Sol-Gel Glasses Doped with Pt-Acetylides and Gold Nanoparticles for Enhanced Optical Power Limiting

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High power laser pulses can be a threat to sensors, including the human eye. Traditionally this threat has been alleviated by colour filters that blocks radiation in chosen wavelength ranges. Colour filters' main drawback is that they block radiation regardless of it being useful or damaging, information is removed for wavelengths at which the filter protect. Protecting the entire wavelength range of a sensor would block or strongly attenuate the radiation needed for the operation of the sensor.

Sol-gel glasses highly doped with Pt-Acetylide chromophores have previously shown high optical quality in combination with efficient optical power limiting through reverse saturable absorption¹. These filters will transmit visible light unless the light fluence is above a certain threshold. A key design consideration of laser protection filters is linear absorption in relation to threshold level. By increasing chromophore concentration the threshold is lowered at the expense of higher linear absorption. This means that the user's view is degraded through the filter.

Adding small amounts of gold nanoparticles to the glasses resulted in an increase in optical power limiting performance. The optimal concentration of gold nanoparticles corresponded to a mean particle distance of several micrometers. The work in this licentiate thesis is about the characterization and explanation of this effect.

The glasses investigated in this work were MTEOS Sol-Gel glasses doped with either only gold nanoparticles of varying shape and concentration, 50 mM of PE2-CH₂OH codoped with gold nanoparticles or 50 mM of PE3-CH₂OH codoped with gold nanoparticles. The glasses only doped with gold nanoparticles showed high optical power limiting performance at 532 nm laser wavelength, but no optical power limiting at the fluences tested at 600 nm. The PE2-CH₂OH glasses codoped with gold nanoparticles showed an enhancement of optical power limiting at 600 nm for the low gold nanoparticle concentration glasses. The enhancement was weak-

¹Standard nomenclature, see section 1.3.3.

ened or not present for higher concentrations. A similar enhancement above noise level for the PE3-CH₂OH glasses was not found.

A population model is used to give a qualitative explanation of the findings. The improvement in optical power limiting performance for the PE2-CH₂OH glasses is explained by the gold nanoparticles helping to more quickly populate the highly absorbing triplet state during the rising edge of the laser pulse by enhancing two-photon absorption. The lack of any marked enhancement for the PE3-CH₂OH glasses is explained by the PE3-CH₂OH chromophore already being of sufficiently high performance to quickly populate the highly absorbing triplet state during the rising edge of the laser pulse. Further work is necessary to validate this model against other chromophores and improving its quantitative predictive power.

Populärvetenskaplig sammanfattning

Laserpulser med hög effekt kan vara ett hot mot sensorer, inklusive människoögat. Traditionellt har detta hot hanterats med färgfilter som stoppar strålning inom valda våglängdsband. Färgfilters huvudsakliga begränsning ligger i att de tar bort strålning oberoende av om den är användbar eller skadlig, information försvinner för de våglängder filtret skyddar för. Skydd över hela det våglängdsband en sensor verkar i skulle stoppa eller kraftigt försvaga strålningen som sensorn behöver för att fungera.

Sol-gel glas högdopade med Pt-Acetylid-kromoforer har tidigare visat hög optisk kvalité i kombination med en effektiv optisk effektbegränsning via omvänt mätbar absorption. Dessa filter transmittar synligt ljus så länge ljusets fluens inte ligger ovan en viss begränsningsnivå. En nyckelfaktor i designen av laserskyddsfilter är linjärabsorption kontra begränsningsnivå. Genom att öka kromoforkoncentrationen så kan begränsningsnivån göras lägre till kostnad av ökad linjärabsorption. Detta betyder att användarens vy genom filtret degraderas.

Genom att lägga till små mängder guldnanopartiklar i glaset ges en förbättring i optisk effektbegränsningsprestanda. Däremot uteblev förbättringen för högre koncentrationer. Arbetet som presenteras i denna licentiatrapport handlar om karakterisering och förklaring av denna effekt.

En populationsmodell togs fram för att förklara experimentens resultat. Förbättringen av optisk effektbegränsningsprestanda förklaras av att guldnanopartiklarna hjälper till att snabbare fylla på den högabsorberande triplettnivån under början av laserpulsen genom förstärkning av två-fotonabsorption. Populationsmodellen förutsäger däremot att denna effekt inte orsakar relevanta prestandaförbättringar för breda klasser av kromoforer och våglängdsområden. Mer arbete behövs för att validera modellen mot andra kromoforer samt öka dess förmåga att kvantitativt förutsäga experiment.

Preface

This licentiate thesis is part of my PhD studies at IFM LiU (The Department of Physics, Chemistry and Biology at Linköping University) and FOI (Swedish Defence Research Institute). My studies has been conducted as a part of my ordinary work as a research engineer at FOI, primarily focusing on protection against lasers.

My work on laser protection began after researchers at FOI lead by C. Lopes had discovered an unexpected and peculiar optical power limiting performance enhancement at 600 nm laser wavelength from adding minute amounts of gold nanoparticles to Pt-Acetylide doped sol-gel glass. Optical power limiting measurements had shown that the optimal concentration of gold nanoparticles corresponded to a mean inter-particle distance of several micrometers.

The origin of the enhancement needed to be identified to answer the questions of how and if the effect could be used to enhance the optical power limiting performance of other filters. Furthermore, an inherent goal of my PhD studies is to develop and consolidate FOI's capability to design new laser protection filters. Finally, an important objective not to be forgotten is to maintain the cooperation with our university partners.

Doping sol-gel bulk glasses with high concentrations of Pt-Acetylide chromophores while retaining the ability to polish the glasses to optical quality had previously been solved in cooperation with Prof. Parola's group at ENS de Lyon [1]. While their group focused on the production of the bulk materials, chromophores and gold nanoparticles, our group polished the glasses (L.-G. Heimdal) and characterized their optical properties.

A long standing cooperation also exists with my LiU supervisor Prof. M. Lindgren from NTNU (Norwegian University of Science and Technology). In this constellation Prof. M. Lindgren and his group has focused on the photophysics and advanced spectroscopic techniques.

As a first step in my studies I traveled to NTNU in Trondheim to learn how to do photophysical measurements on the glasses. While analysing the fluorescence

and phosphorescence lifetimes and relative spectral intensity of the chromophore, a lack of pattern was discerned across the series of different shape and concentration of gold nanoparticles. This contradicted many quenching based models proposed to explain the performance enhancement from *low* concentrations of gold nanoparticles.

At this point our team was at a loss regarding on how this mechanism worked. To increase the number of parameters acting as constraints on any potential future models it was decided to expand the already large series of glasses. Two sub-series were added, one identical to the previous series but only doped with gold nanoparticles and a second smaller one doped with both gold nano-particles and an alternative more high performance chromophore.

I and C. Brännlund then made additional optical power limiting measurement on the glasses. The results for the original series of glasses was reproduced (for the second time). While the results for the glasses solely doped with gold nanoparticles showed good performance at 532 nm laser wavelength, the results contradicted models based on superposition of optical power limiting from the chromophore and nanoparticles. The glasses doped with gold nanoparticles and an alternative high performance chromophore showed excellent performance at 600 nm but no obvious non-linear optical power limiting performance increase from gold nanoparticles. While disappointing, these findings would later turn out to be vital in finding a model explaining the phenomenon.

C. Lopes performed the UV-Vis spectral measurements on the glasses. The spectra showed well defined gold nanoparticle plasmon peaks for all glasses. Though for bipyramidal gold nanoparticles co-doped with the alternative chromophore there was a peak wavelength shift with nanoparticle concentration, indicating an uneven distribution of gold nanoparticles [2, 3].

While trying to find a satisfying model explaining our experimental results we decided that the results from the glasses only with gold nano-particles was interesting in their own right. With ellipsometry, Z. Ghadyani and Prof. M. Kildemo found an interesting self-orientation of bipyramidal gold nanoparticles in the glasses. Though no interesting pattern in regards to enhancement of optical power limiting was found in the ellipsometry data.

I decided to also use an integrating sphere to see if the optical power limiting of the glasses only doped with gold nanoparticles showed optical power limiting due to non-linear scattering as for gold nanoparticles in solution [4]. Due to the expected angle dependence on scattering from a gold nanoparticle [5–7], I was not comfortable in using the more standard Z-scan [8] method. A secondary goal was to detect any strong second harmonic generation. The measurements were consistent with non-linear scattering as a mechanism for optical power limiting in the glasses only doped with gold nanoparticles. No strong second harmonic generation was found, again removing a potential model of optical power limiting enhancement by gold nanoparticles. (Which seemed promising after I developed a model with input from Prof. Patrik Norman.) I thank T. Hallberg for helping in the design of an integrating sphere working in the UV-Vis range. I thank C. Brännlund for taking part in the measurements and practical setup of the experiment.

For the second article the original series of glasses was investigated. Prof. M.

