α polarisabilité β hyperpolarisabilité

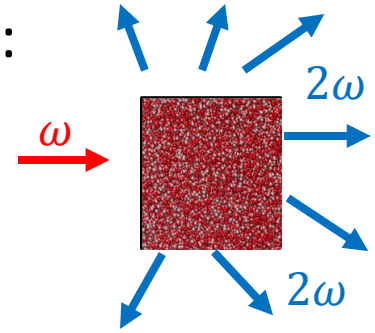


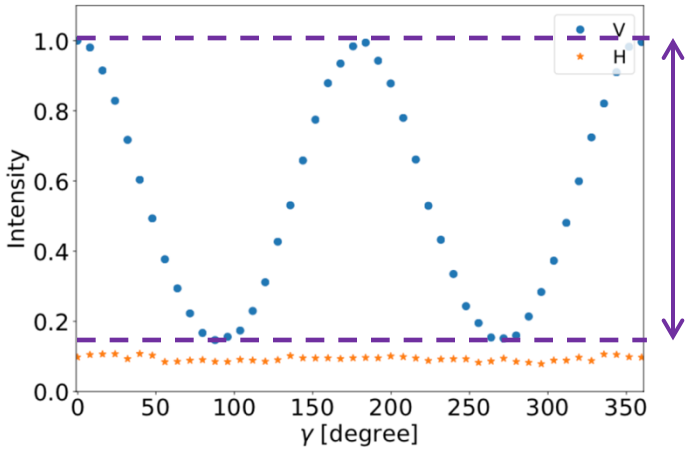
Problème difficile : Phase condensée / Intensité SHG faible (réponse non-résonante)

Génération de second harmonique de l'eau

[Le Breton, JPCL (2023)]

- Intensité SHS de l'**eau pure**
  - Expérimentallement:





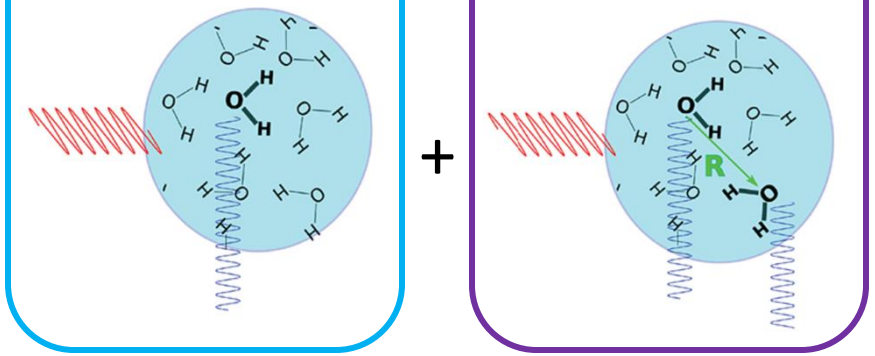
Rapport de dépolarisation
D = 0.14 ± 0.01

  - Numériquement

$$\vec{P}^{SHG} = \sum \overrightarrow{\mu^n} \text{ with } \overrightarrow{\mu^n} = \frac{1}{2}\beta^n : \overrightarrow{E(\omega)}\,\overrightarrow{E(\omega)}$$

$$\Rightarrow I \propto \sum_n (\beta^n)^2 + \sum_{n \neq m} \beta^n \beta^m \, exp[i\Delta q . r_{nm}]$$

