Improving multiphoton spectroscopy standards through the creation of an accurate, high-throughput spectrometer facility

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We describe a high-throughput, high reproducibility setup for the measurement of femtosecond instantaneous degenerate two-photon absorption cross sections in abroad range of visible to near-IR excitation wavelengths. Preliminary results on some common fluorescent dyes such as Rhodamine 6G are presented and analysed in comparison to previously published data. We also introduce a newly created online 2PA spectra database.

INTRODUCTION

Two-photon absorption (2PA), wherein electronic transitions are activated by the simultaneous absorption of two photons,[1] is a topic of growing interest in optics, with applications ranging from optical power limiting,[1] microfabrication,[1] microscopy and phototherapy,[1] to nanothermometry[2] and molecular probes of electric fields.[3] As a second order process by nature, the probability of 2PA shows quadratic dependence on the excitation power, characterized by chromophore's intrinsic two-photon cross section (σ_{2PA}), which is analogous to the one-photon absorption cross section, but is expressed in the units, cm^4 s $photon^{-1}$. Applications can thus be optimized by knowledge of potentially large 2PA cross sections at specific excitation wavelengths; however, determining σ_{2PA} spectra with sufficient reliability and accuracy has been a difficult task, especially due to the need of characterizing the instantaneous photon flux of the excitation.

As an illustrative example, Figure 1 displays the 2PA spectrum of the laser dye Rhodamine 6G, which has been measured numerous times by several groups,[4–9] but with limited reproducibility between measurements. The issues of reproducibility stem from variations between 2PA measurement methods[9] and a lack of standardization of 2PA equipment, which are generally independently assembled. In addition to this, many 2PA measurements are performed at few wavelengths, due to time or capability constraints of the instrumentation, making comparisons difficult. The several techniques for measuring 2PA also do not always agree due to other attenuating processes, such as excited state absorption, or concentration dependent effects which can change the behaviour of absorbers.

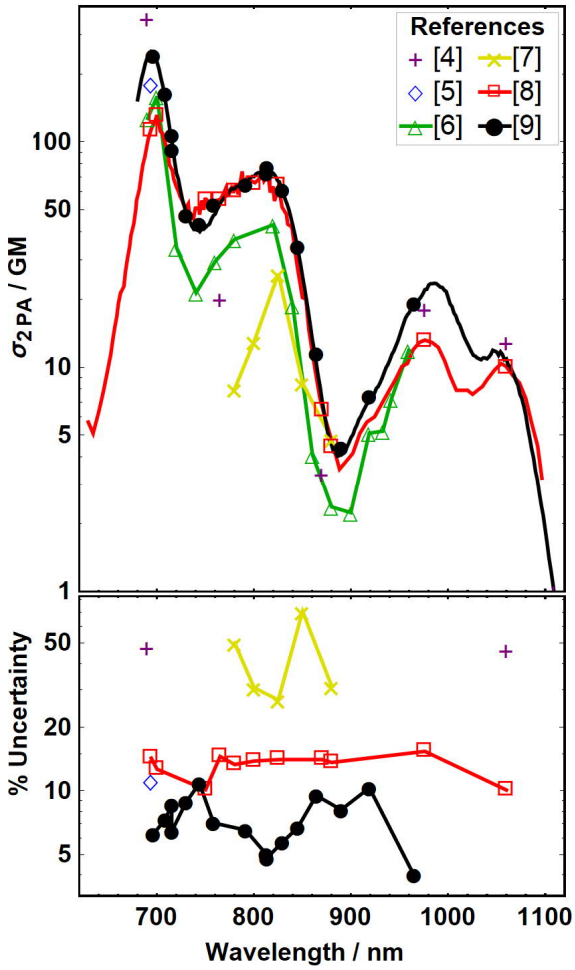

Figure 1. Top: Two-photon cross section measurements of Rhodamine 6G (1 GM = 10^{-50} cm^4 s $photon^{-1}$). Bottom: Reported relative uncertainty (k = 1) in cross section measurements. Both plots are on a log scale showing the wide range of reported cross section and relative uncertainties.

