Stimulated emission of tetrapyrrolic molecules in van der Waals solids

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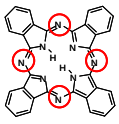
Introduction

Tetrapyrrolic molecules like **Phthalocyanines (Pc)** or closely related **Porphyrines (P)**, have many applications. Among their remarkable molecular properties, they are well known to have very strong electronic oscillator strengths in the UV/visible spectral range.

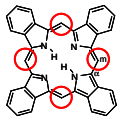
Recent experiments on phthalocyanines species trapped in cryogenic matrices at very low temperature have revealed an unexpected phenomenon: in laser induced fluorescence measurements, a slight increase of the intensity of the exciting laser produced a strong increase of the emission assigned to a specific vibronic band. The corresponding emission line became incredibly intense and dominated completely the normal fluorescence spectrum. This emission possesses all the characteristics of a stimulated emission. This phenomenon was first revealed in free-base phthalocyanine (H_2Pc) and zinc phthalocyanine (ZnPc) doped nitrogen and rare gas matrices under tunable laser excitation [1].

Under studies:

$(H_2)Pc \leftrightarrow (H_2)TBP$
$N \leftrightarrow C$
around the main ring

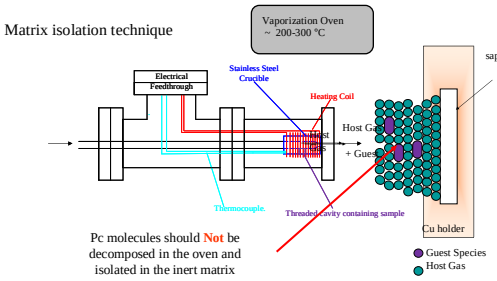


Free-base phthalocyanine (H_2Pc)



Tetrabenzoporphin (H_2TBP)

Experimental set-up

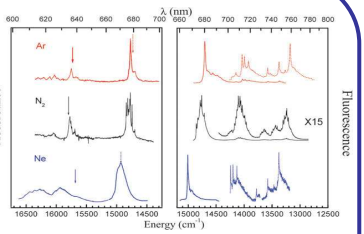


The assistance of Dr. Michel Broquier and Dr. Pierre Çarçabal for the design of the oven used for vaporization of the porphyrin molecules is gratefully acknowledged.

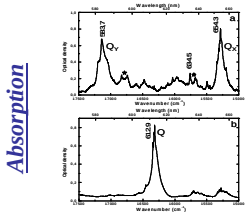
Absorption / Fluorescence

Phthalocyanines:
Left: absorption spectra of H_2Pc isolated in solid Ne, N_2, Ar.
Right: emission spectra of H_2Pc isolated in the three matrices.

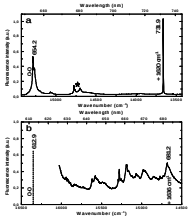
The arrows shown on the left with the absorption spectra indicated the laser excitation wavelengths used in producing the main emission spectra. Q_X excitation is represented by broken arrows while the solid arrows depict higher energy excitation.



Porphyrins:

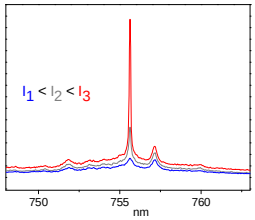


(a) Q_X and Q_Y absorptions bands of H_2TBP.
(b) Unique Q absorption band of ZnTBP. Spectra were obtained in solid Ar at about 8 K.

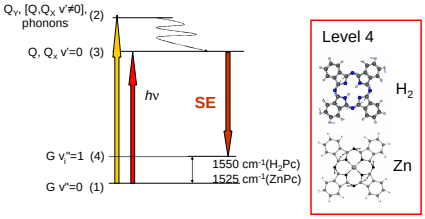


(a) Fluorescence spectrum of free-base H_2TBP recorded under non selective laser excitation at about 583 nm.
(b) Fluorescence spectrum of ZnTBP under resonant excitation wavelength at 612.9 nm.
Both spectra were obtained in solid Ar at about 8 K.

Stimulated Emission observed in H_2Pc/N_2

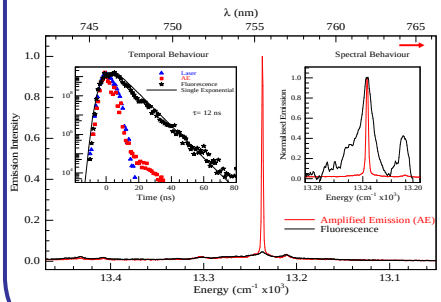


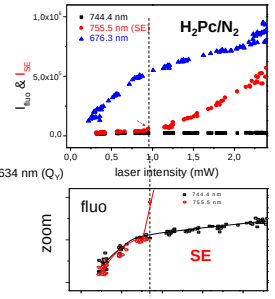
Increasing laser power
↳ from fluorescence
to Stimulated Emission (SE)



