New insights into nonlinear optical effects in fullerene solutions—a detailed analysis of self-diffraction of continuous wave laser radiation

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Abstract
Spatial self-phase modulation (SSPM), i.e. the formation, temporal evolution and subsequent distortion of self-diffraction ring patterns, generated by transmitting a continuous wave 532 nm laser beam through solutions containing C60 or C70 has been investigated. The nonlinear optical response regarding SSPM of such systems was studied, to our knowledge for the first time, in dependence of various solvents, different sample temperatures and viscosities. The SSPM patterns consisted of a number of concentric rings, generated due to induced refractive index changes and start with a central spot, expanding into a series of concentric rings. The number of rings increases steadily and the ring pattern becomes larger with time until a maximum is reached. Thereafter, thermal convection leads to a distortion of the upper part of the ring system, while the lower part keeps its shape. The dependence of temporal and spatial evolution of self-diffraction ring pattern on different sample parameters and not only the functional material itself, leading to our conclusion that thermal effects are responsible for the observed SSPM. For further substantiation, measurements of C60 in toluene at a wavelength of 1070 nm have been carried out. At this wavelength no absorption occurs and no SSPM patterns were observed. Knowing that for ultrashort pulses no significant thermal effects take place, we performed additional measurements at a pulse length of 8 ps and a wavelength of 527 nm. Also in this case no SSPM patterns were generated. In order to gain a deeper understanding of the involved physical processes, we developed a thermal blooming simulation: Thermally-induced refractive index changes and convection caused by locally heating of the solution by the laser beam were taken into account, any other nonlinear phenomena were left aside. A laser beam propagating through an absorbing solution generates similar ring structures under these conditions, what is in fully agreement with our experimental results. Additionally, as a practical application of SSPM a laser protection device is presented.

1. Introduction

Light–matter interaction with a strong external optical field gives rise to a variety of nonlinear optical phenomena. Among other things, it can lead to spatially dependent refractive index changes. Since a laser beam has a spatially varying intensity profile the response of the medium becomes spatially dependent. As a result, self-focusing, self-defocusing or SSPM can occur. SSPM refers to a phenomenon where concentric circular diffraction rings can be observed in the far field, due to constructive and destructive interference within the self-phase modulated beam.

In literature the origin of SSPM is attributed to several different effects. For example to thermo-optical effects in Chloro-Aluminium-incorporated phthalocyanine solutions [1], Ag2S semiconductor nanocrystal dispersions [2] or nitropeptide solutions [3], to $\chi^{(3)}$ third order susceptibility effects like the intrinsic nonlinear
refractive index $n_2$ in dispersions of graphene sheets [4], in black phosphorus dispersions [5] and NbSe$_2$ nanosheet suspensions [6] and to the effect of molecular reorientation in liquid crystals [7, 8]. In older publications SSPM was mainly attributed to the thermo-optical effect, whereas in many recent publications often only the optical Kerr effect is mentioned [6, 9–11] as cause for SSPM. The thermal influence is taken into account only for the phase where the ring system starts to collapse.

As a matter of fact, in absorbing materials already at low power continuous wave radiation thermal processes may occur. They are leading to large and often unwanted nonlinearities: The absorption of light leads to energy deposition in the irradiated material, altering its macroscopic optical properties and resulting in an effective third-order nonlinearity. Thermally induced refractive index changes can easily reach the order of $10^{-5}$ cm$^2$/W, while $\chi^{(3)}$ refractive index changes are usually at least five orders of magnitude smaller [12]. Excluding them without any investigations seems therefore somewhat surprising, Wang et al, for example, have questioned the third order nonlinear susceptibility $\chi^{(3)}$ theory as origin of SSPM in graphene suspensions under continuous wave illumination [13]. After their investigations they found the thermal lens effect responsible for the refractive index changes.