Lindgren and A. A. El-Amay performed a series of photophysical measurements on the chromophore and gold nanoparticles in solution, including excited state absorption. They showed that the excited state absorption increased by gold nanoparticles, secondly that gold nanoparticles quench the triplet state of the chromophore. Though, due to the difference in surrounding medium between solution and sol-gel glass the quenching explanation could not be applied on the glasses. Such a solution could not explain the photophysical results for the glass samples. A new model had to be developed.

Thanks to the two-photon absorption spectra of the two chromophores recently published by M. G. Vivas et al. [9, 10], in combination with an analytical model of field enhancement by K. Tanabe [11] and the concept of feeding a population model the field enhancement field by S. Fischer et al. [12] it was possible for me to create a qualitative model describing system behaviour using photophysical parameters of very similar chromophores published by Rogers et al. [13]. By modeling the relative absorption enhancement from field enhancement of two-photon absorption it was possible to show that the gold nanoparticles caused the highly absorbing triplet state to be populated more quickly during the leading edge of the pulse.

For the third article the lack of obvious enhancement had to be explained not to discredit the model from the second article. My hypothesis was that a more efficient population of the triplet state in the better performing alternative chromophore would cause the field enhancement of two-photon absorption to have less of an impact. Since some relevant photophysical parameters of a very similar chromophore were missing from the literature and we were unable to measure them with meaningful precision in bulk glass, some parameters had to be estimated. Prof. M. Lindgren suggested the linear absorption being larger due to red-shift of the UV-absorption peak of the alternative relative to the original chromophore. Postulating a 10x increase of the very weak linear absorption of the original chromophore showed a marked decrease in optical power limiting enhancement.

The path leading to the creation of this model was not straight. For brevity I've not included all tested hypotheses and measurements. Working with the philosophy "When you have found something unexpected, you are most probably doing something wrong.", I've had ample opportunity to scrutinize our experimental methods. I've therefore chosen to include a frank and thorough investigation of potential weaknesses in our previous optical power limiting measurement protocol used during the measurements presented in this thesis. I've also chosen a selection of hypotheses for which I explain why they are less probable than the two-photon field enhancement model.

I believe this extra caution is necessary since my theoretical work resulted in novel ways to evaluate the performance enhancement of non-linear chromophores. By investigating the relative absorption enhancement for each point in time during a laser pulse, new understanding of relative chromophore performance can be gained. This method of evaluating the time evolution of population models have the power to aid in both the design of excited state absorption systems and interpreting experiments. The scientific impact of this model is wider than on the limited system/application we were investigating.

Acknowledgements

I want to thank my university supervisor, Prof. M. Lindgren. Not only for acting as any good supervisor should, but also taking the extra time and effort to advice me during his parental leave. His experience in photophysics, laboratory work, and supervising PhD students has been invaluable.

The efforts of my FOI project leader C. Lopes can not be ignored. He has not only been a project leader, but also as a secondary supervisor of my studies. He has always been able to combine the requirements of utility to the project with the needs of my studies, finding ways to create win-win situations. C. Lopes has taught me about chromophores, sol-gel glasses and much about the fine craft of scientific writing.

The head of department at FOI, M. Armgarth, is thanked for his insistence on me focusing on my studies while other projects vied for my attention. Without his support my studies would not have been possible.

My colleague C. Brännlund is thanked for teaching me how to perform optical power limiting measurements. He also wrote the computer code for our laboratory's optical power limiting setup.

Prof. Parola and his group at ENS de Lyon is thanked for their substantial part in this work. Since I consider myself primarily an experimentalist, interesting samples is of utmost importance for my work. The very long series of glasses required for this work, in combination with their large effort on the articles is strongly appreciated.

Both Lindgren and Lopes are thanked again for their help with proofreading this thesis.

I'm very grateful for the funding from the Swedish Armed Forces allowing me to pursue my PhD studies while working at FOI.

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CHAPTER 1

Introduction

Optical power limiting (OPL) is a nonlinear optical effect, attenuating optical radiation more strongly when there is more radiation. Optical power limiting is useful for multiple applications including eye protection and self-activating optical switches [14]. The purpose of this work is to explain and find ways to enhance this attenuation.

This introduction chapter will first describe the laser threat from an eye/sensor safety perspective, the application motivating this work. The next section, 1.2, explains why the properties of the laser threat invites a solution based on self-activating filters. In section 1.3 an overview of mechanisms for optical power limiting is given. The basics of molecule population models is described in section 1.4.

The chromophores used in this work PE2-CH₂OH and PE3-CH₂OH are very similar to the Pt-acetylides PE2 and PE3 [15, 16]. Both PE2 and PE3 have been well characterized and reported about in the literature [9, 10, 13]. A summary of relevant photophysical parameters from the literature is given in section 1.6.

A previously used method to increase OPL performance is by increasing the concentration of chromophores in the filter, though the increase in performance decline with higher concentration [1]. Sol-gel glasses have proven to be versatile since they can be doped with gold nano-particles and/or high concentrations of Pt-ethynyl chromophores while retaining their ability to be polished for optical use [1, 15, 17]. A short overview of sol-gel glasses relevant to the matrix of the glasses used in this work is given in section 1.7.

This work investigates the enhancement of optical power limiting from gold nanoparticles. A short introduction in the physics of gold nanoparticle in nonlinear optics is given in section 1.8.

1.1 The laser threat

Not long after the discovery of the laser the importance of laser safety was understood due to the damage potential to human eyes [18–20]. From a military perspective, the use of laser technology has caused both accidental and intentional damage to human eyes [21, 22]. While international law protects the unenhanced human eye from intentional permanent damage, the legal protection is far from complete [22].

Traditionally partial protection has been achieved by eye-patches, mono-ocular optics and colour filters [22]. Colour filters have the draw-back of degrading the image [22, 23]. A colour-degraded image induce varying degrees of "induced colour blindness" [24]. The larger wavelength span protected, the larger amount of information never reach the image sensor.

When evaluating different methods for protection against lasers, multiple threat parameters are of importance. When evaluating incoming radiation from a point source, the most important parameters are:

Pulse energy Maximum incident energy before failure of a sensor is a central parameter for describing sensor susceptibility to laser damage [14]. The limit is often expressed in J m^{-2} on the entrance pupil of the optical system (pupil for the human eye). Note that sometimes it is expressed as fluence on the detector (retina in the eye).

Peak power Combined with pulse energy, another central parameter is peak power received by a sensor [14]. It is often expressed as irradiance in W m^{-2} . Again, a distinction between entrance pupil and detector surface needs to be made.

Pulse duration Shorter pulse length with the same pulse energy results in higher peak power. For the human eye the dominant damage mechanism and thresholds depend on pulse length [25].

Continuous power For a train of multiple laser pulses the average irradiance is also important to consider [25].

Wavelength Maximum allowable exposure depend on the wavelength of the laser radiation [25]. Also, colour filters only protect at wavelengths where they block radiation.

Beam quality A laser beam of lesser quality will not be focused into as small a spot as a perfect gaussian beam. This mean that in many cases the threat to the sensor would be lower due to lower fluence/irradiance compared to a diffraction limited beam.

The main physical mechanisms causing damage to the human eye are thermoacoustic transients, thermal effects and photochemical processes [25]. Thermoacoustic transients are mainly relevant at pulses in the nanosecond regime or shorter, thermal effects in the intermediary 0.1s to 10s range and photochemical for long term exposure [25].

Figure 1.1. An ideal reverse saturable absorber according to multiple sources [14, 23, 27]. The dashed line show the transmittance of a linear material or a reverse saturable absorber in its linear regime. The dotted line shows the so called clamping level of the filter, preferably below the damage threshold of the detector. The red line shows the input fluence versus output energy characteristics of an ideal reverse saturable absorber.

According to Swedish workplace safety regulations, the maximum permissible single pulse exposure for nanosecond pulses in the visible wavelength range is 5 mJ m^{-2} [25]. A 7 mm diameter pupil results in a maximum pulse energy of $0.2 \mu\text{J}$, in agreement with other sources [14]. The filters investigated in this work are optimized for nanosecond pulses of visible light.

1.2 Self-activating filters

No information can travel faster than the speed of light [26]. This means that the connection between the triggering and attenuating mechanism of a filter must be shorter than it takes any damaging levels of radiation to reach the attenuation mechanism, which is especially important when dealing with pulses in the nanosecond regime or shorter. [6]. By choosing a laser protection method that is self-activating this constraint can be bypassed [6]. A secondary advantage of self-activating filters is lowering the complexity of the laser protection system, avoiding the need for active feedback [6].

Dini et al.'s recent comprehensive review of the subject summarize a wide variety of materials proposed as optical power limiters, including but not limited to nanocrystalline materials, metal nanoparticles, hybrid organic-inorganic materials such as Pt-ethynyls and carbon based materials like graphene [14]. The behaviour of an ideal optical power limiter, in this case a reverse saturable absorber (section 1.3), is shown in figure 1.1.

