Stimulated emission of tetrapyrrolic molecules in van der Waals solids

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Introduction

Tetrapyrrolic molecules like Phthalocyanines (Pc) or closely related Porphyrins (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 produces 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 the unsubstituted phthalocyanine (Pc) and in a tetrapyrrylene (ZnPc) doped nitrogen and rare gas matrices under tunable laser excitation [1].

Under studies:

- (H3Pc ∼→ H3TBP)
- (N ∼→ C)

Free-base phthalocyanine (H3Pc)
Totamiphthalocyanine (H3TBP)

Absorption / Fluorescence

Phthalocyanines:
- Left: absorption spectra of H3Pc isolated in solid N2, N2, Ar.
- Right: emission spectra of H3Pc isolated in the three matrices.

The arrows shown on the left with the absorption spectra indicate the laser excitation wavelengths used in the main emission spectra. Q0 emission is suppressed by broken arrows while the solid arrows depict higher energy excitation.

Porphyrins:

Absorption

Fluorescence

(a) Q and Q0 absorption bands of H3Pc
(b) Unique Q0 absorption band of H3TBP. Spectra were obtained in solid N2 at about 8 K.
(c) Fluorescence spectrum of free-base H3TBP recorded under non selective laser excitation and blue laser excitation wavelengths 652.0 nm. Both spectra were obtained in solid Ar at about 8 K.

Experimental set-up

Matrix isolation technique

Stimulated Emission observed in H3Pc/N2

Increasing laser power \( P \) from fluorescence to Stimulated Emission (SE)

Stimulated emission in H3TBP/Ar

Other observations

H3TBP/N2: Spectral Hole-Burning

ZnPcTBP/N2: Phosphorescence, no SE

Conclusions and perspectives

✓ Unexpected stimulated emission (SE) in thin solid films
✓ Observation made possible because:
- high-resolution spectroscopy
- pulsed laser excitation
- narrow emission bands
- SE allows a high-resolution spectroscopy and a better site characterization.

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