# Femtosecond fluorescence spectroscopy based on the optical Kerr effect

R. Mundt, G. Ryseck, P. Gilch, Femtosecond spectroscopy group, Chemistry,
University of Düsseldorf, Germany (May 2014)

## Application Note

### Introduction

The period of vibrational motions in molecules (10 – 300 fs) sets a lower limit for the time scale of chemical processes [1] [2]. This femtosecond time scale is nowadays directly accessible [3]: An ultra-short laser pulse (pump) triggers the molecular process of interest. A second pulse (probe or gate) records changes in spectroscopic or diffraction patterns induced by the pump. Commonly, the pump pulse promotes the molecule into an electronically excited singlet state. Fluorescence emission is a hallmark of such an excitation [4]. Tracing the fluorescence emission as a function of time and frequency, thus, yields information on the fate of this state. The technique we apply to resolve the fluorescence in time and frequency relies on the optical Kerr effect [5].

### Principles and realization of a Kerr gate

On the femtosecond time scale, fluorescence spectra are often recorded by means of an optical gate (see Figure 1a). An optical gate cuts temporal slices out of the fluorescence decay. The timing of this "cutting" is controlled by a delay stage which sets the time interval $t_d$ between excitation by the pump pulse and the gating. Repeating the experiment with different setting for $t_d$ will yield the decay trace. The Kerr effect is one mechanism an optical gate can rely on (see Figure 1b).

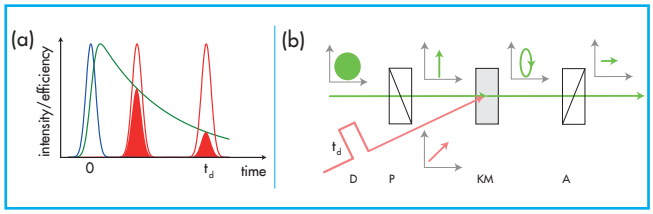


Figure 1: a) Principle of a pump-gate/probe experiment b) Principle of an optical Kerr gate.

In a Kerr gate, the fluorescence first passes a linear polarizer P. A second linear polarizer, the analyzer A, is set perpendicular to P, hence extinguishing the emission. In between A and P a (Kerr) medium KM is placed. It is an isotropic and transparent material not altering the polarization state of the transmitted light. While exposed to the gate pulse, an anisotropy is induced which leads to birefringence of KM. This alters the polarization state of the fluorescence light and a portion of it can pass the analyzer. If employing glass plates as Kerr media it remains open for $\sim\tau_g/\sqrt{2}$ whereby $\tau_g \approx 50 - 100$ fs is the duration of the gate pulse.

The design of the present setup is similar to the one described in reference (6) and is depicted in Figure 2.

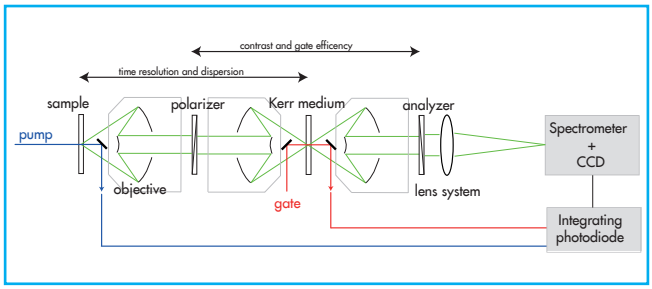


Figure 2: Realization of the optical Kerr gate. Key features are reflective objectives and wire grid polarizators.

Pump and gate pulses are derived from a single femtosecond laser/amplifier system (Coherent Libra-HE, repetition rate of 1 kHz). This ensures synchronization of the pulses. By non-linear optics its 800 nm light is frequency converted. The frequency of the pump light is tunable to match the absorption of the molecules under study. Pulses for gating are converted to 1200 nm avoiding spectral overlap with the fluorescence light. Reflective optics guide the fluorescence light from the sample towards the Kerr medium and the detector. Two crossed wire grid polarizers embrace the Kerr medium (a fused silica plate). The design minimizes the dispersion of arrival times for different frequency components. The detection system consists of a pre-calibrated combination of an Andor iDus DU420A-BU CCD detector in combination with a Shamrock SR-303i-B spectrograph equipped with a 150 l/mm grating blazed for 500 nm. The power of pump and gate light is measured by photodiodes connected to a low-noise integrator (WieserLabs, IPD4A). With the aid of these signals fluctuations in light power can be corrected. The integrator is synchronized via the "fire out" connector of the iDus CCD detector. The whole system is controlled by LabVIEW using the Andor Software Development Kit.

### Requirements for the detection system

The number of photons per second (flux) which will impinge on the CCD can be estimated as follows: The energy per pump pulse typically amounts to ~0.3 µJ; higher energies could lead to non-linear response and saturation effects. For an excitation wavelength of 370 nm as applied here and a repetition rate of 1 kHz, this translates into a flux of $\sim 6 \cdot 10^{14}$ $s^{-1}$. We as-

# Femtosecond fluorescence spectroscopy based on the optical Kerr effect

R. Mundt, G. Ryseck, P. Gilch, Femtosecond spectroscopy group, Chemistry,
University of Düsseldorf, Germany (May 2014)

## Application Note

sume that all photons will be absorbed by the sample. When gating the fluorescence, the maximal flux which can be recorded reduces by a factor of $\tau_g/\sqrt{2}\tau_{rad}$ to ~$4 \cdot 10^9$ $s^{-1}$. Hereby, a typical value for the radiative lifetime $\tau_{rad}$ of 10 ns [4] [7] was inserted. This value applies only for delay times $t_d$ around zero. Fluorescence emission is close to isotropic and the optics employed collect only a fraction $\eta_{col}$ of 0.05. The throughput $\eta_{tp}$ of the whole setup was measured independently and amounts to ~0.004. The efficiency $\eta_{Kerr}$ of the Kerr gate, that is the relative throughput in the open state, is 0.02. The gate fluorescence is spectrally dispersed and impinges on around 200 spectroscopic pixels. Taking all these factors into account, one may expect a maximum of 80 photons per second and pixel.