Since their discovery, fullerenes are attracting a great deal of research interest, but some aspects still remain unexplored. The existence of fullerenes was predicted and theoretically described by Eiji Osawa in 1970 [14] for the first time, but being published in Japanese only, his article remained unconsidered for many years. As a consequence of this, his work has been recognized as the first known suggestion that C$_{60}$ might be stable [15] only a long time later, after their experimental discovery. Thus, the third allotropic form of carbon, was attributed to Robert F Curl, Sir Harold W Kroto and Richard E Smalley. In 1985 they made the first experimental observations of the fullerene C$_{60}$ [16] and in 1996 they were jointly awarded the Nobel Prize in chemistry for their discovery. C$_{60}$ is the best known representative of the fullerene family, but meanwhile nearly spherical hollow carbon molecules with 60, 70, 76, 78, 84 carbon atoms and many more have been synthesized and characterized. Theoretically all molecules according to the formula C$_{2n+2}$ with $F \equiv 1$ and $F \geq 0$ are producible. Nowadays, fullerenes are widely used in many applications like organic solar cells, fuel cells or biopharmaceuticals [17–21]. Studies on their nonlinear optical properties in the nanosecond time domain using 532 nm pulsed laser radiation have shown strong nonlinear absorption due to reverse saturable absorption (RSA) in C$_{60}$ solutions [22, 23], whereas for solutions with larger fullerenes self-defocusing was observed [24] in addition.

In this publication, we report on the SSPM effect of C$_{60}$ and C$_{70}$ fullerene solutions using 532 nm continuous wave laser radiation. In order to understand the underlying mechanisms, SSPM was analysed in dependence of laser power, sample temperature, type of solvent and viscosity of the solvent. Furthermore, C$_{60}$ in toluene was examined at a wavelength of 1070 nm. Additionally, we developed a time-dependent thermal blooming simulation with a temperature-dependent refractive index. To our knowledge, this is the first analysis in this level of detail of SSPM in C$_{60}$ and C$_{70}$ solutions. In the last part of this work, we investigate a practical implementation of SSPM based on fullerene solutions. Their nonlinear properties make them potential candidates for laser protection applications.

2. Experimental

C$_{60}$ (fullerene powder, 99% C$_{60}$), C$_{70}$ (fullerene powder, 99+% C$_{70}$) and 1,2-dichlorobenzene (99%) were purchased from Alfa Aesar. Toluene (ACS reagent, $\geq 99.5\%$) and poly(methyl methacrylate) (PMMA) powder (average Mw 120,000 by GPC) were purchased from Sigma-Aldrich. Four different C$_{60}$ and C$_{70}$ solutions in toluene and 1,2-dichlorobenzene (C$_{60}$/toluene (C$_{60}$/T), C$_{60}$/1,2-dichlorobenzene (C$_{60}$/DCB), C$_{70}$/toluene (C$_{70}$/T) and C$_{70}$/1,2-dichlorobenzene (C$_{70}$/DCB)) were prepared via sonication. To generate samples with high viscosity PMMA powder was dissolved in toluene and mixed with C$_{60}$ and C$_{70}$ in toluene afterwards (samples: C$_{60}$/PT and C$_{70}$/PT).

For all optical measurements cuvettes with a 10 mm optical path length were used. The sample concentrations in both solvents were adjusted to the same transmittance using a spectrophotometer (Shimadzu UV-3600 UV-Vis-NIR) (see figure 1) to exclude concentration effects.