$=$ Terme incohérent $+$ Terme cohérent



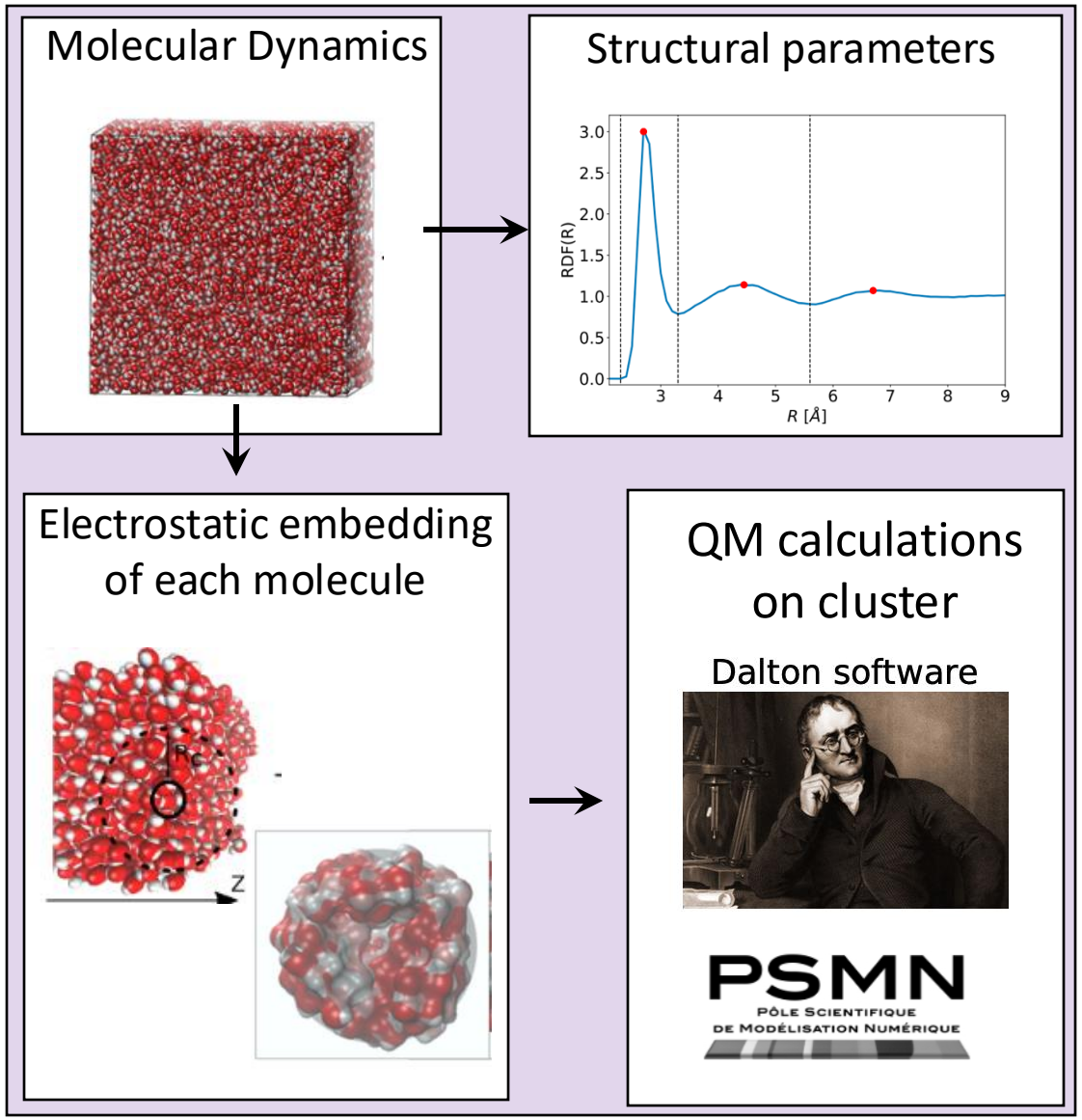
Modéliser la réponse SHS: calculs QMMM

FROG

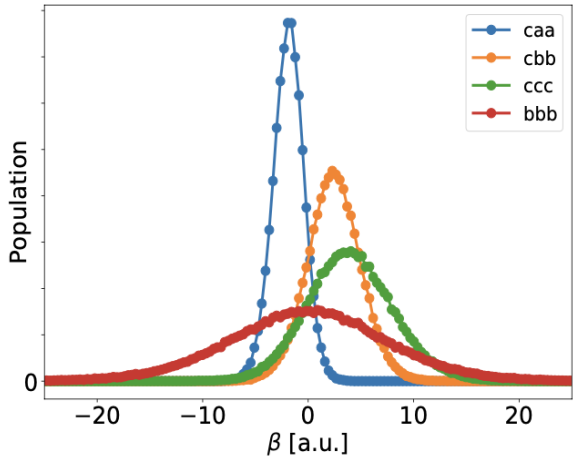
FROm molecular dynamics
to second harmonic Generation