The filters investigated in this work are MTEOS sol-gel glasses doped with gold nanoparticles (section 1.8) and/or platinum acetylides (section 1.6) [15–17]. Due

Figure 1.2. To achieve optical power limiting from a self-activating filter the laser pulse needs to be focused into the material [27].

to the high clamping level of today's materials the laser pulse needs to be focused into the material to sufficiently lower the clamping level, see figure 1.2 [27].

1.3 The photophysics of optical power limiting

There are multiple potential mechanisms to achieve optical power limiting by self-activating filters [14]. In this section different classes of optical power limiting will first be defined and compared from a functional perspective. Secondly, relevant mechanisms for nonlinear absorption and methods to characterize them will be described.

1.3.1 Classes of optical power limiting

Functionally, self activated optical power limiting in bulk materials can be divided into three classes, nonlinear scattering, nonlinear refraction and nonlinear absorption. This classification scheme for optical power limiting materials is derived considering how a material can be optically described.

In linear optics a material can be described by a complex index of refraction $N(\lambda) = n(\lambda) + ik(\lambda)$, where $n = \sqrt{\epsilon}$ is the index of refraction, k the extinction coefficient and λ the wavelength [28]. If inhomogeneities of N in a material is not significantly smaller than λ , scattering can occur [28].

All of these three parameters can be varied nonlinearly [6, 14]. Since these nonlinear effects can occur simultaneously it is important to distinguish between them when analyzing experiments [6, 14].

Another useful classification scheme is the distinction between instantaneous and accumulative nonlinearities [6]. Instantaneous nonlinearities depend on intensity (W cm^{-2}) while accumulative nonlinearities depend on fluence (J cm^{-2}) [6].

Nonlinear refraction

When light traverses a medium with changes in the refractive index, the light might be refracted according to Snell's law [28].

Different mechanisms for nonlinear refraction include thermal lensing or carrier generation leading to an optically induced Kerr-effect [6, 14]. By placing an aperture after the self-activating filter, optical power limiting can be achieved due to self-(de)focusing [6, 14].

The photorefractive effect can be used for optical power limiting [6]. The mechanism is explained by a grating of refractive index variations formed by the electro-optic effect from mobile carriers excited by an interference pattern of two coherent beams [29]. Optical power limiters employ the photorefractive effect to cause beam fanning of coherent light [6].

A strength of filters based on nonlinear refraction is their lower susceptibility to damage [6].

Nonlinear absorption

With nonlinear absorption excess radiation is absorbed by the filter. Assuming a low fluorescence and phosphorescence quantum yield the amount of removed radiation again being collected by following optical elements is lowered. Two examples of mechanisms are two-photon absorption (section 1.3.2) and reverse saturable absorption (section 1.3.3) [6, 14].

Nonlinear scattering

When radiation can induce scattering centers in a material the result is nonlinear scattering [6]. In solution metal nanoparticles can act as scattering centers due to microplasmas forming around them during a laser pulse [14, 30]. Though in solid materials permanent damage is an expected problem [6].

Scattering centers much smaller than the wavelength can be described by Rayleigh scattering [31]. The scattering and absorption of spherical metal nanoparticles has been described by Mie theory [32]. Mie scattering has been used to explain the microplasma scattering in carbon-black suspensions [33].

Another drawback of nonlinear scattering is that the optics after the filter will collect a part of the scattered light. For simple calculations regarding performance limits in the design of optical systems employing nonlinear scattering for laser protection, see section 1.5.2.

Z-scan measurements

In the optical power limiting field the z-scan measurement is an often used method to characterize optical power limiting materials [6, 14]. The method allows for quantitative measurements of nonlinear absorption and refraction [6, 14, 34]. Though nonlinear absorption and scattering can not be distinguished by a z-scan [6].

Figure 1.3. A z-scan measurement setup [34]. The insert show the z-scan result for a filter with negligible nonlinear refraction. The aperture may or may not be present.

The measurements are performed by transposing the sample along the beam path through the focus, see figure 1.3 [6, 14, 34]. When the filter is closer to the laser focus the intensity gets larger. By measuring both with and without the aperture, absorption and refraction can be distinguished [6, 14, 34].

By fitting the measured data to a model assuming that the nonlinear refraction and absorption can be described by

$$n(I) = n_0 + \gamma I \quad (1.1a)$$

$$\alpha(I) = \alpha_0 + \beta I \quad (1.1b)$$

it is possible to estimate the γ and β parameters [34]. By using a picosecond laser it is possible to avoid the influence of the triplet state (section 1.3.3) [6]. It is also possible to approximate the behaviour of reverse saturable absorption by a β parameter [14].

While the original z-scan method assumes a gaussian beam and thin sample, more recent improvements to the z-scan method allows for non-gaussian beams and thick samples [14, 23, 35]. It is possible to apply this formalism for fluence, F , instead of irradiance, I [23]. Though the validity for nanosecond pulses is questionable [23].

Nonlinear transmission or Optical Power Limiting (OPL) measurements

A straight-forward measurement method often used is placing the laser focus in the sample and varying the incoming irradiance or fluence [14]. But there is a danger of nonlinear refraction corrupting the results [14]. For a more thorough description of an OPL measurement setup, see section 2.1. Example results are shown in figure 1.4.

A nonlinear transmission measurement is often a simple way to evaluate a filter. But due to variation of optical setup, beam quality etc. it is important

Figure 1.4. OPL measurement of 50 mM PE3-CH₂OH in MTEOS glass [16].

to realize the limited potential for comparing data across measurement setups or even different calibrations. A solution to this problem is to always use a reference sample when measuring a series of filters.

A strength of this method apart from its simplicity is that the measurement is conceptually close to the engineering problem of protecting a sensor. A carefully designed setup allows for a good estimation of real world filter performance.

1.3.2 Two-photon absorption

Two-photon absorption is an instantaneous nonlinearity where the energy from two photons is absorbed [6]. Two-photon absorption was first postulated by Göppert-Mayer in 1931, though required the development of the laser for real world applications [14, 23]. The nonlinear absorption coefficient, β , can be described by

$$\alpha(I) = \alpha_0 + \beta I \quad (1.2a)$$

$$-\frac{\partial I}{\partial z} = \alpha_0 I + \beta I^2 \quad (1.2b)$$

[6, 23, 27]. For a quantum mechanical explanation of the mechanism an introductory quantum electronics book is recommended [36].

Two-photon absorption has been used as a mechanism for optical power limiting [6, 14]. Since two-photon absorption depend on intensity, I , instead of fluence the mechanism is not expected to give adequate laser protection for nanosecond pulses or longer [6, 23]. But in combination with reverse saturable absorption (section 1.3.3) two-photon absorption has potential for protection against longer

Figure 1.5. Five level Jablonski diagram of a reverse saturable absorber [6, 23, 27].

pulses [23, 27]. Population modelling (section 1.4) has shown that the presence of two-photon absorption can lower the clamping level of reverse saturable absorbers [27].

Measurements

Equation 1.1b and 1.2a from the z-scan formalism have the same form. Open aperture z-scan method has often been used to determine β , the nonlinear two-photon absorption coefficient [14, 27]. However, care must be taken with pulse length and repetition rate to avoid the influence of reverse saturable absorption [9, 10, 23].

1.3.3 Reverse saturable absorption

Reverse saturable absorption is an accumulative nonlinear mechanism (depends on fluence, F) used for optical power limiting [6, 14, 23, 27]. Most relevant chromophores for reverse saturable absorption can be described by a five-level population model, see figure 1.5 [23, 27]. When a chromophore in its ground state, S_0 , absorbs a photon an electron gets excited into the higher singlet state S_1 . If the inter system crossing time, τ_{isc} , is short compared to fluorescence and quenching, τ_{S1S0} , the electron might reach the triplet state, T_1 . When the absorption cross section of the triplet state is much larger than the singlet state, $\sigma_{T1T2} \gg \sigma_{S0S1}$, the chromophore can act as an optical power limiter [14, 23, 27]. Often the relaxation times of S_2 and T_2 are assumed fast enough that these levels can be ignored [23, 27]. Long enough triplet lifetime, τ_{T1S0} , is important for reverse saturable absorption of less intense light sources [37].

Figure 1.6. The left plot is the ground state absorption of PE2-CH₂OH in THF (1), with varying amounts of 45 nm diameter spherical gold nanoparticles **S1** & **S2** and only gold nanoparticles in THF **AuNP**. The dashed lines show the result of bleaching. The right plot shows the transient absorption. Excitation was from single 5 ns, 355 nm laser pulses. Both plots reproduced with permission, measured by Lindgren [15].

Measurements

Apart from luminescence strength and lifetime measurements (section 1.3.4) excited state absorption measurements can be used to investigate reverse saturable absorbers [15, 27]. Flash photolysis used for excited state absorption measurements was pioneered by Porter in 1950 [27, 38].

For an overview of the technique, see Glimsdal's PhD thesis [27]. A short recapitulation is given here. By first measuring the absorbance spectrum of the sample in its ground state and then comparing it to the absorbance spectrum in its excited state, it is possible to measure absorption spectra of the triplet state. The excitation source might be either a pulsed flashlamp, LED or laser depending of the characteristics of the sample. Shortly after the excitation pulse, the probe flashlamp is fired and the transmitted light collected.