A sketch of the experimental setup used to measure the SSPM effect is shown in figure 2. A continuous wave laser at a wavelength of 532 nm (CONQUEROR CW_12, Compact Laser Solutions) or 1070 nm (Daten) was focused onto the sample by a lens ($f = 120$ mm), respectively. A screen was placed behind the sample to observe the diffraction rings in the far field. Images from 1 ms up to 50 s were recorded by a high-speed camera (Phantom V711, Vision Research) to analyse the dynamics of the diffraction pattern. To cover that large time range, videos at different frame rates were taken, ranging from 5000 fps down to 100 fps. The exposure times were adapted in order to minimise blooming and smearing of the diffraction rings. Thus the intensity of the rings is determined by the exposure time.
In order to analyse the practical use of the SSPM effect in fullerene solutions regarding laser protection applications, we investigated its nonlinear transmittance. Therefore the laser beam was focused into the sample with the help of a lens. Behind the sample the beam was recollimated by a second lens. Since the SSPM effect leads to larger beam diameters an aperture was positioned right in front of the second lens. The size of the aperture was adjusted to the unaffected beam diameter. The transmitted power was measured using a detector placed behind the second lens. Figure 3 shows a typical scheme of a laser protection device.
3. Results and discussion

To investigate and understand the underlying physical processes, a broad range of measurements in dependence of a variety of parameters were performed. In order to determine whether SSPM is a thermal effect or caused by the optical Kerr effect ($\chi^{(3)}$ process), studies at different sample temperatures, wavelengths, pulse durations, types of solvent and viscosities of the solvent at different laser powers have been carried out. If the refractive index change would be caused by intrinsic $\chi^{(3)}$ the SSPM behaviour should not depend on these parameters.

Our investigations discussed in the following sections revealed a clear dependence of the SSPM pattern on the solvent and temperature. These findings and the absence of SSPM pattern outside the absorption band, as well as at short picosecond time scales at 527 nm indicate that the induced refractive index change can be explained by thermal effects solely. The thermally induced refractive index changes ($n_\text{r}$) of our samples are in the order of $10^{-7}$ cm$^2$/W (equation (7) with $L_e = 300 \mu$m, $n_0 = 1.5$) at an input power of 105 mW.

3.1. Evolution of diffraction rings

Figure 4 shows images of the laser beam after traversing C$_{60}$ and C$_{70}$ in two different solvents at three input laser powers (56 mW, 84 mW and 105 mW). The diffraction-pattern starts with a central spot and already within the first millisecond a single ring is generated. Thereupon the spot begins to expand and a series of concentric rings appear. The number of rings increases steadily and the SSPM pattern becomes larger with time until a maximum is reached. In the further course of the dynamic process the upper part of the ring pattern distorts until a stable collapsed pattern is reached.

The number of rings gained from the high-speed camera images as a function of time are plotted in figure 5. It can be clearly seen, that for both types of fullerenes and at each input power the number of rings increase faster in toluene than in 1,2-dichlorobenzene.

The refractive index changes due to temperature variation is given by [25]

$$n(r, t) = n_0 + \frac{\partial n}{\partial T} \Delta T(r, t) + \frac{\partial n}{\partial c} \Delta c(r, t)$$

(1)
The first part of the equation is the change of the refractive index with respect to the temperature where \( r \) is the radial coordinate, \( \frac{\partial n}{\partial T} \) the thermo-optic coefficient and \( \Delta T \) the temperature variation. The thermo-optic coefficient of liquids is generally negative, as the induced density reduction leads to a decreasing refractive index [26]. In general, \( \frac{\partial n}{\partial T} \) is negative for highly expansive and loosely bonded materials and positive for strongly bonded materials.

The second part of the equation is the refractive index change with respect to the local change of concentration \( c \). It has been shown that a temperature gradient in a mixture containing nanoparticles or molecules induces thermal diffusion and migration of these particles within the thermal gradient [25, 27–29]. This effect is known as the Soret effect. Particles will migrate either to the hotter or to the colder region of the mixture depending on the elements composing the mixture and their mass fraction. This migration leads to a concentration gradient locally affecting the refractive index. This concentration gradient may also affect the absorption coefficient (less absorption in regions with less concentration), which can in turn affect the temperature increase and consequently the refractive index change. The magnitude of the thermally induced concentration gradient is proportional to the ratio between the coefficient of thermal diffusion \( D_T \) and the coefficient of mass diffusion \( D_M \). In order to determine if we need to take the Soret effect into account, we calculate the characteristic time \( t_M \) required to form the concentration gradient and compare it with the characteristic time constant \( t_T \) of the thermal lens induced by the thermo-optic coefficient. This can be calculated according to [27]

\[
t_T = \frac{\omega^2}{4D_T}, \quad \text{with} \quad D_T = \frac{\kappa}{\rho C_p}
\]

where \( \kappa \) is the thermal conductivity of the solvent, \( \rho \) the density, \( C_p \) the specific heat capacity and \( \omega \) the radius of the laser beam.