Home-made Python code
Available on demand

Coll. C. Loison, iLM



Hyperpolarisabilités $(\beta, \gamma, \ldots)$



- Large fluctuations de β dans la phase liquid Tocci, JPCL, 2016

effets important du milieu environnant

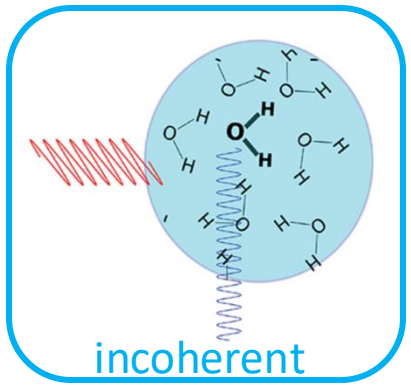
- Effets électrostatiques longue distance (4nm)

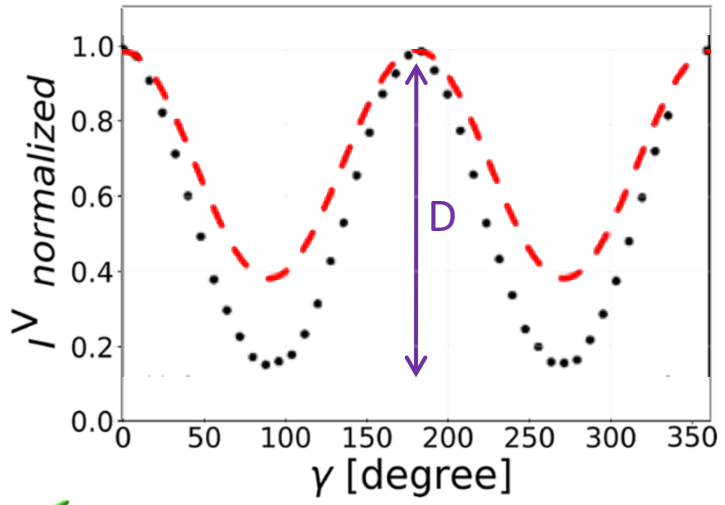
[Le Breton, PCCP (2022)]

Modéliser la réponse SHS de l'eau

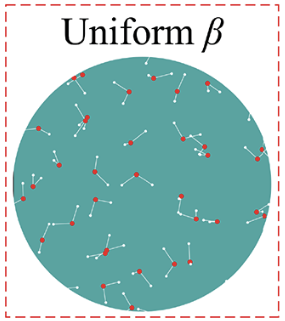
[Le Breton, JPCL (2023)]

