



**HAL**  
open science

## Can Non-Photochemical Laser induced Nucleation be a stereoselective Process?

Melody Briard, Clément Brandel, Valérie Dupray, Gérard Coquerel

### ► To cite this version:

Melody Briard, Clément Brandel, Valérie Dupray, Gérard Coquerel. Can Non-Photochemical Laser induced Nucleation be a stereoselective Process?. ISIC21 (International Symposium on Industrial Crystallization), Aug 2021, Online event, France. hal-03832240

**HAL Id: hal-03832240**

**<https://normandie-univ.hal.science/hal-03832240>**

Submitted on 23 Nov 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## Context

**NPLIN** stands for **N**on-**P**hotochemical **L**aser **I**nduced **N**ucleation.

- Nucleation process discovered in 1996 by Garetz *et al* (1)
- Laser pulses triggers nucleation from supersaturated solution
- How does it works? ➔ Different Hypotheses

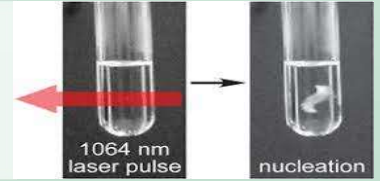
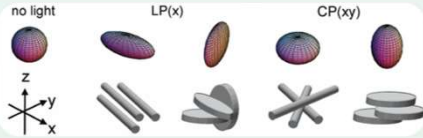


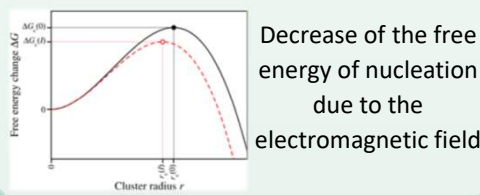
Figure adapted from (2)

### OKE : Optical Kerr Effect

Alignment of the dipole along the electromagnetic field

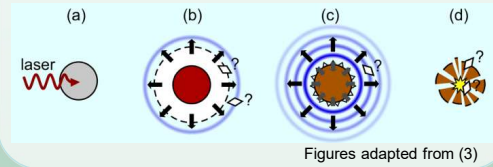


### DP : Dielectric Polarization



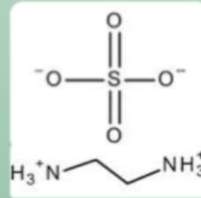
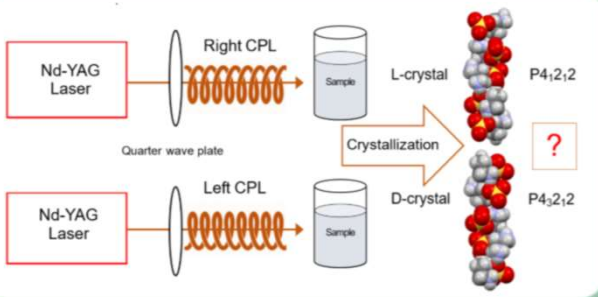
Decrease of the free energy of nucleation due to the electromagnetic field

### Cavitation : bubble generation



Figures adapted from (3)

## Can chirality be used to identify the NPLIN mechanism?

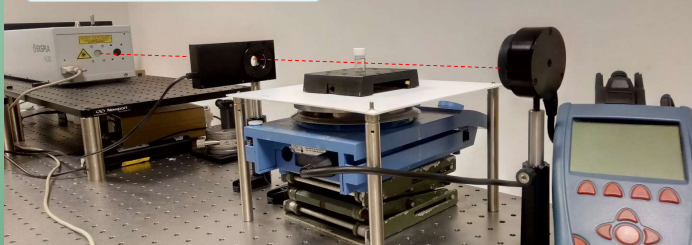


### Ethylenediamine sulfate (EDS)

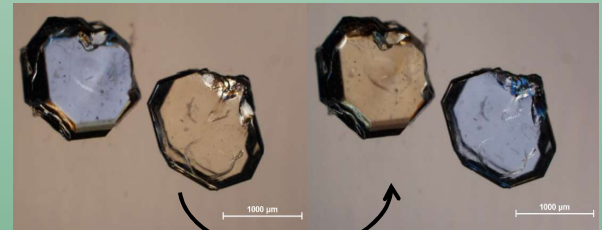
- Supramolecular chirality P4<sub>1</sub>2<sub>1</sub>2 or P4<sub>3</sub>2<sub>1</sub>2
- Easy to distinguish enantiomorphs
- The nucleation can be triggered by laser pulses