\[
t_M = \frac{\omega^2}{4D_M}, \quad \text{with} \quad D_M = \frac{k_B T}{6\pi \eta r}
\]

where \( k_B \) is the Boltzmann constant, \( \eta \) the viscosity and \( r \) is the radius of the molecule or particle. In the case of \( C_{60} \) in toluene we obtained \( t_T = 65 \times 10^{-6} \, \text{s} \) and \( t_M = 5.8 \times 10^{-3} \, \text{s} \) using parameter values of toluene at 20 °C [30]. Similar results were obtained with \( C_{60} \) in 1,2-dichlorobenzene and \( C_{70} \) in both solvents. Obviously, the Soret effect can be considered as negligible since \( t_M \gg t_T \). Even if we take account of the fact that all the aforementioned parameters are temperature dependent and their values will change once the laser is switched on, the characteristic times will not change by these orders of magnitude. A model based solely on thermal blooming is therefore a sufficient approximation, i.e. Equation (1) can be simplified to:

\[
n(r, t) = n_0 + \frac{\partial n}{\partial T} \Delta T(r, t)
\]

The spatial variation in the refractive index leads to a nonlinear phase shift of the traversing beam that depends on the transverse distance from the beam axis. The phase shift (\( \Delta \phi \)) can be determined by [31].
\[ \Delta \phi(r, t) = \frac{2\pi}{\lambda} L \Delta n \]  

where \( \lambda \) is the laser wavelength and \( L \) is the sample length. The number \( N \) of SSPM rings depend on the phase shift

\[ N \approx \frac{\Delta \phi}{2\pi}, \]  

but also on the position of the sample with respect to the beam waist and the nonlocality of the nonlinearity [32].

The refractive index change as a function of the number of diffraction rings can be written as [5]

\[ n_2 = \frac{\lambda N}{2n_0L_cI} \]  

where \( n_0 \) is the linear refractive index and \( L_c \) the effective optical interaction length.

In materials with intrinsic \( \chi^{(3)} \) SSPM effect, the efficiency depends only on the functional material. Is the SSPM effect thermally induced the efficiency depends on the functional material itself but also on the host material. In the case of thermal effects the relation between host material and refractive index change applies: The higher the thermo-optic coefficient, the larger the refractive index change (equation (4)). Toluene exhibits higher thermo-optic coefficient than 1,2-dichlorobenzene which results in a larger refractive index change and thus a larger phase shift and more SSPM rings are formed.

### 3.2. Distortion of diffraction rings

The distortion of the diffraction pattern starts at around 150 ms in toluene and 200 ms in 1,2-dichlorobenzene solutions and is completed around 600 ms and 700 ms, respectively. The deformation process is attributed to laser induced thermal convection in [33, 34]. In an absorbing liquid the temperature is at maximum at the centre of a gaussian beam and decreases radially. Subsequently the heated liquid rises and is replaced by cooler parts. A convection current primarily from the beam centre upwards is formed. Due to liquid motion the upper part of the pattern become squeezed, the lower part of the pattern is less affected [35, 36]. It can be seen in figure 4 and figure 8 that the collapsed SSPM can be tilted to the left or to the right. This phenomenon can be explained by an asymmetric convection, for example due to positioning of the cuvette with respect to the laser beam. If the sample is irradiated closer to the left or the right edge of the cuvette an unbalanced SSPM pattern occur. Therefore, it is much likely that thermal convection is the main effect in the deformation process.

