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THE EXCITED STATE OF CIS-THIOINDIGO

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Résumé - Dans le cadre de l'étude de la photoisomérisation cis-trans réversible du thioindigo, des mesures spectroscopiques à basse température des isomères cis et trans isolés en matrice ont été réalisées. C'est la première observation, pour l'isomère cis, de spectres ayant une structure vibrationnelle résolue. Différentes évaluations du rendement quantique de fluorescence de ce composé indiquent que la durée de vie de l'état excité est dans le domaine subpicoseconde.

Abstract - Spectroscopic measurements at low temperature of matrix isolated cis- and trans-thioindigo are presented and are discussed in relation to the photoinduced reversible isomerization of this molecule. For the cis isomer these data represent the first vibrationally resolved spectra. Estimates of the emission quantum yield for this species show that the excited state decays on a subpicosecond timescale.

I - INTRODUCTION

The reversible trans-cis photoisomerization of some indigo dyes is a prototype example of light induced conformational changes in polyatomic molecules and has been extensively studied.

Thioindigo

While the trans isomer is well characterized and the trans + cis reaction is generally thought to proceed via the triplet state /1,2,3/, little is known about the inverse reaction /4/. The metastable cis isomer (lifetime in the range of minutes in various solvents at room temperature) is not well characterized: no vibrationally resolved spectra exist, no emission has been detected, and the excited state potential is hypothetical.

We have started an extensive investigation of thioindigo: for the stable trans isomer the absorption and fluorescence spectra are very regular, the vibrational frequencies change only little upon electronic excitation and remain harmonic up to several quanta in both the ground and excited electronic state, indicating that the changes in the potential are small.

The present work is concerned with the cis isomer: stabilized by matrix isolation, vibrational spectra in the ground and excited state have been obtained. Emission was detected and estimates of the emission quantum yield could be made.

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II - EXPERIMENTAL

Sample preparation:
- For the absorption spectra: a solution of thioindigo in n-nonane is irradiated during 1 minute with a 150 W iodine lamp, using a filter to eliminate $\lambda > 500$ nm, and then quickly plunged into liquid nitrogen.
- For the emission spectra: the sample of thioindigo in liquid 2,5-diphenyloxazole (M.P.: 72°C) is irradiated and rapidly cooled by sputtering on a glass plate.

In both solutions it was verified that the photoinduced species, ascribed to the cis isomer, reverts in the dark to trans-thioindigo. The irradiated samples still contain a large amount of trans-thioindigo.

III - ABSORPTION SPECTRA

Fig. 1 shows absorption spectra of trans- and cis-thioindigo in n-nonane. The non-irradiated sample contains trans-thioindigo only. The amount of the cis isomer in the irradiated sample is estimated to be at least 15% of the total amount of thioindigo.

![Absorption Spectra](image)

Fig. 1 - Absorption spectra of trans- and cis-thioindigo in a n-nonane matrix at 4 K.

This is the first vibrationally resolved absorption spectrum of cis-thioindigo. It shows one progression with a spacing of 500 cm$^{-1}$; the FWHM of the lines varies from 300 to 400 cm$^{-1}$. The trans isomer under identical conditions exhibits lines of 15 cm$^{-1}$ width. The inhomogeneous contributions to the width of the cis spectrum are thus thought to be negligible. The observed linewidth could be due to a strong electron-phonon coupling and/or to a very rapid decay (20 fs) of the excited state (see below).

IV - EMISSION SPECTRA

Fig. 2 shows the fluorescence spectrum of the cis-thioindigo isomer in a 2,5-diphenyloxazole (DPO) matrix between 20400 and 18000 cm$^{-1}$. Residual impurities and unrelaxed emission from the trans isomer contribute to the weak background signal in this spectral region, such that less than 30% of the fluorescence intensity comes from the cis isomer. The right part of Fig. 2 shows the intense fluorescence of the trans isomer (note the change in the intensity scale between the two parts of the spectrum).
In addition to the broad emission background, sharp lines are observed, most of which correspond to Raman lines of the matrix; some Raman lines of both thioindigo isomers could also be identified.

Fig. 2 - Fluorescence spectra of cis- and trans-thioindigo in a DPO matrix at 1.6 K. Excitation = 4880 Å Ar+ laser line. A: this spectral region is shown in expansion in fig. 3.