Stimulated Emission is characterised by:
- high relative intensity
- narrow linewidth
- shorter lifetimes than fluorescence

SE upon one specific vibronic band:
Asymmetric stretch of bridge C-N-C bonds in central ring [3]

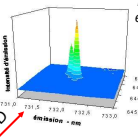




This work and the data shown here were obtained with the invaluable help of Nadia Dozova and Ciaran Murray from Department of Chemistry, N.U.I. Maynooth, Irlande (See ref. [1])

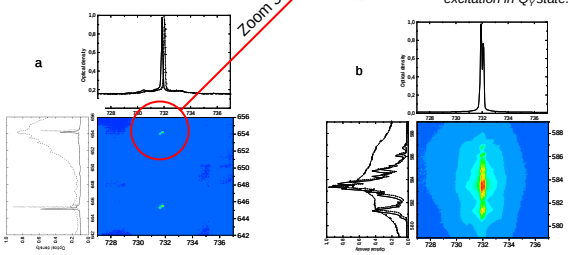
Stimulated emission in H_2TBP/Ar

SE generated under selective excitation at 654.43 nm and 654.25 nm inside the broad Q_X absorption band : existence of 2 stimulated emissions, assigned to 2 distinct sites.



The 2 peaks correspond to the emissions from 2 distincts sites.

Same shifts from one site to another in Q_X and Q_Y states, but congested excitation in Q_Y state.



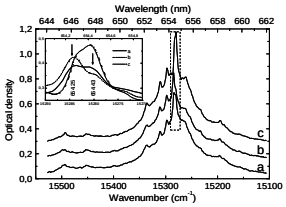
2D-Emission-Excitation spectra of free-base H2TBP/Ar at 8 K recorded under selective laser excitation. Emission spectra are shown on top, excitation spectra, together with the absorption spectra (dotted lines) are on the left.
a) Analysis of the 2D-spectrum under SE conditions of QX region around 654 nm.
b) Analysis of the 2D-spectrum under SE conditions of QY region around 584 nm.

Clearly excitation spectra recorded for the SE signal provide greatly enhanced spectroscopic information over what can be extracted from either conventional fluorescence excitation or absorption spectroscopy.

Stimulated Emission involves a vibrational mode of ~1640 cm^{-1} in the ground state: asymmetric stretch of bridge C-C-C bonds in central ring.

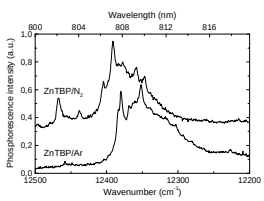
Other observations

$H_2TBP/N2$: Spectral Hole-Burning



Extended view of the absorption spectrum around the Q_X absorption band of H_2TBP/Ar at 8 K. a, b and c are the traces recorded before irradiation, after irradiation at 654.43 nm and after irradiation at 654.25 nm. The insert shows evidence of persistent spectral changes (hole-burning effect) between two specific sites in the Q_X origin region.

ZnTBP/N2: Phosphorescence, no SE



Phosphorescence spectra of ZnTBP/Ar and ZnTBP/N_2 recorded under selective laser excitation at about 612nm .The spectra were recorded at about 8 K.

For H_2Pc and ZnPc, SE was observed in Ne, Ar, Kr and N_2 matrices, but SE was very difficult to obtain in Xe.
For H_2TBP, SE could be observed in Ar and N_2, but also Hole-Burning effects were reported. For ZnTBP in Ar or N2, no SE but a strong phosphorescence was reported.

From results obtained on SE in cryogenic matrices, with H_2Pc, ZnPc as well as H_2TBP, we can predict that SE should be observed for these molecules in other solid materials with narrow linewidths like Shpol'skii matrices (n-octane). Other possible candidates could also be sol-gel or polymer hosts.

Conclusions and perspectives

✓ Unexpected stimulated emission (SE) in thin solid films.
✓ Observation made possible because :
- large extinction coefficients
- pulsed laser excitation
- narrow emission bands

✓ SE allows a high resolution spectroscopy and a better site characterization.

*[1] N. Dozova, C. Murray, J. G. McCaffrey, N. Shafizadeh and C. Crépin, "Amplified emission of phthalocyanine isolated in cryogenic matrices", Phys. Chem. Chem. Phys. **10**, p 2167 (2008). [2] C. Crépin, N. Shafizadeh, W. Chin, J.-P. Galaup, J. G. McCaffrey and S.M. Arabei, "Unveiled optical properties of tetra-pyrrolic pigments in cryogenic environments", Low Temperature Physics, **36**, p 451 (2010).*
[3] C. Murray, N. Dozova, J. G. McCaffrey,S. FitzGerald, N. Shafizadeh and C. Crépin, ""Infra-red and Raman spectroscopy of free-base and zinc phthalocyanines isolated in cryogenic matrices", Phys. Chem. Chem. Phys. DOI 10.1039/c0cp00055h (2010).

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