To illustrate symmetric and asymmetric convection, the temperature and velocity magnitude of a laser heated absorbing fluid is simulated using Comsol Multiphysics in figure 6. The laser beam is horizontally positioned in the centre of the sample in the temperature simulation in row 1 and velocity magnitude simulation in row 2. In the simulations row 3 (temperature) and row 4 (velocity magnitude) the laser beam was shifted to the right side of the sample. If the beam is positioned in the horizontal centre the temperature and velocity distribution is symmetric to the vertical axis leading to a symmetric SSPM pattern. If the laser beam is shifted to
one side the convection is not symmetric. At the closer distance to the border of the cuvette (right border) an upward movement of the fluid arises while on the left side of the laser beam a downward movement occurs, which leads to a tilt of the SSPM pattern.

In samples with high viscosity (figure 7) no distortion occurs up to 10 s and only minimal distortion up to 40 s. It can also be seen that in an undistorted sample more rings appear within the measurement period, while the collapse of the pattern prevents further ring evolution. Thus the suppression of thermal convection helps to increase the SSPM effect.

3.3. Temperature dependency of diffraction rings

Figure 8 shows the SSPM pattern of C60/T and C70/T at 5 °C measured at 105 mW laser power. The samples at 5 °C show less rings and the distortion of the upper part starts earlier at around 30 ms compared to the measurements at 25 °C.

Many solvent parameters, like viscosity, heat transfer coefficient or density are temperature dependent. The two-dimensional temperature isosurface plots in figure 9 show the temperature distributions of C60 in toluene at 5 °C and 25 °C. At 25 °C the isosurfaces of the laser heated area expand faster to the top of the cuvette compared to the simulation at 5 °C. The reason is that at 5 °C the temperature gradient is confined in a smaller area compared to 25 °C. This leads to pronounced concentrated circular fluid vortices near the laser spot at 5 °C with lesser upward movement than at 25 °C as shown in figure 10. The differences in fluid movement influences the SSPM pattern and causes quenching and faster distortion in the samples at the lower temperature.

The dependence of the SSPM pattern on the solvent and temperature in C60 and C70 solutions indicates that the refractive index change is a thermal effect. The evolution of the ring formation can be explained as follows: A considerable amount of the laser energy is absorbed by fullerenes. The thermal energy is transferred to the solvent which leads to an axially symmetric temperature gradient and thus to a spatial density profile.

3.4. Dependency of diffraction rings on wavelength and interaction time

To further substantiate our hypothesis, measurements outside the absorption band of C60 in toluene at a wavelength of 1070 nm were performed. The laser beam pattern in the far field, taken at an input power of 80 mW, is shown in figure 11. In case of a $\chi^{(3)}$ effect, the refractive index change compared to 532 nm should be about twice as large due to the linear dependence of $\chi^{(3)}$ on the wavelength ($\chi^{(3)} \propto \lambda^{3}$) [37].

Even after several seconds of illumination no SSPM pattern arises, only a static bright spot can be observed. The absence of self-diffraction outside the absorption range of C60 is further evidence that the refractive index change causing the ring pattern is a thermal effect.

Knowing from [12] that for ultrashort pulses no significant thermal processes will take place, we performed additional measurements at a pulse length of 8 ps and a wavelength of 527 nm. With an input energy of 36 μJ, only a bright spot was generated. In contrast, for 3 ns pulses at 532 nm and an input energy of 500 μJ we do
observe ring patterns. A large amount of energy is deposited in the irradiated area of the sample due to nonlinear absorption (RSA) of the fullerenes in the nanosecond time domain. This leads to a local heating of the functional material itself and subsequently to the surrounding solvent due to heat transfer. The induced temperature gradient and thus the density gradient change the refractive index profile within the beam profile, causing a spatial phase modification. Self-diffraction due to constructive and destructive interference within the self-phase modulated beam occurs. For single pulses in the picosecond regime, the thermally induced refractive index change does not have time to develop. In other words, the density does not change significantly resulting in no refractive index changes during this short pulse duration [12, 38]. If the material would exhibit a Kerr nonlinearity with a response time in the order of picoseconds and shorter [39], a ring pattern should have easily

Figure 8. Self-diffraction patterns of C$_{60}$/T and C$_{70}$/T at 5 °C measured at 105 mW (T: Toluene).

