Kerr-gated Raman experiment driven by 100 kHz Ytterbium based OPCPA laser system

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Introduction

Raman spectroscopy is a vibrational spectroscopy technique providing important information on the structure and composition of the material under study. However, Raman scattering effect is quite weak by its very nature and cannot compete with fluorescence. So, when studying fluorescent materials or those with fluorescent impurities, the fluorescence background can easily overwhelm the weak Raman signal.

Over the last few decades, a number of approaches have been offered to circumvent the fluorescence background in Raman experiments, and the most efficient approach so far has been the optical Kerr gating. It was initially proposed in the 1980's by Deffontaine et al. [1] and implemented experimentally at CLF in 1999 [2]. The first Kerr gated Raman setup at CLF was driven by a 1 kHz amplified Ti:Sapphire laser system. Over the years, the Kerr gated Raman setup has continued to evolve and commissioning the ULTRA laser system [3] has enabled to upgrade the setup to 10 kHz, improving signal-to-noise ratio and data acquisition times [4].

The recent advances in the Ytterbium laser technology are leading to the gradual replacement of Ti;Sapphire lasers with the new Ytterbium based lasers in many areas of time-resolved laser spectroscopy. Very recently, CLF has commissioned the new 100 kHz OPCPA laser system, pumped by the Yb:YAG laser Dira 200-100 from Trumpf Scientific. From the very beginning, this laser looked very promising to drive the Kerr-gated Raman experiment, and this setup was the first we built around the new laser system. In the present publication, we report on our preliminary results obtained with this setup.

Experimental

The general principle of optical Kerr gate relies on the induced birefringence in the Kerr medium due to the electric field of the intense laser pulse. When placed between the two crossed polarizers, this Kerr medium acts as an optical gate. The basic layout of the Kerr gated Raman setup is shown in Figure 1, as presented in our earlier publication [4]. The detailed description of the Kerr-gated Raman technique has been provided in earlier publications from our group [2, 4-5]. The laser Dira 200-100 delivers up to 200 W average power at 100 kHz at 1030 nm, with a near-transform-limited pulse duration of ~850 fs. A small fraction of the laser fundamental output beam is split to generate the 2nd harmonic beam (at 515 nm) in the BBO crystal to be used as Raman probe. The main fraction of the laser fundamental beam is used to drive the Kerr gate. To adjust the gating beam power, half-wave plates and thin-film polarizers are used.

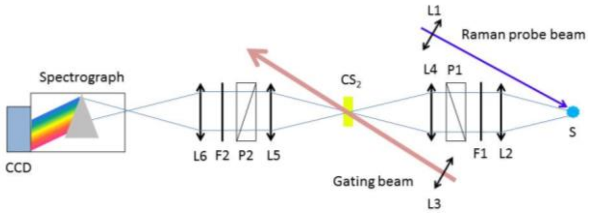

Figure 1. Schematic diagram of the Kerr-gated Raman setup, where: S – sample, L1 – L6 – lenses, F1, F2 – cut-off filters, P1, P2 – polarisers, CS_2 – the Kerr cell filled with carbon disulfide. Reproduced from [4].

The data reported in this publication has been taken with CS_2 as the Kerr medium. Due to the higher repetition rate of the new 100 kHz Yb:YAG laser, the average gating beam power at the Kerr medium is significantly higher than what was used before with the 10 kHz Ti:Sapphire ULTRA laser. To prevent the degradation of CS_2 in the high power gating beam, we use a demountable liquid cell DLC-S25 from Harrick with a large optical aperture (25 mm), filled with CS_2 (with 2 mm pathlength and 1 mm thick fused silica removable windows). This cell with CS_2 is then rastered in X and Y directions to reduce the degradation of CS_2 in the beam.

The key aspects we aimed to test with this setup were the following: i) the performance of the Kerr gate at the conditions of the small (ca. 0.75 mm) and large (ca. 3 mm) gating beam spot size; ii) the best achievable spectral resolution in the Kerr-gated Raman experiments with the new laser.

Small gating spot size tests

First, we have demonstrated the operation of Kerr gated Raman experiment with the gating beam spot size of 0.75 mm diameter FWHM. Such a spot size is comparable to that used with the ULTRA Ti:Sapphire laser at 10 kHz, where the pulse energy available for gating is limited. The corresponding probe beam spot size at the sample is 80 µm diameter FWHM. With such gating spot size, it takes ca. 5 W average power of 1030 nm / 100 kHz gating beam to achieve efficient gating. This number gives the lowest average power required to drive the Kerr gate. Such experimental conditions are optimal when studying photostable samples with sufficiently high Raman cross-section. To narrow down the linewidth of the probing 515 nm beam, a Fabry-Pérot etalon was used in the 515 nm beam. The illustration of the data obtained at such conditions is shown in Figure 2A, where Kerr gated Raman spectrum of toluene is presented.

To estimate the gating efficiency, we used the "inverted gating" approach. To do that, the transmission plane of the entrance and exit polarizers were set parallel to each other (i.e. "gate open" configuration) and the gating beam was on. Then the induced birefringence in CS_2 rotates the polarization of the signal beam coming through the entrance polarizer which leads to the attenuation of the signal beam by the exit polarizer. The result of that experiment is illustrated in Figure 2B, where the intensity of the signal coming through the gate is plotted vs. time delay between the gating and probing pulses. The plot in Figure 2B