Example data is given in figure 1.6. Transient absorption is the excited state absorbance subtracted by the ground state absorbance.

1.3.4 Luminescence

Radiative relaxation from the S_1 and T_1 state cause fluorescence and phosphorescence respectively [39]. By investigating luminescence spectra and lifetimes it is possible to estimate decay constants including quenching, see figure 1.5 [27, 39].

Quenching is a process where the energy of an excited electron find alternative pathways than luminescence to relax to a lower state, for example collisional quenching, resonant energy transfer and Dexter interaction [39].

Gold nanoparticles can quench chromophores [39–42]. They can also increase radiative decay and rate of excitation [39, 42].

Considering the importance of the decay constants for reverse saturable ab-

Figure 1.7. Luminescence spectrum of a 50 mM PE2-CH₂OH in MTEOS Sol-Gel glass.

sorption (section 1.3.3), the luminescence properties of the filters investigated in this work needed to be investigated.

Measurements

Two methods used to measure the luminescence properties of a sample is emission spectroscopy and Time-Correlated Single-Photon-Counting (TCSPC) [27]. Again, Glimsdal's PhD thesis gives an excellent introduction to these two techniques [27]. A short recapitulation is included here for completeness: Emission spectroscopy is achieved by first exciting the sample by for example a flashlamp/monochromator combination, LED or Laser. Then the luminescence is measured by monochromator or spectrometer. TCSPC is a widely used technique where a low fluence light source is used to excite the sample. When the emitted photons from the sample are few enough that less than two photons per 100 pulses are detected, a timing histogram can be created.

Example data is given in figure 1.7 and 1.8. In figure 1.7 the fluorescence peak is at 430 nm while the phosphorescence peak is at 526 nm. The phosphorescence decay of similar sample is shown in figure 1.8. It has been fit to a two-exponential decay model, often used to investigate the dynamics of chromophores [39].

1.4 Population models

Population modelling is widely used to model the photophysical dynamics of chromophores [9, 10, 12, 23, 27, 43]. The technique can basically be described as a numerical implementation of a Jablonsky diagram (figure 1.5), evolved stepwise with Δt in [s]. If Δt is short enough a single step of a population model can be implemented by

$$dN_i = \sum_{j \neq i} \sigma_{ji} J \Delta t N_j + \sum_{j \neq i} \omega_{ji} J^2 \Delta t N_j - \sum_{j \neq i} \frac{\Delta t}{\tau_{ij}} N_i \quad (1.3)$$

where N_i is the population density of orbital i in [cm^{-3}], J the photon flux density in [$\text{cm}^{-2}\text{s}^{-1}$], σ_{ji} the single photon cross section for electrons in orbital j being excited into orbital i expressed in [cm^2], ω_{ji} the two-photon cross section in

Figure 1.8. TCSPC measurement of the phosphorescence decay of a 50 mM PE2-CH₂OH in MTEOS Sol-Gel glass.

[cm⁴s] and τ_{ij} the relaxation time into orbital j expressed in [s]. This algorithm can favourably be implemented in matrix notation. Care must be taken to avoid using too long time steps, Δt , compared to photon flux density and relaxation times. The attenuation coefficient α in [/cm] can then be calculated by

$$\alpha = \sum_i \sum_j (\sigma_{ji} N_j + \omega_{ji} J N_j) \quad (1.4)$$

1.4.1 Conversion of units

To aid in the implementation of population modelling software, unit conversion formulas from more widely used units are included here. Numerical density is often expressed in molar concentration, N_M , in [mol L⁻¹], the starting numerical density can then be expressed by

$$N_0 = N_M \cdot n_0 / 1000 \quad (1.5)$$

where n_0 is the Avagadro constant. The photon flux depends on both the irradiance, I [W cm⁻²], and wavelength, λ [m],

$$J = \frac{I \lambda}{h \cdot c} \quad (1.6)$$

where h [Js] is the Plank constant and c [ms⁻¹] the speed of light [44]. The two-photon cross-section can be converted from [GM] (Göppert-Mayer units) by

$$\omega_{ji} = \omega_{GM} \cdot 10^{-50} \quad (1.7)$$

[10]. The linear cross section, σ_{ji} , is often expressed in absorbance, A [/Mcm], as

$$\sigma_{ji} = 1000 \ln 10 \cdot A/n_0 \quad (1.8)$$

, observe the change in base.

1.5 Optics

Both the z-scan and OPL-measurements employ a focused laser beam (section 1.3.1). A reverse saturable absorber is placed at the focus to achieve optimal optical power limiting [6, 14, 23, 27].

1.5.1 Laser focus size

A gaussian beam is recommended for both OPL and z-scan measurements [14]. Though alternative beam shapes can be handled numerically, and often necessary to contemplate due to imperfections in lasers [23]. A perfect gaussian beam focus, ω_0 , can be described by

$$\frac{\omega_0}{\omega} = \frac{\frac{f\lambda}{\pi\omega^2 n}}{\sqrt{1 + (\frac{f\lambda}{\pi\omega^2 n})^2}} \quad (1.9)$$

where f is the focal length of the lens, ω the beam radius at the lens and n the index of refraction in the medium [36]. Assuming that $\lambda \ll f/\omega$ and Taylor expanding around $\lambda = 0$ we get the well known rule of thumb

$$\omega_0 \approx \frac{f\lambda}{\pi\omega n} \quad (1.10)$$

. Any imperfections will result in a larger spot size [23].

Another variant of a perfect beam is that of flat wave cut by a circular aperture with radius a and focused into a spot at distance f , an Airy disk [44]. Assuming the spot size is much smaller than the focal length of the lens the Airy disk is

$$I(r) = I_0 \left[\frac{2J_1(\frac{2\pi ar}{\lambda R})}{\frac{2\pi ar}{\lambda R}} \right]^2 \quad (1.11)$$

where r is the distance from spot center and J_1 the first Bessel function [44]. A comparison between a gaussian and airy disk spot is shown in figure 1.9, where the functions have been multiplied by $2\pi r$. It shows how even an ideal reverse saturable absorber (figure 1.1) will show a slope after the cut-off level has been reached due to the low fluence but large area rings not being caught by the filter. This problem has been known in the field for a long time [45].

Figure 1.9. Comparison between Gaussian and Airy disk focus. The intensity at position r from the center is multiplied by the circumference $2\pi r$. The multiplication by $2\pi r$ is done to show the impact of the large area of Airy rings. The beam radius of the gaussian beam at the lens is set to $a/\sqrt{2}$, where a is the lens radius for the Airy disk. $f = 0.1$ m, $\lambda = 600$ nm, $a = 1$ cm, $n = 1$ and $I_0 = 1$ W m⁻².

1.5.2 Optical system design for optical power limiting

While the nonlinear scattering is not expected to be spherically distributed [6], the spherical approximation can be used to gain an understanding of an inherent limitation of nonlinear scatterers as self-activating filters. Since the filter is placed in an intermediary image plane, scattered light collected by following optics will still be imaged on the sensor. The same is true for non-linear absorbers with high fluorescence and/or phosphorescence efficiency. If the entrance pupil of the optics after the filter has the radius r and a distance R from the filter the fraction of light transmitted is

$$\frac{r^2}{4R^2} \quad (1.12)$$

. This means that to achieve an optical density of OD4 for a half inch diameter lens after a non-linear scatterer, a 30 cm focal length would be necessary. This would in most cases put unacceptable design constraints on the optical system as a whole.

1.6 Platinum acetylides

Platinum acetylides are a class of hybrid metal-organic molecules used for optical power limiting [14]. Platinum acetylides are also known as platinum phenyl-ethynyls and Pt:ethynyl complexes [9, 10, 13, 14].

Metal organic complexes in general are appreciated for the ability to combine the advantages of organic and inorganic materials for optical power limiting [14]. Strengths include strong non-linear response, fast response times and large design flexibility [14]. More specifically metal acetylides are known for large nonlinear optical properties while retaining good transparency in the visible wavelength region [14].

Platinum acetylides are known as very good broadband optical power limiters in the visible wavelength range. [9, 10, 14]. The Platinum center cause inter-system crossing due to its weakly bound electrons in combination with the ligands' electron transporting acetylide groups, while the ligands give high two-photon absorption [9, 46]. The platinum acetylides are characterized by fast inter system crossing times, high excited state absorption, good two-photon absorption and long triplet lifetimes [9, 47]. The singlet absorption peak is often in the UV/deep blue range while the triplet absorption cover a wide wavelength range [13, 46–51]. The low ground state absorption of platinum acetylenes in the visible make them excellent reverse saturable absorbers (section 1.3.3) [47]. For blue light the dominant mechanism is one-photon absorption into the singlet state with intersystem crossing into the highly absorbing triplet state [47, 48]. For green, a forbidden direct transition into the triplet state is important [47, 48]. While in the yellow/red region two-photon absorption followed by intersystem crossing dominates [47, 48].