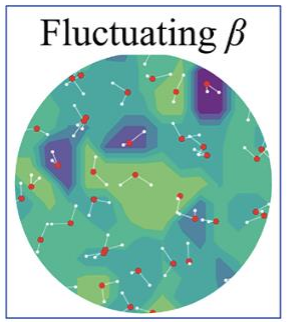
Intensité SHS =

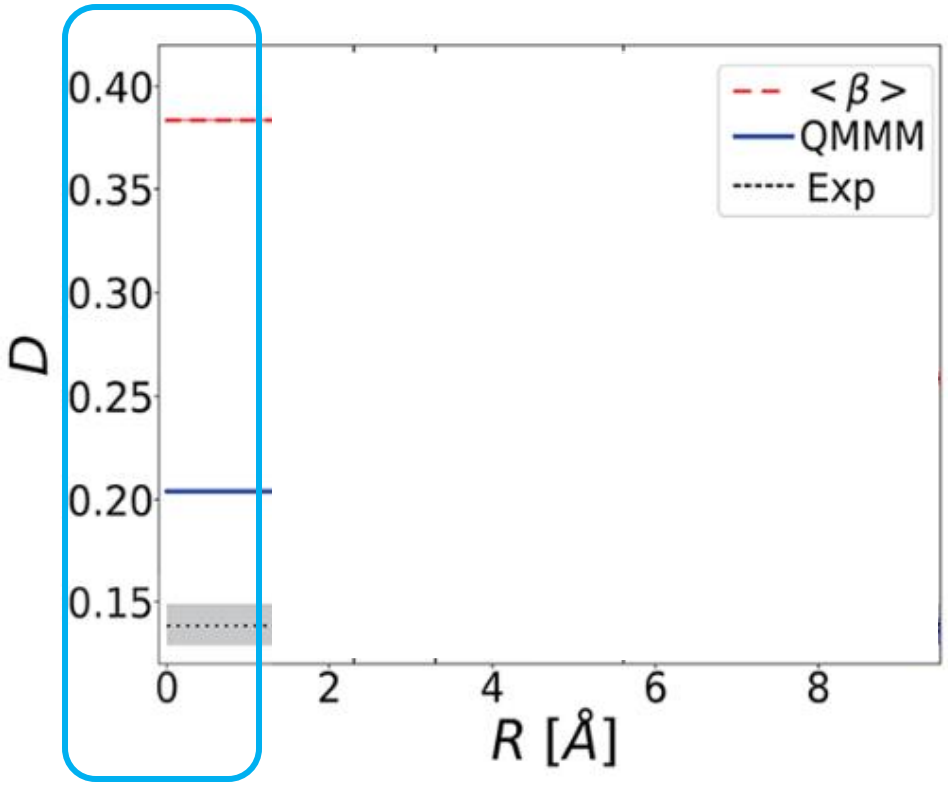




Exp.
< β >, incoherent





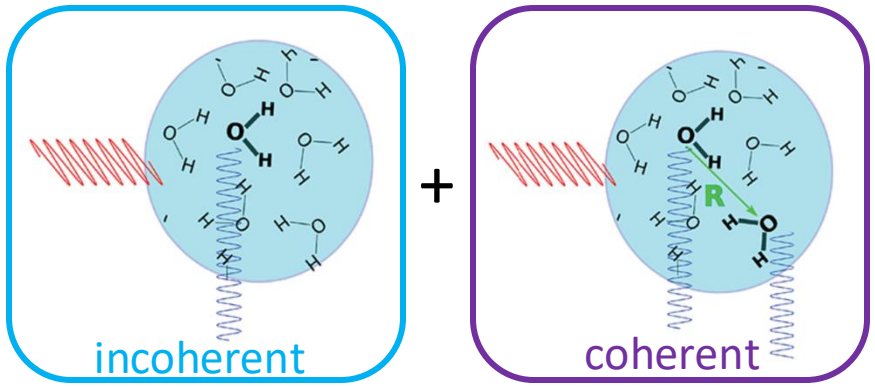


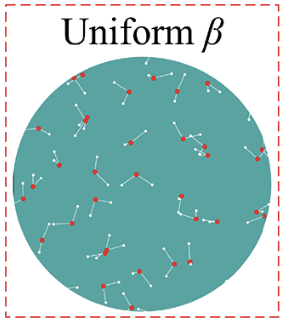
rôle important des fluctuations de β

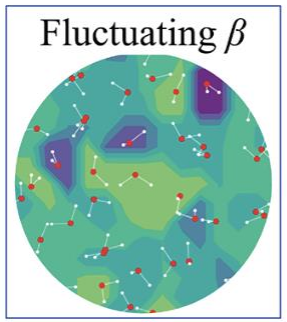
Modéliser la réponse SHS de l'eau

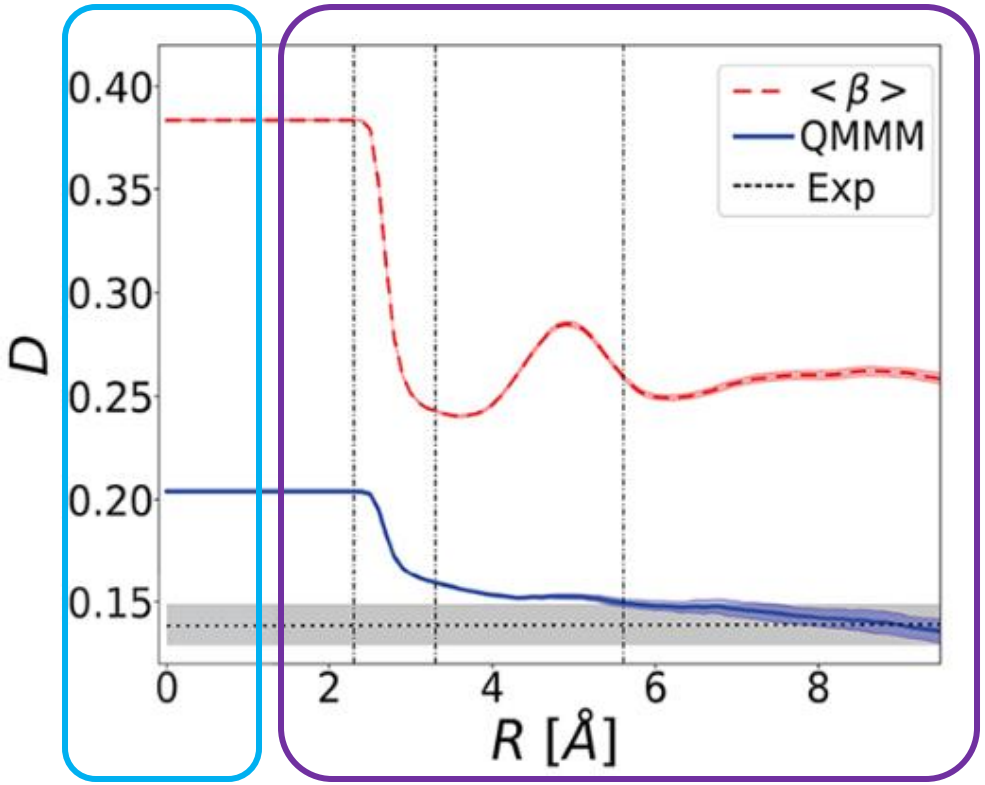
[Le Breton, JPCL (2023)]

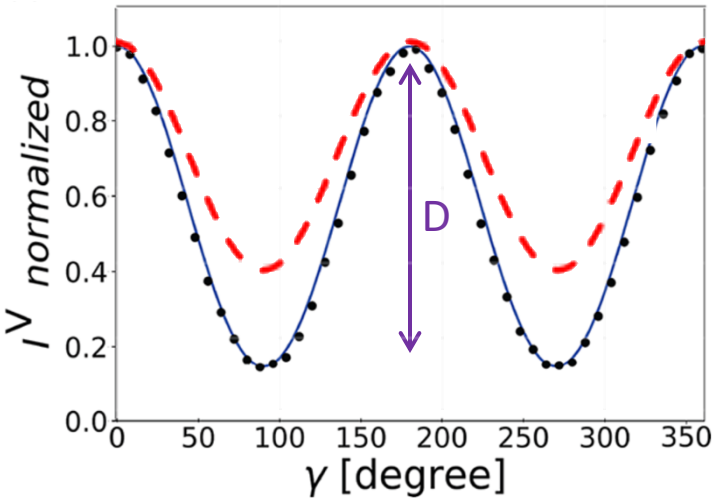
Intensité SHS =











Exp.
< β >, incoherent
QMMM, tot

- rôle important des fluctuations de β
- Les 3 premières couches de solvatation remodèle l'intensité SHS
- Courbe résolue en polarisation obtenue **sans paramètres ajustables**

Conclusions

- La diffusion de second harmonique a permis de sonder l'organisation à l'échelle moléculaire
- L'intensité SHS a pu être simulée par des calculs QM/MM
- L'intensité SHS est sensible aux fluctuations d'hyperpolarisabilité et à l'organisation à l'échelle de 3 couches de solvatation.