## Results & Discussion

### Set-up



Crystals obtained



Anticlockwise rotation of the polarizer of the optical microscope

### Results :

Polarization	N <sub>vial</sub>	N <sub>crystal</sub>	N <sub>D</sub>	N <sub>L</sub>	Cee±σ
Left Circularly Polarized Light	89	194	99	95	0.02±0.07
Right Circularly Polarized Light	86	190	81	109	-0.14±0.07
Linearly Polarized Light	91	251	129	122	0.03±0.06

Supersaturated solution ( $\beta=1.1$ ), exposed to 1 laser pulse at 34.8mJ (1064 nm)  
The Crystal Enantiomeric Excess (Cee) shows no significant change upon changing laser polarization geometry  
It is in our experience that the NPLIN process of NaClO<sub>3</sub> from aqueous solutions is also not stereoselective (data not shown here)

### Why is there no influence of polarized light ?

#### Option n° 1

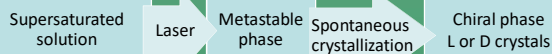
#### OKE mechanism is invalid

The electromagnetic field of the laser can not influence the orientation of the molecules

#### Option n° 2

### Potential Metastable phase

As in the case of NaClO<sub>3</sub>(3), an achiral phase nucleates first and transforms non stereoselectively into the chiral one (monotropic system). So the laser can not induce any stereoselective effect.



Existence of a High-Temperature phase of EDS, likely centrosymmetric  
Does laser trigger its nucleation first?  
It is unlikely : due to the high transition temperature (ca. 230°C)  
(Enantiotropic system)

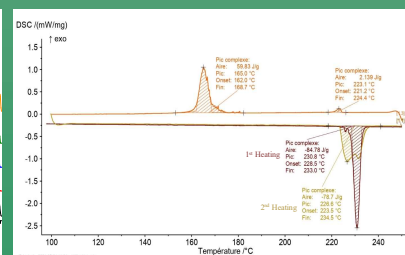
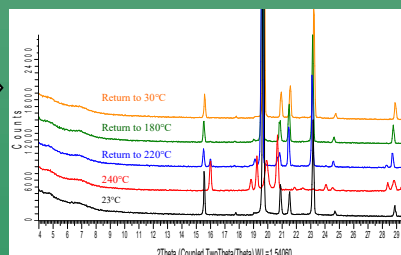
### Conclusion & perspectives

NPLIN seems to be non-stereoselective

BUT experiments with chiral molecules are needed to confirm it EVEN IF

OKE is already controversial (4),(5) (invalid option 1)

Another option would be another mechanism : we think that Cavitation mechanism is more likely and we will focus our next studies on it



### References

- (1) Garetz, B. A.; Aber, J. E.; Goddard, N. L.; Young, R. G.; Myerson, A. S. *Physical review letters* 1996, 77 (16), 3475.
- (2) R. Ward, M.; McHugh, S.; J. Alexander, A. *Physical Chemistry Chemical Physics* 2012, 14 (1), 90-93.
- (3) Alexander, A. J.; Camp, P. J. *Non-Photochemical Laser-Induced Nucleation*. *J. Chem. Phys.* 2019, 150 (4), 040901.
- (4) Barber, E. R.; Kinney, N. L. H.; Alexander, A. J. *Crystal Growth & Design* 2019, acs.cgd.9b00951.
- (5) Knott, B. C.; Doherty, M. F.; Peters, B. *The Journal of Chemical Physics* 2011, 134 (15), 154501.
- (6) Irimia, D.; Jose Shirley, J.; Garg, A. S.; Nijland, D. P. A.; van der Heijden, A. E. D. M.; Kramer, H. J. M.; Eral, H. B. *Crystal Growth & Design* 2020.