The two platinum acetylides chromophores used in this work are based upon PE2 and PE3. These two chromophores show a strong triplet state absorption in the order of 10^4 to 10^5 /Mcm in the visible while the singlet absorption peaks are in the UV [13]. The chromophores have been functionalized with CH_2OH to facilitate dissolving into the matrix precursor [1].

1.6.1 PE2

The PE2 chromophore is a molecule well characterized in the literature. A comparison between PE2 and PE2- CH_2OH is shown in figure 1.10. Due to their similarity photophysical constants for PE2 is used in the population modelling work (chapter 4). The singlet absorption peak is located in the UV, with a large absorbance up to $9 \cdot 10^4$ /Mcm at around 355 nm (in benzene solution) [13]. The triplet absorption peak is broadband and covers the visible range [13, 48]. The absorbance varies between $1 \cdot 10^4$ and $4 \cdot 10^4$ /Mcm for visible light [13]. The singlet absorption in the visible is low, around 6 /Mcm at 450 nm and 0.2 /Mcm at 600 nm [13]. There is a short inter-system crossing time of less than 300 ps while the inter-system crossing quantum efficiency is high at 0.92 [13, 48]. The phosphorescence decay time for PE2- CH_2OH in MTEOS Sol-Gel glass is around 1-2 μs [1]. At 595 nm there is a two-photon absorption peak of 290 GM [10].

1.6.2 PE3

PE3 is like PE2 but with an extra phenyl-ethynyl group at the two phenyl-ethynyl ligands. A comparison between PE3 and PE3- CH_2OH is shown in figure 1.11. As expected this extra phenyl-ethynyl group increases non-linear absorption perfor-

Figure 1.10. Comparison between PE2 (upper) and PE2-CH₂OH (lower) [1, 13, 15]. PBu₃ is tributylphosphine.

Figure 1.11. Comparison between PE3 (upper) and PE3-CH₂OH (lower) [1, 13, 16]. PBu₃ is tributylphosphine.

mance [9]. A stronger, compared to PE2, two-photon absorption peak of around 680 GM is located at 610 nm [9]. The singlet absorption peak is somewhat red-shifted to 377 nm [13]. The excited state absorption is significantly larger, especially in the red, up to $4 \cdot 10^8$ /Mcm [13]. However, the inter-system crossing quantum efficiency is lower at 0.72 [13]. Still, the inter-system crossing time is shorter at around 20 ps [9].

1.7 Sol-Gel glasses

Dyes doped into solids instead of dissolved into solution has obvious advantages for practical applications [1]. Chromophore doping of glasses can be characterized into two classes, either Class 1 where the dye molecules are embedded in the glass matrix or Class 2 where the chromophores are covalently bound to the matrix [52]. Class 1 materials have shown better clamping level performance than Class 2 materials, but puts requirements on solubility of the chromophore into the glass matrix [1, 52].

A glass matrix widely used for nonlinear optical materials is PMMA, an organic glass (Commonly known as acrylic glass and is not a Sol-Gel.) [14, 47, 52]. It is known for its good mechanical properties [47, 52]. Bulk PMMA has been both Class 1 and 2 doped with high concentrations of PE2 derivatives [52].

Recent advances in Sol-Gel technology allow for the glasses to be made far more quickly, a problem that earlier has hindered their use in real applications [1, 47, 53]. Compared to PMMA the Sol-Gel glasses have better optical quality, thermal stability and less susceptibility to damage [47]. Also, the process is relatively low temperature, increasing the number of potential chromophores [1]. Both Class 1 and Class 2 doping is possible [1, 53]. Extremely high concentrations of up to 400 mM of PE2-CH₂OH has been achieved with Class 1 doping [1]. But the clamp-

ing level did not lower linearly with increasing chromophore concentration [1].

1.7.1 Pores

It is possible to control the pore size by modifying the matrix of the Sol-Gel glass [1]. This can be done by changing the precursor of the glass, such as MTEOS¹ (methyltriethoxysilane) [1]. Thereby controlling the amount of quenching of the triplet state from the formation of singlet oxygen [1]. Controlling the chromophore exposure to oxygen and thereby increasing the lifetime of its triplet state has been used to increase reverse saturable absorption of less intense light [37].

1.8 Gold nanoparticles

Gold nano-particles are particles small enough that when light strikes them, the free electrons in the gold metal form resonances depending on the shape and size of the particle [54]. Modern methods such as the "discrete dipole approximation" are able to accurately model the absorption and scattering cross-sections of different shapes and constellations of gold nanoparticles [54–56]. By controlling the shape of gold nanoparticles it is possible to choose where the plasmon resonance is located in the wavelength spectrum [54, 56, 57]. The change in plasmon resonance wavelength due to different sizes/shapes of bipyramidal gold nanoparticles is demonstrated in figure 1.12 [17]. Gold nanoparticles in close proximity to each other show a shift in plasmon resonance wavelength [2, 3, 58, 59].

1.8.1 Enhancement of chromophores

Gold nanoparticles can both enhance and quench the fluorescence of dyes [39–41, 54, 60]. At a few nanometers distance quenching is dominant while at around 10 nm field enhancement dominates [39, 54, 60]. Longer distance effects, such as increased radiative rate or chromophore to gold nanoparticle energy transfer due to overlapping fluorescence and plasmon resonances, have shown longer interaction ranges of several tens of nanometers [39, 61, 62].

Chromophore two-photon absorption enhancement by gold nanoparticles has been reported from multiple sources [47, 48]. Two-photon absorption depend on the fourth power of the electric field enhancement around a gold nanoparticle [63]. Surrounding a spherical nanoparticle the intensity enhancement ($\sim |E|^2$) field can be described by Tanabe's analytical model

$$\eta = \left| 1 + 2 \frac{a^3}{r^3} \frac{\epsilon_1 - \epsilon_m}{\epsilon_1 + 2\epsilon_m} \right|^2 \cos^2 \theta + \left| -1 + \frac{a^3}{r^3} \frac{\epsilon_1 - \epsilon_m}{\epsilon_1 + 2\epsilon_m} \right|^2 \sin^2 \theta \quad (1.13)$$

where a is the nanoparticle radius, r the distance from the nanoparticle center to the observing point, ϵ_1 is the dielectric constant of the surrounding medium, ϵ_m the dielectric constant of the nanoparticle and θ the angle between the electric field and the vector between the particle position and observing point [11].

¹The glass samples used in this work were MTEOS glasses.

Figure 1.12. MTEOS glasses doped with different sizes/shapes of bipyramidal gold nanoparticles. The Au^0 concentration is 0.125 mM. A glass without gold nanoparticles is included for comparison. Measured by Lopes [17].

CHAPTER 2

Measurements

The purpose of this chapter is to describe and evaluate the measurements of the published papers included in this thesis in a more thorough manner than in the articles. The focus will be on the optical power limiting measurements (section 2.1) due to their central importance for this work. Then several short sections will give an overview of the other techniques that this work depend on (section 2.1, 2.2, 2.3, 2.4 & 2.5). Finally, potential weaknesses in the measurement method and sample limitations are discussed in section 2.6.

2.1 Optical power limiting measurements

The optical power limiting measurement (section 1.3.1) setup used in this work is based on the $f/5$ standard setup often used to test the performance of optical power limiting materials [23, 64–68]. The principle of operation is that a plane wave pulse of known energy strikes the 2 cm aperture of a $2.5\times f/5$ telescope, with the sample placed in the focus of the 10 cm focal length lens, see figure 2.1 [23, 64–68]. The setup is optimized to answer the question of how good a filter attenuates a laser pulse. It is not designed to answer what mechanisms that cause the optical power limiting (section 1.3.1).

2.1.1 Experimental setup

The main components of the optical power limiting setup used in this work, see figure 2.1, can be described by: a Brilliant B + Rainbow OPO, two motorized filter wheels allowing for OD 0 to OD 3 in OD 0.1 increments, a galilean telescope (3.33x) for beam expansion, a beam clean-up system, an 8% pellicle beam splitter, an Ophir PE9-SH reference pulse energy detector, a second galilean telescope

Figure 2.1. Highly schematic view of the $f/5$ setup used in this work [23, 64–68].

(2.66x), a 20 mm aperture, a 10 cm focal length lens L_1 , a sample positioned by micrometer stepper motors, a 4 cm focal length lens L_2 , a 8 mm aperture, a 100 cm focal length lens L_3 and a Ophir PD10-V1-SH signal pulse energy detector.

This setup has three main differences compared to most other implementations of the $f/5$ setup.

First, a beam clean-up by a $f = 30$ cm, $d = 200$ μ m pin-hole filter was necessary due to the low quality beam from the optical parametric oscillator (OPO). The pinhole filtering was also done for the second harmonic beam during the 532 nm measurements. The pin-hole diameter was not chosen from the wavelength of the laser pulses, but from practical beam quality/pin-hole damage considerations. The necessary pinhole diameter was large due to the laser beam quality being low due to the OPO crystal being damaged (a small spot was visible in the crystal).