Figure 9. Simulated temperature isosurfaces of C$_{60}$/T at 25 °C and at 5 °C. Temperature scale at 5 °C: 5.17 °C to 17.39 °C at 25 °C: 25.24 °C to 36.96 °C.

Figure 10. Simulated velocity magnitude of C$_{60}$/T at 25 °C (left) and at 5 °C (right) at 100 ms.
been observed for the picosecond pulse, since the intensity of the picosecond pulse is more than a factor of 20 higher compared to the nanosecond pulse. Thus, the absence of SSPM patterns at short picosecond time scales is further evidence of the thermal nature of induced refractive index changes in our samples.

3.5. Simulation of thermally-induced SSPM

We developed a time-dependent thermal blooming simulation with a temperature-dependent refractive index. In this simulation, no other nonlinear effects are taken into account, in particular no $\chi^{(3)}$ nonlinearity was considered. The laser induced temperature increase, and the subsequent change of the refractive index can be seen as similar to a $\chi^{(3)}$ nonlinearity, as the refractive index is ultimately depending on the intensity of the laser, but it is the linear part of the refractive index, which is here temperature dependent and is changing. The interesting difference of this thermally induced nonlinearity with other nonlinearities is that it grows over time, since the temperature increase takes time itself, generally several milliseconds (depending on the absorption coefficient and the intensities involved), which is much longer than $\chi^{(3)}$ nonlinear effects.

In order to simulate the thermally-induced SSPM, we will consider only a small portion of length $L$ of the sample in which thermal blooming is highest, specifically a portion centred on the beam waist of length $L = 2z_R$, with $z_R$ being the Rayleigh length of the beam. We simplify the simulation by considering that the beams size is constant over this length, meaning that the intensity is constant. Furthermore, we will only simulate C60 in toluene. The temperature increase $\Delta T$ is given by:

$$\Delta T(r, t) = \frac{(I(r) - I(r) \exp(-\alpha L)) \Delta t}{C_p \rho L}$$

where $I(r)$ is the intensity, $\alpha = 0.2 \text{ m}^{-1}$ is the absorption coefficient and $\partial n/\partial T = -5.8 \times 10^{-4} \text{ K}^{-1}$[40]. The other parameters were defined in section 3.1. The phase change is then calculated using equations (4) and (5). This phase is applied to the electric field of a Gaussian beam and propagated to a distance $D = 5z_R$, which corresponds to the far field of a Gaussian beam, using a beam propagation method described in [41], commonly used to propagate laser beams in random media.

In the first simulation, we varied the beam waist in order to see the impact of a change of the beam size on the ring pattern. The laser power is 105 mW. No heat transfer phenomena are taken into account, only the absorption of laser power. Two beam waists were chosen: 6.5 $\mu$m and 20 $\mu$m radius. The results are shown in figure 12.

In this case, since no heat transfer, i.e. no cooling mechanism is considered, the sample is continuously heated by the laser. The ring structure grows over time and no flattening of the ring structure was observed, which is similar to our measurements of the high viscosity samples (figure 7).

The ring structure with a beam radius of 6.5 $\mu$m in figure 12 grows quickly over time, and by around 1.8 ms, the grid size becomes too small for the size of the ring structure and aliasing effects start to appear. For a larger beam radius of 20 $\mu$m the ring structure and the number of rings does not grow as fast as before, which shows the intensity dependence of a thermally induced SSPM effect.