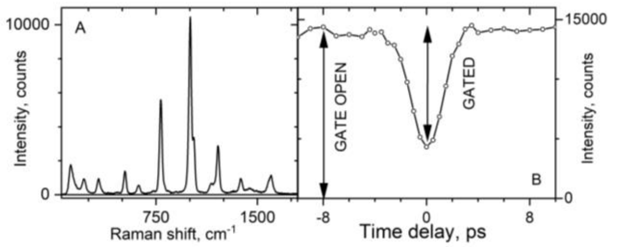

Figure 2. (A) The representative Kerr-gated Raman spectrum of toluene obtained with the gating beam spot size of 0.75 mm x 0.75 mm. (B) The time profile of the Kerr-gated Raman signal of toluene at 1006 cm^{-1} obtained in the "inverted gating" approach with the gating beam spot size of 0.75 mm x 0.75 mm. The Kerr gate efficiency is estimated as the ratio of the negative "GATED" peak intensity to the "GATE OPEN" intensity.

also shows the temporal response function of the setup. As can be seen from Figure 2B, the gating efficiency approached 70%, and the time response was ca. 3 ps FWHM. The 70% gating efficiency indicates that the performance of the Kerr gated Raman setup driven by 100 kHz Ytterbium laser is as good or even better as that driven by the ULTRA Ti:Sapphire laser. As for the response function duration of 3 ps, there are two factors contributing to that. The first is the longer pulse length of the 515 nm probe beam going through Fabry-Pérot etalon (the etalon narrows the linewidth of the probe beam and at the same time stretches the pulse) as compared to the gating 1030 nm beam (which is ~ 850 fs). And the second factor is the rotational relaxation time of CS_2 which is known to be 1.5 ps [6]. Having the 1030 nm gating pulse of the same pulse length as the probing 515 nm pulse would help to improve the gating efficiency, however to do that would require building a pulse stretcher in the gating beam. This capability is planned to be implemented in the next version of the Kerr gated Raman setup.

Large gating spot size tests

One of the limitations of the current ULTRA laser when doing Kerr gated Raman experiments is the pulse energy available to drive Kerr gate, which translates into keeping the gating beam spot size rather small (< 1 mm FWHM) to maintain sufficient gating efficiency. This in turn limits the size of the probe beam spot at the sample, which typically is kept at ca. 100 µm FWHM. This is acceptable when studying photostable samples. However, when the sample is prone to photodegradation, the probe beam power has to be reduced, which is accompanied by a drop in the signal intensity. Therefore, the high average power and higher repetition rate of the new 100 kHz Ytterbium laser comes as a great advantage, as it enables to expand the probe beam spot size at the sample and yet maintain Kerr gate performance. Also, for the same average power at the sample, at 100 kHz the probe pulse energy is reduced by 10x, preventing sample damage. To demonstrate how that extra power can be utilized efficiently, we performed Kerr gate experiments with a large spot size of the gating beam, imaging an increased probe beam spot size at the sample. For this demonstration, the Kerr gated Raman data was taken with 3 mm x 3 mm gating spot size FWHM. To achieve efficient Kerr gating at such conditions, 75 W average power was used in the 1030 nm gating beam. The gating efficiency was 46% (Figure 3). In that experiment, the probe beam spot size at the sample was set to 0.6 mm x 0.6 mm, which corresponds to an increase of the sample spot area by a factor of ca. 35, compared to the current ULTRA system. Potentially, this can allow boosting the Kerr gated Raman signal intensity accordingly, when working with sensitive samples.

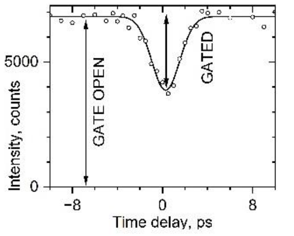

Figure 3. The time profile of the Kerr-gated Raman signal of toluene at 1006 cm^{-1} obtained in the "inverted gating" approach with the gating beam spot size of 3 mm x 3 mm. The data was fitted with an offset negative Gaussian peak. The Kerr gate efficiency is estimated as the ratio of the negative "GATED" peak intensity to the "GATE OPEN" intensity.

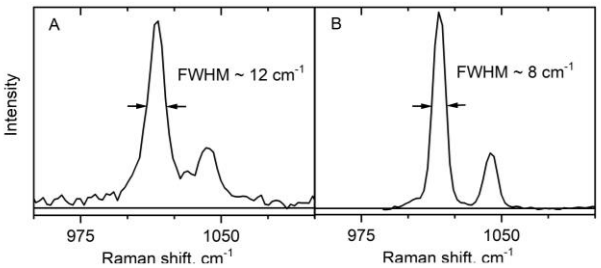

Figure 4. (A) The illustration of the spectral resolution obtained in the Kerr-gated Raman experiment, toluene used as a sample. (B) The spectral profile of Raman signal of the same sample recorded with the same setup but in the gate-open mode without the gating beam.

Spectral resolution tests

In the next set of tests, we replaced the etalon in the 515 nm probe beam with a folded grating-based pulse shaper. The pulse shaper involves a diffraction grating (1200 l/mm) and an adjustable spectral slit arranged in an auto-collimating geometry. As shown in Figure 4A, this setup was capable to deliver the linewidth of the Kerr-gated Raman signal of ca. 12 cm^{-1}. However, we could clearly see that the interaction of the gating beam with the signal in CS_2 was causing some broadening of the Raman lines, since the linewidth of the same Raman line detected in the CW mode (recorded with the same setup with the Kerr gate open and gating beam blocked) was ca. 8 cm^{-1} (Figure 4B).

Conclusions

In this publication, we report on the first implementation of the Kerr gated Raman experiment, driven by 100 kHz Ytterbium laser. The driving laser Dira 200-100 from Trumpf Scientific offers a substantial increase in the pulse energy available for Kerr gating, which enables to expand the probe beam spot at sample. This opens a unique opportunity to study photosensitive samples, which before were not suitable for Kerr gated Raman. In this setup, we have achieved efficient Kerr gating, reaching 70% and demonstrated 12 cm^{-1} spectral resolution.

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