Secondly, the large pinhole/aperture after L_3 was not considered necessary due to the high optical quality of the glass samples.

Thirdly, there was no 7 mm aperture ahead of L_2 to stop scattered light.

Integrating sphere

To investigate the mechanism of the optical power limiting from gold nanoparticles an integrating sphere was used. Z-scan was not used due to non-linear scattering being expected [14, 30]. A 7.5 cm diameter integrating sphere was placed around the sample while L_2 , A_2 and L_3 was removed. The signal detector was placed against a secondary port of the integrating sphere located perpendicular to the beam. Measurements were also performed with a UV short-pass filter in front of the signal detector to see if there was any strong second harmonic generation.

2.1.2 Calibration

The reference detector was calibrated by measuring a series of varying fluence laser pulses with the signal detector in the sample position. The losses through L_2 , A_2 and L_3 was implicitly assumed to be zero.

The area of the beam was estimated by the 10/90 knife edge method. By moving a sharp edge across the beam with sub-micrometer precision it was possible to measure the horizontal profile of the beam. The beam area was defined as $\pi(D/2)^2$ where D is the distance between 10% transmittance and 90% transmittance.

The integrating sphere was calibrated by measuring the output pulse energy for varying input fluences without the sample inserted [17].

2.1.3 Quantification and analysis of the results

A quantification of optical power limiting performance was made by point plots as in figure 1.4, page 7. The x-axis was calculated from the calibrated reference pulse energy divided by beam area. The y-axis was the measured signal pulse energy. The x-axis unit was selected due to fluence [J/cm^2] being the relevant parameter for photophysics of reverse saturable absorbers. The y-axis was selected to aid in the detection of data-points outside the linear range of the detector, secondly to aid in any discussion about damage threshold in any optical system placed after the laser protection filter.

Since the measurement method is optimized for measuring filter performance instead of physical parameters, it is important to always include reference samples in any measurement series. Since the results are very dependent on beam quality (which might vary between setups or even measurement campaigns), any comparison between measurements without a proper reference could be considered questionable.

Due to the stochastic variation in laser pulse energy the placement of laser pulses across the input fluence x-axis was not evenly distributed. Secondly, the sample propensity to attract dust caused some laser pulses to have significantly lower transmitted pulse energy.

By tradition any dense accumulation of sample points were trimmed from lower transmitted pulse energy and upwards. Secondly, any obvious outliers were removed. This was done to avoid reporting too good performance of the filters due to the random variation in transmitted energy having a tendency to lower the OPL-curve. Also, a data point at origo was always added.

2.2 Thickness measurements

Sample thickness was measured by a digital slide caliper across multiple locations of the glass edge.

2.3 Photophysical measurements

The setup used for photophysical measurements in Lindgren's laboratory at NTNU, Trondheim, is described in Glimsdal et al.'s 2009 article [69]. Excited state absorption measurements of PE2-CH₂OH and/or gold nanoparticles in THF solution were performed. Also, luminescence spectra and lifetimes of the glasses were measured. The fluorescence lifetimes of the Pt-acetylides were too short to collect with the available hardware.

The fluorescence spectra were very sensitive to placement of the glass sample and dirt. To increase measurement precision a mechanical sample holder was constructed instead of using the earlier double sided tape method. The luminescence spectra and phosphorescence lifetimes were measured at three occasions, twice by me, once by Lindgren.

2.4 UV-Vis Measurements

Transmission spectra of the glass samples were recorded with a CARY 5G UV-Vis-NIR spectrometer [15–17]. The measurements were performed by Lopes.

2.5 Ellipsometry

Ellipsometry is a method where the change in polarization for different angle of incidence and/or wavelength is measured [28]. Ghadyani and Kildemo used Mueller matrix ellipsometry to show that the bipyramid gold nano-particles were self-oriented in some of our samples [17].

2.6 Weaknesses

Due to the unexpected nature of the findings (chapter 3), extra impetus for a more thorough reporting of potential error sources exist. Two areas were identified as most critical, the optical power limiting measurements and sample quality.

2.6.1 Optical power limiting measurements

The optical power limiting measurement setup and methodology used was not optimized to identify different physical processes behind optical power limiting, but instead answer the engineering question of what the practical performance of a specific filter is. The potential error sources reported below all stems from this optimization.

Deletion of data points

While the trimming of the data is justifiable from an engineering standpoint since it avoids reporting of too good performance due to stochastic variation in the data (section 2.1.3), the trimming of data has scientific pitfalls. Not due to any risk

of the perceived result differing, but that the quality of data looks to be *slightly* higher than it should. This step has been removed from our current measurement method.

Insufficient control of beam quality

The beam quality was only estimated by moving a knife edge across the beam (section 2.1.2). Not only does this only measure the beam quality in the horizontal but not vertical direction, but also assumes a somewhat nice top-hat or gaussian beam. The nature of any deviation from a flat wave on the f/5 lens was not investigated. In a worst case scenario hot-spots could have been present in the beam.

This risk was managed by including reference glasses into the measurement series and redoing the measurements with new alignment of the optical system each time. The results were reproduced.

The quantitative reproducibility (absolute cut-off level in μJ) of the setup has been improved by placing a CMOS camera near the sample position during alignment. Secondly, 3-axis stepper motors will allow for a secondary vertical knife-edge measurement.

Unknown amount of nonlinear refraction

The measurement setup is not able to distinguish between nonlinear refraction and absorption/scattering. Though care was taken that the laser spot on the detector did not change drastically in size with input fluence. Since the measurements were performed multiple times any large nonlinear refraction should have been noticed. Secondly, a nonlinear refractor at the focus is not expected to cause much refraction of the beam, for the same reason that a thin lens placed in a focus will not [6].

Performing both open and closed aperture Z-scans would fully rule out nonlinear refraction as a relevant mechanism. A more simple solution is to always make extra measurements with the 8 mm aperture removed.

Incomplete calibration

The losses of L_2 , A_2 and L_3 was not zero. Investigation of the undoped MTEOS glass data found losses of up to 18% that were unaccounted for. Part of the difference was found to arise due to a faulty anti-reflection coating. It is possible that placing the filter in the optical path changed the beam width at A_2 .

Since reference samples were used and optical power limiting measurements only should be used for intra-series comparison this was not a large problem. The calibration method has been updated to include any losses after the sample.

No measurement of damage

Since there were only two axes for the stepper motors (along the optical axis and horizontal perpendicular to it) it was not possible to systematically investigate any

damage to the glasses. Pairing any damage to a specific pulse considering wavelength and pulse energy was not possible with the current measurement method. That the glasses had a strong tendency to attract dust made microscope studies hard.

A possible solution would be to photograph the sample at each pulse [70]. This would allow the hypothesis of the optical power limiting for glasses only doped with gold nanoparticles being from microfractures in the glass testable. Expected results would be no fractures in the chromophore/gold nanoparticle doped glasses and fractures in the glasses only doped with gold nanoparticles.

2.6.2 Samples

While most measurements were reproduced multiple times, a weak link was that the same samples were used several times. Using several identical samples to test for reproducibility would have further strengthened the results.

Thickness

The PE2-CH₂OH glasses' thickness were within specifications of 1 ± 0.05 mm (but the broken glass piece was within measurement uncertainty outside this range), though there was a pattern of more highly gold nanoparticle doped glasses being slightly thinner within specifications. Due to the glass holder in the optical power limiting measurements always placing the front surface at the same position, the impact of this pattern was judged to be negligible.

After publication it was found that the series of glasses only doped with gold nanoparticles was not fulfilling specifications. They were $\approx 7\%$ too thick (varied between 1.04 mm and 1.10 mm), but showed acceptable intra-series variation.

The PE3-CH₂OH doped glasses were $\approx 7\%$ too thick and had a slight wedge shape within the thickness variation specification. Since the front surface was placed correctly by the sample holder and the deviation was noticed before publication, this was not deemed a problem.

Gold nanoparticle stability

A colour shift in the bipyramidal gold nanoparticles' plasmon resonance was detected after a few months. This was attributed to the tips being eroded.

This resulted in that we choose not to make an additional series of optical power limiting measurements with a new laser.

Surface durability and cleanness

The surface of the glasses were found to be extremely easy to scratch. This was an unfortunate property in combination with the glasses' strong propensity to attract dust.

This made it difficult to model the surface properties for ellipsometric models. This in turn made it impossible to measure the weak linear absorption at 600 nm of the chromophores in MTEOS glass. This would give too many free parameters in

the theoretical modelling (chapter 4), resulting in ambiguities in the interpretation of the model compared to experimental results.

Refractive index inhomogeneities

It is common practice in the research field to show sample optical quality by photographing the sample on a background with for example the university logotype [14, 47]. While this method detects many defects such as transmittance variations, cracks and bubbles, it will not detect even moderate refractive index variations. The proper way to detect such inhomogeneities is holding the sample at an arms length and looking at a far away object. Photographing the sample and a far away background with a large f-number lens would be a better practice for publication.