Once the liquid is being heated, natural convection will occur, i.e. the heated part of the liquid will move upwards because it is lighter than the colder parts of the liquid. Natural convection is a complex phenomenon to simulate as it involves solving the Navier–Stokes equations. Instead, we will simplify the problem by assuming a constant flow with speed $v$ of liquid going upwards as it would be the case for pure advection. In our simulation, this flow will not happen immediately at the start, but will occur after a time $t_{flow} = 1$ ms, once the sample has been sufficiently heated.

Figure 11. Laser beam pattern at a wavelength of 1070 nm without sample (left) and with C60/T (right) at an input power of 80 mW.
It has to be pointed out that it was not our intention to make an exact simulation. Our simulation of course simplifies the complexity of the phenomena occurring inside the sample. We were interested in seeing if thermal blooming with advection can lead to similar intensity patterns as the observed SSPM.

In the second simulation (Figure 13), natural convection in the form of advection with two different convection velocities (25 mm/s (figure 13 top) and 12.5 mm/s (figure 13 bottom)) and a beam radius of 6.5 μm is modelled.

A constant heat flow upwards starting at 1 ms provokes a flattening of the ring structure. The ring structure and the number of rings grows slower than in the first simulation, because advection acts here as a cooling mechanism, i.e. the hottest parts of the liquid are driven upwards, while unheated parts are replacing them. A convection velocity of 25 mm/s leads to an immediate collapse of the ring pattern at 1.5 ms preventing a further growth of the SSPM pattern. Since $\partial n/\partial T$ is negative and the liquid flows upwards, the upper part of the probe shows a smaller refractive index than the lower part. This beam is therefore deviated to the lower part. This observation is exactly the same as thermal blooming in the atmosphere, when dealing with high energy laser [42], in which a laser beam is deviated to parts of the atmosphere with higher refractive index (i.e. deviated in the opposite direction of the wind). With a convection velocity of 12.5 mm/s, the intensity reaches the size of the calculation grid after 2.5 ms and aliasing effects start to appear. The same flattening of the ring structure is observed, but with half advection the ring structure and the number of rings can evolve over a longer period of time. We know that we overestimated the convection velocity, actually it is in the order of 1 mm/s [43]. Due to the limited grid size aliasing effects occur after a few milliseconds, therefore it was not possible to simulate convection with lower velocities. In addition, this simulation does not include some phenomena like diffusion, which could be useful to fully predict the observation. Diffusion could be leading to a slower temperature increase and therefore a slower thermal blooming effect, since the heat would be transported away from the laser beam. Overall, this simplified simulation can produce similar ring patterns, despite the lack of thermal diffusion. It is in accordance with our hypothesis that we observed a thermal phenomenon.

3.6. SSPM materials for laser protection applications

Exposure of the human eye to continuous wave laser radiation in the visible region in the low double-digit milliwatt range can cause permanent retinal damage in less than 250 milliseconds [44]. The temporal evolution
of diffraction rings in C₆₀ and C₇₀ solutions is a fast process compared to many other materials, like NbSe₂ nanosheets [6] or Bi₂Se₃ nanosheets [45]. The SSPM pattern formation of the fullerene solutions start within 1 ms, within 5 ms the diameter has doubled and within 150 ms the diameter has increased around one order of magnitude.

A laser protection device based on SSPM materials can be realized as schematically already shown in figure 3. In the low power regime the beam can pass the device undisturbed. Beyond the threshold of the functional material, SSPM pattern formation occurs and a considerable amount of the laser beam is blocked by the aperture. To create an efficient device functional materials with fast response times and large SSPM pattern are required. The collapse of the pattern can be suppressed by using high viscosity host materials. In the measurements of the high viscosity fullerene samples shown in figure 7 the ring pattern were stable up to 40 s. In figure 14 red circles representing an aperture are plotted into the SSPM pattern of C₆₀ in toluene (low viscosity) and C₆₀ in PMMA-toluene (high viscosity). For both samples the majority of the laser intensity is blocked by the aperture but at different levels. That is as in the case of C₆₀/PT the power is homogeneously distributed over a wider area (low intensity at the aperture), while for C₆₀/T the power concentrates more in the vicinity of the aperture (high intensity at the aperture).