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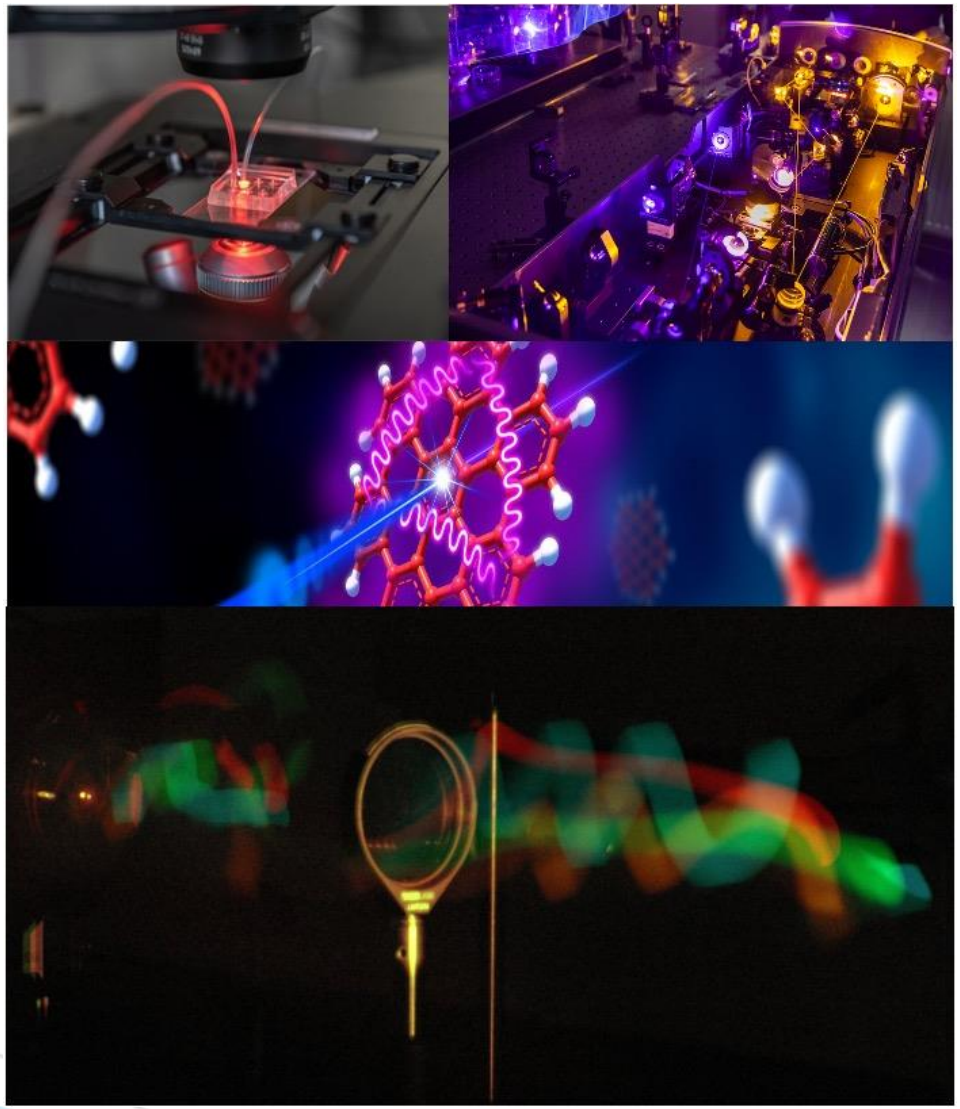
Parcours Q-Light



Q-LIGHT : Quantique, Lumière et Interactions
(Quantum, Light and Interactions)

Q-Light est un parcours du master de physique fondamentale et applications de l'université Claude Bernard Lyon 1.

La formation est consacrée à l'étude des interactions entre la lumière et la matière à l'échelle microscopique, où les effets quantiques et non linéaires jouent un rôle fondamental.

Ce programme explore des thématiques essentielles en physique théorique et expérimentale, notamment l'optique quantique, l'optique non linéaire, la physique des lasers, la photonique, la spectroscopie et l'optique ultra-rapide.

https://master-physique.univ-lyon1.fr/qlight/