These measurements are used to make two independent evaluations of the emission quantum yield of the cis isomer.

A) We estimate that at the wavelength of excitation (4880 Å) both isomers absorb equal amounts of light; the ratio of the integrated emissions attributed to the two species therefore equals the ratio of the emission quantum yields. As the fluorescence quantum yield of trans-thioindigo is known to be $\phi^{\text{trans}}_{F} = 0.7$ /5/, we obtain for the cis-isomer $\phi^{\text{cis}}_{F} < 7 \cdot 10^{-5}$.

B) A second estimate of this quantum yield can be made using the intensity of a Raman line of the matrix for the calibration /6/:

$$
\phi^{\text{cis}}_{F} = \frac{\sigma_{R} \times N_{R}}{I_{R}} \times \frac{I^{\text{cis}}_{F}}{\sigma_{\text{abs}} \times N_{F}}
$$

where $\sigma_{R}$, $N_{R}$, and $I_{R}$ are the Raman cross section, the number of scattering matrix molecules, and the intensity of the considered matrix Raman line. $\sigma_{\text{abs}}$ and $I_{F}$ are respectively the absorption cross section and the fluorescence intensity of the cis isomer, and $N_{F}$ is the number of cis molecules.

The Raman cross section of suitable lines was calibrated against known values of liquid benzene by measuring the Raman spectrum of a 50% solution of DPO in benzene.
The concentration of thioindigo was measured by taking absorption spectra in solution, and the relative concentration and the absorption cross section of the cis isomer were evaluated from our and literature spectral data (Ref. 7). This determination yielded \( \Phi_F^{\text{cis}} \approx 10^{-6} \).

Both evaluations of this quantity suffer from the fact that the measurements are made on strongly scattering polycrystalline material and that different amounts of each isomer may not be matrix isolated but are rejected from the matrix in the preparation process. Measurements on room temperature solutions, which avoid these problems, are limited in the present case by the fact that, at high temperatures, the very weak cis emission becomes masked by the stronger trans-emission.

Fig. 3 is a blow-up of the spectral region A in Fig. 2, where strong Raman lines of both isomer species can be observed.

**Fig. 3 - Resonance Raman spectra of thioindigo in a DPO matrix at 1.6 K.**

For cis-thioindigo a 490 cm\(^{-1}\) mode gives rise to the strongest Raman line and is observed also in two quanta; very likely it correlates with the mode appearing in the strong 500 cm\(^{-1}\) progression in absorption. The cross section of this line was measured to be \( 2 \times 10^{-31} \text{ cm}^2 \text{ molecule}^{-1} \) (\( \lambda_{\text{exc}} = 4880 \text{ Å} \)). All other Raman lines are considerably weaker and are at or below our detection limit.

**V - DISCUSSION**

The quantitative evaluation of very weak emission is subject to great uncertainties; in the present study it becomes even more difficult due to the strong fluorescence of the always present trans isomer. Our results do nevertheless clearly indicate that the emission quantum yield of cis-thioindigo is very low, lying in the range of \( 10^{-5} \) to \( 10^{-8} \). The lifetime of the first excited state therefore is very short (\( \xi \approx 200 \text{ fs} \)), as the radiative lifetime can be estimated to be similar for the two isomers and is known to be \( \frac{1}{k_F} = 20 \text{ ns} /5/ \) for trans-thioindigo. Such a short lifetime would make a significant - if not dominant - contribution to the width of the lines observed in the absorption spectra. One of the fundamental questions concerning the excited state potential of cis-thioindigo is its shape along the reaction coordinate, that is the torsion around the central double bond. In the ground state of trans-thioindigo, the frequency of the corresponding torsional mode lies at \( \approx 200 \text{ cm}^{-1} /8/ \), and its value in the metastable ground state of cis-thioindigo is likely to be smaller. In the excited state of the cis-isomer, the force constant for this motion is further reduced and may even be negative. Our measurements show that the excited state decays on a timescale which is comparable to or less than one vibrational period of this
torsional mode. We suggest that this rapid decay is indicative of an unstable nuclear configuration of the excited state of the cis isomer along this coordinate. The exact pathway of this rapid electronic relaxation process remains however to be determined.

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