Improved experimental technique for determining double hydrogen transfer rates in porphycenes with the use of transient absorption anisotropy

**Introduction**

The use of transient absorption anisotropy decay for determining double hydrogen transfer rates in porphycenes and its derivatives has been recently proposed by our laboratory [1, 2]. Contrary to stationary and time-resolved emission anisotropy, this technique allows determination of ground state relaxation times, however, to take full advantage of the technique, there is a need for more sensitive and more robust instrumentation. Experimental setup and detection systems presented here greatly decreases the influence of short term intensity instabilities. It allows us to obtain good results with small number of scans, which reduces scan time and in turn minimizes occurrence of error caused by long term instabilities.

**Tautomerization & anisotropy**

Tautomerization products of porphyrines. Note the location of hydrogen atoms on upper porphyrine plane. Arrows indicate dipole transition directions for relevant transitions.

**Experimental setup**

- **Data acquisition**: Using TOPAS WinX, the data is collected for each experiment and a single scan is collected for each measurement.
- **Data processing**: The data is processed using TOPAS WinX software.

**Finding optimal workflow**

- **Linearization of pump pulse energy on absorption change for N,N-dimethyl (500) and porphycene (500)**: The influence of pump pulse energy on absorption change for N,N-dimethyl and porphycene is shown.
- **Temporal resolution** (retrieved from rise time of ground state bleach): The temporal resolution of the experiment is shown.

**Results**

- **Sensitivity**: The sensitivity of the experiment is shown.
- **High sensitivity**: The high sensitivity of the experiment is shown.

**Conclusions**

The overall performance of our technique is very promising, and we believe that this technique could be as much as two orders of magnitude more sensitive than current methods.

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**Notes**

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**References**