Due to the glass samples being made in small crucibles there are refractive index changes towards the edges. This make the glasses into weak lenses. The impact on the measurement results are expected to be small.

The practice of using small glass making crucibles for saving glass material has been discontinued.

Summary of article results

The three articles that this work rest upon are highly connected. Not only were many of the measurements performed at the same occasion, but the analysis was done taking the results from all three articles into account (chapter 4).

The first article reported on a wide variety of different shapes and concentration of gold nanoparticles doped in MTEOS glasses. The second article investigated glasses doped as in the earlier article together with 50 mM PE2-CH₂OH. The third article was about a more limited set of glasses doped with gold nanoparticles and 50 mM PE3-CH₂OH. The different shapes and concentrations of gold nanoparticles are compiled in table 3.1. For more in-depth information about the samples, see the supplementary information of the articles [15–17].

3.1 Glasses with only gold nanoparticles

The MTEOS glasses doped with gold nanoparticles showed good optical power limiting performance for 532 nm pulses, but none at all for 600 nm pulses at the tested fluences [17]. At 532 nm the optical power limiting was better than for glasses doped with both chromophores and gold nanoparticles. The optical power limiting at 532 nm was absent when collecting the nonlinearly scattered light by an integrating sphere [17]. The linear transmittance spectra showed well defined plasmon peaks that did not show any marked widening or shift with increased gold nanoparticle concentration.

3.2 Glasses with gold nanoparticles and PE2-CH₂OH

The MTEOS glasses doped both with gold nanoparticles and 50 mM PE2-CH₂OH showed at 600 nm lower optical power limiting clamping level for low concen-

Table 3.1. The different series of gold nanoparticle doping used in article 1 (only gold nanoparticles in MTEOS glass), article 2 (also doped with 50 mM PE2-CH₂OH) and article 3 (50 mM PE3-CH₂OH). Reference glasses for each article with no gold nanoparticles were also made. The Largest Surface Plasmon Resonance (LSPR) is the peak wavelength of absorption corresponding to the longitudinal resonance in the bipyramidal gold nanoparticles. The LSPRs in this table are for the particles in solution and not bulk glass. For calculation of particle concentrations see [17].

Particle shape	Concentration		Article
	Gold (mM)	Particle (nM)	
Spheres 23 nm	0.125	0.06	1,2,3
	0.25	0.13	1,2,3
	0.50	0.25	1,2,3
	1.00	0.5	1,2,3
Spheres 45 nm	0.031	0.006	1,3
	0.063	0.013	1,2,3
	0.125	0.026	1,2,3
	0.25	0.052	1,2,3
	0.5	0.1	1,2,3
Bipyramids LSPR=640 nm	0.063	0.29	1,2
	0.125	0.58	1,2
	0.25	1.15	1,2
Bipyramids LSPR=700 nm	0.063	0.12	1,2
	0.125	0.24	1,2
	0.25	0.48	1,2
Bipyramids LSPR=770 nm	0.063	0.048	1,2,3
	0.125	0.097	1,2,3
	0.25	0.19	1,2,3
Reference	0	0	1,2,3

Figure 3.1. Optical power limiting measurement of MTEOS glasses doped with 50 mM PE2-CH₂OH and varying concentrations of bipyramidal gold nanoparticles with a largest surface plasmon resonance of 700 nm (as measured in solution) [15].

trations of gold nanoparticles compared to particles or high concentrations, see figure 3.1 [15]. At 532 nm a similar pattern was not found. As with the previous glasses, the UV-Vis measurements showed well defined plasmon peaks without any marked widening or shift with gold nanoparticle concentration. The luminescence spectra and phosphorescence lifetimes of the glasses showed no apparent systematic differences regarding to gold nanoparticle concentration or shape. Excited State Absorption measurements in THF solution showed a larger absorption and a decrease in phosphorescence yield with gold nanoparticles, also phosphorescence lifetime decreased with more gold nanoparticles in the solution.

3.3 Glasses with gold nanoparticles and PE3-CH₂OH

The glasses doped with gold nanoparticles and PE3-CH₂OH did not show any pattern of improvement of clamping level above noise level compared to the glasses only doped with PE3-CH₂OH [16]. At 600 nm all PE3-CH₂OH glasses showed a clamping level much lower than the PE2-CH₂OH glasses. Secondly, the cut-off was very sharp. The UV-Vis spectra showed a wavelength shift with concentration of bipyramidal gold nanoparticles.

Phosphorescence lifetime measurements were not possible due to a lack of discernible phosphorescence peak.

CHAPTER 4

Population Model

To account for and explain the results reported in chapter 3, a model with predictive power had to be created to allow for the design of future composite chromophore/gold nanoparticle materials. Several questions had to be answered simultaneously, either by one mechanism or several acting together:

1. Why was there clamping level enhancement of PE2-CH₂OH at 600 nm but not at 532 nm?
2. Why was there optical power limiting at 532 nm but not at 600 nm for glasses only doped with gold nanoparticles? Why was performance better at 532 nm compared to glasses also doped with a chromophore?
3. Why was no second harmonic generation detected as expected for gold nanoparticles [71, 72]?
4. Why was there only clearly noticeable enhancement for PE2-CH₂OH but not for the PE3-CH₂OH chromophore?
5. Why is there enhancement at only low concentrations of nanoparticles? The doping concentrations of the gold nanoparticles corresponded to an average particle distance in the micrometer scale.
6. Why does the enhancement disappear at higher concentrations of gold nanoparticles?
7. Why didn't the enhancement correlate to any changes in luminescence spectra or phosphorescence lifetimes?
8. Why was there excited state absorption enhancement for PE2-CH₂OH in solution together with gold nanoparticles?

9. Why was there signs of quenching in the phosphorescence decay times for PE2-CH₂OH with increasing concentration of gold nanoparticles in solution?

These questions were able to discredit several hypotheses:

Quenching/rate changes Since any large quenching or rate changes would have changed the photophysical measurement results (question 7) this hypothesis was weak. Secondly, considering the low concentration of gold nanoparticles, the expected range of quenching [39, 54, 60] would have a hard time to influence large enough percentage of the glass material (question 5). While resonances between chromophore fluorescence band and nanoparticle plasmon band can increase the interaction range [61, 62], the lack of enhancement of the clamping level at 532 nm excitation wavelength would be difficult to explain with this mechanism. Collisional quenching [39] can explain the quenching of phosphorescence in solution (question 9).

Hot electrons A potential solution to the long range problem (question 5) would be excited electrons from the gold¹ [73]. This mechanism would be problematic to combine with question 4 and 1. It's hard to see why any excited electrons would influence PE2-CH₂OH but not PE3-CH₂OH. Secondly, the wavelength dependence would be difficult to explain considering both 532 nm and 600 nm being above the resonances of gold [74].

Superposition A combination of optical power limiting from chromophores and gold nanoparticles is an unlikely explanation considering question 2. A simple superposition is not compatible with the lowering of performance at 532 nm with the addition of a chromophore.

Linear field enhancement Considering the lack of enhancement at 532 nm (question 1) this was not a probable explanation. It is known that similar platinum acetylides' main mechanism around this wavelength is linear absorption followed by intersystem crossing into the triplet state [13, 47, 48].

Second harmonic generation An interesting solution to the questions above would be second harmonic generation from the gold nanoparticles. It would have explained the wavelength dependence due to the higher matrix absorption and lower chromophore absorption at 532/2 nm. Secondly, PE2 in solution has an absorption peak at 600/2 nm [13]. But no second harmonic generation was found (question 3).

Considering that at 600 nm the expected mechanism for reverse saturable absorption in similar platinum acetylides is two-photon absorption followed by intersystem crossing into the triplet state [47, 48] and that field enhancement of two-photon absorption has been reported in the literature [63, 75, 76], it is apt to investigate how a two-photon field enhancement model could answer the questions above.

¹Idea from Mårten Armgarth.

1. At 532 nm the dominant mechanism is linear absorption followed by inter-system crossing [13, 47, 48]. This would explain the lack of enhancement for green light.
2. An alternative mechanism not present or dominant in glasses also doped with chromophores would be necessary to mesh well with a two-photon absorption enhancement model. Considering that the optical power limiting from gold nanoparticles in solution originates from non-linear scattering from microparticles [14, 30], the high doping of chromophores might make it harder for microcracks to form in the glass. This hypothesis should be considered untested.
3. Since no strong second harmonic generation was detected from the gold nanoparticles, this mechanism was not deemed probable.
4. For reasoning why enhanced two-photon absorption will not influence the performance of PE3-CH₂OH glasses as much, see section 4.2.
5. Two-photon absorption enhancement can be both powerful and long range. See section 4.1.
6. The dependence on I^2 for two-photon absorption is more sensitive than linear absorption ($\sim I$). This means that any linear absorption before the focus have more impact, see section 4.3.
7. The photophysical measurements were made at different wavelengths. This mechanism does not require quenching.
8. The excited state absorption measurements were performed by exciting the UV singlet absorption peak [15]. This question neither supports nor discredits the two-photon absorption enhancement model.
9. The quenching of chromophores in solution is different from when the chromophores are stuck in a glass matrix. Moving chromophores and gold result in collisional quenching [39].