The transmitted laser power over time of C₆₀/T and C₆₀/PT at 56 mW, 84 mW and 105 mW is shown in figure 15. In the PMMA-toluene (PT) sample the transmitted laser power is decreasing continuously during the evolution of the SSPM pattern. Within less than one second the majority of rings are generated, leading to a strong drop in transmittance, and subsequently the transmittance decreases slowly further. In the case of the toluene sample a strong reduction of transmittance in the beginning was observed as well, but due to the collapse of the SSPM pattern the transmitted power was increasing afterwards. The transmittance stabilised after the distortion of diffraction rings was completed.

In materials with intrinsic χ(3) SSPM effect, the efficiency depends only on the functional material. Is the SSPM effect thermally induced the efficiency depends on the functional material itself but also on the host material. So a further optimisation of the SSPM effect is possible by using a host material with a high thermo-optic coefficient (see equation (1)). Table 1 shows the attenuation results after 2 s of illumination. At each measured input power C₆₀/PT reaches higher attenuation values, compared to C₆₀/T. Thus, it is useful to suppress convection to reach better protection.

Figure 14. Self-diffraction patterns of C₆₀/T (top) and C₆₀/PT (bottom) for an irradiation of 84 mW taken at the following times: 1 ms, 150 ms and 10 s. The red circles are representing an aperture as used in the laser protection device.

Figure 15. Transmitted laser power over time of C₆₀/T and C₆₀/PT at 54 mW (left), 84 mW (middle) and 105 mW (right).
4. Conclusion

We have investigated self-diffraction of 532 nm continuous wave laser radiation passing through solutions containing C60 or C70. The measurements were performed on two different solvents and at two different sample temperatures. The dependence of the SSPM pattern on the solvent and temperature and the absence of SSPM pattern outside the absorption band and at short picosecond timescales indicates that the induced refractive index change can be explained by thermal effects solely. Moreover, our thermal blooming simulation underpins that absorption induced thermal heating alone can explain our findings. Since no other nonlinear effects were taken into account we conclude that in particular electric field dependent $\chi^{(3)}$ nonlinearities do not matter in our investigations.

The temporal evolution of diffraction rings in C60 and C70 solutions is a quite fast process compared to many other SSPM materials [6, 45–47], which makes them suitable for continuous wave laser protection applications. Thermal convection can be suppressed by using high viscosity host materials, which prevents the SSPM pattern from collapsing, keeping the concentric circular diffraction rings stable on a longer time scale. The ring pattern formation depends also on the host material, which provides an additional opportunity to optimise the SSPM effect.

Fullerenes are known as efficient RSA materials used for optical limiting purposes in the nanosecond time domain. Studies on the nonlinear optical properties using 532 nm pulsed laser radiation have shown strong nonlinear absorption due to RSA in C60 solutions [22, 23]. In solutions with larger fullerenes self-defocusing was observed [24] in addition to RSA. In the continuous wave regime, fullerenes have also been investigated e.g. by means of the z-scan technique, see for example [48]. Z-scan measurements are suitable to investigate refractive index changes. Refractive index changes are usually associated with $\chi^{(3)}$ and the fact that thermal effects can also be involved is often neglected. From z-scan measurements it is not possible to distinguish between thermal effects and Kerr nonlinearity. With our detailed analysis in dependence of laser power, sample temperature, wavelength, pulse duration, type of solvent and viscosity of the solvent we were able to bridge this gap.

According to our results, we have demonstrated that C60 and C70 solutions have the potential to protect against continuous wave laser radiation as well, especially in high viscosity host materials. Thus, using C60 and C70 as functional materials offers the possibility for laser protection against pulsed nanosecond and continuous wave laser radiation within one setup as depicted in figure 3.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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