The iDus CCD detector has a peak quantum efficiency of 0.9 and a high conversion of 2 electrons per count. Still, at room temperature the contributions will be lost in the background fluctuations due to dark current. The ability to cool the CCD chip to -100 °C solves this problem. In contrast to cooling with liquid nitrogen, the iDus uses thermo-electric elements simplifying daily operation.

### Results

To illustrate the performance of the setup and the detector, a measurement on N,N-dimethyl-para-nitroaniline dissolved in acetonitrile is presented (Figure 3).

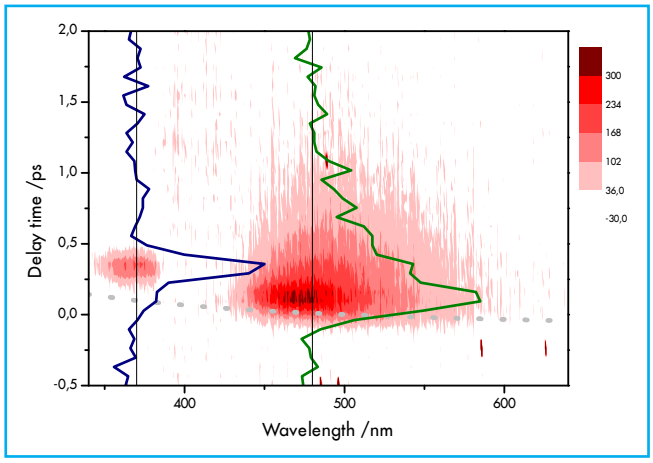


Figure 3: Spectrally and temporally resolved fluorescence of DMpNA dissolved in acetonitrile. The color scale for the contour plot represents the number of counts. The time trace at the excitation wavelength (blue line) holds information on the instrumental response time, the one at 480 nm (green line) on the fluorescence lifetime. The gray dotted line describes the apparent shift of time zero due to dispersion.

The molecule is known to undergo ultrafast internal conversion, thereby depleting the emitting singlet state [8]. In the spectrally and temporally resolved scan, subsequent spectra were taken with a time interval of 67 fs between them. The acquisition time was set to 3 s per spectrum and the detector was cooled to -40 °C. Beside the subtraction of the first spectrum, which serves as reference for the background contributions, no further data manipulation was undertaken. The maximal signal with respect to the delay time and wavelength (or frequency) amounts to approximately 100 counts per second and pixel in accordance with the estimate given above.
The signal at 370 nm is due to scattered pump light and inspection of the respective time trace yields the instrumental response time (FWHM) of 180 fs. At 480 nm, where fluorescence peaks, the time trace informs on the lifetime of the excited singlet state which here amounts to 480 fs.

The signal quality can be improved further by correction for intensity fluctuations in pump and gate light powers. The capability of the Andor detector to synchronize the reference diodes offers a way to do so.

### Conclusion

We presented highly time resolved broadband fluorescence spectroscopy based on the optical Kerr effect. It is shown that an optical Kerr gate is well-suited for the study of ultrafast decays of excited states. We have estimated the expected gated signal and have shown that the iDus CCD detector can be used as a detector for optical Kerr gating.

### Acknowledgement

Financial support by the Deutsche Forschungsgemeinschaft (GI 349/4-1) is gratefully acknowledged. We thank Martin Schramm for technical support.

# Femtosecond fluorescence spectroscopy based on the optical Kerr effect

R. Mundt, G. Ryseck, P. Gilch, Femtosecond spectroscopy group, Chemistry,
University of Düsseldorf, Germany (May 2014)

**Application Note**

## References

[1] A.H. Zewail, Femtochemistry: Atomic-Scale Dynamics of the Chemical Bond, J. Phys. Chem. A, 104, (2000), 5560-5694
[2] A. Nitzan, Chemical Dynamics in Condensed Phase, Oxford, New York: Oxford University Press, (2006)
[3] C. Rullière, Femtosecond laser pulses: principles and experiments, New York: Springer Science+Business Media, LLC, (2005)
[4] J.R. Lakowicz, Principles of Fluorescence Spectroscopy, Third Edition. s.l.: Springer, New York, (2006)
[5] M.A. Duguay, The ultrafast optical Kerr shutter, Prog. Opt., 14, (1976), 161-193
[6] B. Schmidt et al., A broadband Kerr shutter for femtosecond fluorescence spectroscopy., Appl. Phys. B, 76, (2003), 809-814
[7] S. Strickler and R. Berg, Relationship between Absorption Intensity and Fluoresence Lifetime of Molecules, J. Chem. Phys., 37, (1962), 814-822
[8] Q. An et al., In-situ Determination of Fluorescence Lifetimes via Inverse Raman Scattering, Opt. Comm., 202, (2002), 209-216

## Contact

Prof. Dr. Peter Gilch
Femtosecond Spectroscopy Group
Department of Chemistry
University of Düsseldorf
Universitätsstraße 1
40225 Düsseldorf
Germany

Phone: +49 (211) 81-15400
E-mail: peter.gilch@hhu.de
Web: www.gilch.hhu.de/en.html