While the two-photon absorption enhancement model meshes well with earlier findings in the literature and at least at a superficial level explains the results, constructing a numerical population model to evaluate it at a qualitative level was considered necessary. Photophysical parameters were selected from the similar chromophores PE2 and PE3 (section 1.6).

4.1 Two-photon field enhancement

From equation 1.2b we know that the amount of photons two-photon absorbed is linear to

$$-\frac{\partial I}{\partial z} \sim \beta_0 I^2 \quad (4.1)$$

where

$$I = \eta I_0 \quad (4.2)$$

and β_0 is two-photon absorption coefficient of the chromophore. η is the Tanabe field enhancement factor [11] from equation 1.13 and I_0 the intensity of the incoming laser pulse. An effective two-photon absorption coefficient can then be defined as

$$\beta = \eta^2 \beta_0 \quad (4.3)$$

giving

$$-\frac{\partial I}{\partial z} \sim \beta I_0^2 \quad (4.4)$$

. In the direction of maximum field enhancement

$$\eta = \left| 1 + 2 \frac{a^3}{r^3} \frac{\epsilon_1 - \epsilon_m}{\epsilon_1 + 2\epsilon_m} \right|^2 \quad (4.5)$$

from equation 1.13 [11]. For 23 nm and 45 nm gold [77, 78] spheres in a $n = 1.43$ material, the field enhancement at 600 nm wavelength is shown in figure 4.1 [15]. In the plot, only the enhancement further away than 10 nm from the gold surface is filled in as a conservative measure considering the quenching seen in solution (question 9).

4.2 Absorption enhancement factor

Applying this effective two-photon absorption into a population model (section 1.4) combined with photophysical parameters from similar platinum acetylides (section 1.6) it is possible to calculate the absorption $\alpha(\eta^2, t)$ from equation 1.8. The idea to feed a population model a field enhancement factor was taken from Fischer et. al's modelling of luminescence enhancement [12]. In an analogue manner an absorption enhancement factor can be defined as

$$\gamma(\eta^2, t) = \frac{\alpha(\eta^2, t)}{\alpha(1, t)} \quad (4.6)$$

Instead of the spatial variation of η , the time evolution t of the reverse saturable absorption is investigated. The results for PE2 and PE3 (section 1.6) are shown in figure 4.2. Since the linear absorbance of PE3 at 600 nm is not known two different values were selected, the same as PE2 or 10 times as much. A higher linear absorption would not be considered surprising considering the red-shift of the singlet absorption peak in PE3 compared to PE2 [13].²

The enhancement for the PE2 model shows how the leading edge of the pulse more easily populate the triplet state in the presence of gold nanoparticles. After

²Idea from Mikael Lindgren.

Figure 4.1. Field enhancement from gold nanoparticles of diameter 23 nm or 45 nm in 50 mM PE2-CH₂OH doped MTEOS glass [15]. The x-axis is the direction of maximum enhancement. The two vertical lines are the surface of the gold nanoparticles. The part of the curves filled in are at the distances where field enhancement can be assumed to dominate quenching [39, 54, 60].

the leading edge of the pulse the triplet state is already populated enough, resulting in most light being blocked. This explains the increased performance from co-doping with gold nanoparticles and PE2-CH₂OH.

The lower enhancement of the PE3 model with higher linear absorption compared to the PE2 model shows how an already high performing reverse saturable absorber will not get the same relative enhancement due to the highly absorbing triplet state already being populated quick enough. Considering the higher performance of PE3-CH₂OH compared to PE2-CH₂OH while measurement noise being comparable between the different series, it would not be impossible that the enhancement is hidden below the noise level of the measurement³.

4.3 Linear absorption before the focal point

It is a well known that having an absorbing medium in front of the focus in a non-linear material will lessen the optical power limiting effect [16]. The linear absorption before the focus can interfere with the non-linear scattering of nanodiamonds [79]. The losses from gold nanoparticles before the focus can be estimated to

$$T_{AuNP} = \sqrt{\frac{T}{T_0}} \quad (4.7)$$

³Idea from Mikael Lindgren.

Figure 4.2. Field enhancement factor for a 5 ns, 10 J/cm² pulse [16]. PE2 and two potential variants of PE3 are investigated. Expected η^2 values selected from figure 4.1.

where T is the transmittance of the glass and T_0 is the transmittance of a reference glass without any gold nanoparticles. The effective two-photon absorption coefficient can then be expressed by

$$\beta = \eta^2 T_{AuNP}^2 \beta_0 \quad (4.8)$$

Since the T_{AuNP}^2 acts over the entire glass volume while η^2 is only strong near a gold nanoparticle, even the estimated T_{AuNP}^2 values between 0.97 to 0.76 for the glasses with highest concentration of gold nanoparticles could have larger influence than η^2 .

4.4 Potential pitfalls of the model

While the two-photon enhancement model survived the qualitative test described above, it must be stressed that the numerical model has several issues that need to be explained in deeper detail.

- The photophysical values of PE2 and PE3 were measured in solution [9, 10, 13]. Secondly, the chromophores used in the glasses were functionalized with CH₂OH. The impact of the glass matrix has not been taken into account but for quenching of the triplet state (which had no impact since 1 μ s is much longer than the 5 ns laser pulse). This means that the photophysical parameters used only can be considered as coarse estimates.
- The linear absorption of PE3 is unknown. However, any other method for more efficient population of the triplet state, such as a forbidden S_0 to T_1 transition could replace the assumption of higher linear absorption.

- The model does not take into account the beam propagation, only a single point at the focus. To fully test the validity of this model, a spatial model with stochastic placement of gold nanoparticles would be necessary. This is especially necessary for modelling the interplay between linear absorption before the focus and two-photon absorption at it.
- The numerical model is intended as a test for the two-photon enhancement model. Other effects such as linear field enhancement, quenching etc. has not been included in it. To make such a test meaningful a more complicated spatial model would have to be constructed.
- To fully test the model, a greater range of chromophores with varying two-photon absorption, linear absorption, intersystem crossing rate and excited state absorption need to be investigated, preferably in solution to allow for greater variation.⁴

While the qualitative numerical model is useful as a first test for the two-photon absorption enhancement hypothesis, it needs further work to give more quantitative predictions.

The assumption of higher linear absorption in PE3-CH₂OH in MTEOS glass at 600 nm creates an unwanted free variable that lessens the persuasive power of the model. The shifting plasmon resonance wavelength with different concentration of bipyramids in the PE3-CH₂OH glasses (section 3.3) begets the question if the changing of this variable is an attempt to shoe-horn a failed experiment into a theoretical model. A shift in plasmon resonance wavelength could indicate that the gold nanoparticles were not evenly distributed in the glass [2, 3, 58, 59]. Though a similar shift is not seen for the spherical nanoparticles. Secondly a marked widening of the absorption peaks with increased nanoparticle concentration due to random group sizes is not seen.

⁴Idea from Mikael Lindgren.

Conclusions and future work

The work that this report is based on shows how gold nanoparticles can enhance reverse saturable absorption. Also, a qualitative model has been developed to explain how some chromophores can be enhanced more than others.

The qualitative model shows that only at wavelengths where the dominant mechanism of the chromophore is two-photon absorption large enhancement of reverse saturable absorption is expected. Secondly, if the chromophore already is sufficiently populated during the leading edge of the pulse, the enhancement is not expected to be as large.

Due to limitations in the available measurement methodology and chromophores investigated, a more quantitative model would be premature. Further work is necessary to both test the qualitative model with chromophores with varying photo-physical parameters and creating a quantitative model of predictive value.

Considering the predicted limitations regarding two-photon absorption enhancement for laser protection (wavelength and chromophore choice), alternative methods for enhancing chromophore performance should be investigated. Current efforts include chromophore alignment by electric field during the glass making process and creating glasses with less pores resulting in protection against continuous wave lasers.

CHAPTER 6

Errata

Minor errors in the articles have been found after publication.

Dispersion and self-orientation of gold nanoparticles in sol-gel hybrid silica - optical transmission properties

- The reference detector was a PE9-SH not PE9.
- The gallilean telescope was 2.66x not 2x.

Long distance enhancement of nonlinear optical properties using low concentration of plasmonic nanostructures in dye doped monolithic sol-gel materials

- The pure two-photon absorption without reverse saturable absorption was overestimated in the absorption enhancement factor by η . Secondly, all the linear absorption was underestimated by $\ln 10$. The correct plot is shown in figure 6.1. Any changes to the discussion or conclusion is not necessary since the relevant qualitative behaviour of the model was the same.

Figure 6.1. Correction to the absorption enhancement factor in article 2.

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