To address the issues of reproducibility and accuracy, we have developed a high throughput instrument for the automated characterization of two-photon cross section and spectra. This instrument has pulse characterization, coupled with the ability to measure multiple samples, as well as a broad spectral range, so our results may be easily comparable to other systems.

METHODS

Our 2PA setup, depicted in Figure 2, measures the two-photon excited fluorescence of samples. Excitation pulses (1 mJ, <150 fs) are generated by a Yb laser (Pharos-SP, Light Conversion), followed by an optical parametric amplifier (OPA, Orpheus-HE, Light Conversion) and second harmonic generation (SHG), which allow for wavelength tunability from 315-2600 nm. These pulses can be characterized in terms of bandwidth, pulse duration, pulse energy and beam diameter. Power is adjusted using a neutral density filter, providing a quadratic fluorescence response which is recorded via PMT. Collecting emission, rather than direct absorption helps eliminate other nonlinear processes, such as excited state absorption.

The key advantages of this system lie in the automation of many of its functions. It is capable of measuring power dependent spectra over a broad range of wavelengths, with comparisons of up to four samples in a single run. Comparisons can also be made to the corresponding one-photon absorption, which is achieved via SHG using a BBO crystal.

In conjunction with this spectrometer, our research group has also implemented the first online database of two photon absorption spectra (www.kbfi.ee/mpa), providing reference compounds for other facilities to measure 2PA.

INITIAL RESULTS AND FUTURE PLANS

Initial measurements indicate 2PA spectra are highly reproducible, with variations of spectral shape <5%, and of absolute cross section <10%, which we plan to improve shortly. In addition to the emission detection we currently have, we plan to install a nonlinear transmission detector, which will allow us to determine what circumstances these two techniques agree or disagree. We also have tentative discussions with national metrology institute (AS Metrosert) towards establishing a certified and SI-traceable 2PA measurement service.

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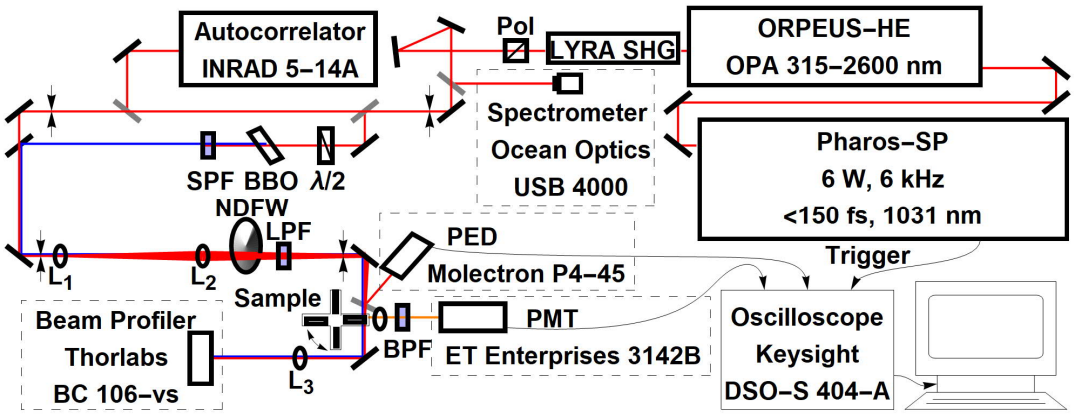

Figure 2. Schematic of the automated femtosecond 2PA spectrometer. Pol – polarizer; FM – flip-mirror; LPF – long-pass filter; SPF – short-pass filter; BPF – band-pass filter; L_n – lenses; $\lambda/2$ – half-wave plate; BBO – barium borate crystal; NDFW – neutral density filter wheel; PED – pyroelectric detector; PMT – photomultiplier tube.