

Article

Stokes Components of Raman-Induced Singlet Oxygen

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Abstract

We studied the Stokes signals generated following the Raman photoexcitation of dissolved oxygen in water. When a water sample is pumped with intense nanosecond radiation, Stokes signals of different origins are generated. These signals form a characteristic non-linear diffraction pattern, comprising a central spot and concentric rings whose radii depend on the Stokes wavelengths. Although most of the Stokes signals correspond to the stretching vibrations of water molecules, we also observed a small contribution from dissolved oxygen molecules. This contribution can be separated from the others using appropriate spectroscopic filters, then analyzed with a spectrometer. In this study, we report on Stokes components assigned to singlet oxygen excitation detected in the central spot, as well as in the diffraction pattern's ring structure. The signal detected in the central spot exhibits a single peak, while that from the ring shows a two-peak structure. These two observed peaks are interpreted as Stokes signals corresponding to Raman transitions to the two lowest vibrational sublevels of the singlet-oxygen electronic state. We also report exponential growth in the Stokes signal with the pulse energy, in agreement with the standard stimulated Raman theoretical model.

Keywords: Raman spectroscopy; singlet oxygen photoexcitation; singlet oxygen Raman spectrum

1. Introduction

Singlet oxygen ($^1\text{O}_2$) is a reactive oxygen species (ROS) widely used in photochemistry, photobiology, and photomedicine [1–6], which corresponds to the lowest excited electronic level of the oxygen molecule. $^1\text{O}_2$ excitation via direct photon absorption is not effective, as the dipolar transition from the ground to the $^1\text{O}_2$ state is heavily forbidden by quantum mechanics selection rules. As such, photosensitizing is the commonly used $^1\text{O}_2$ excitation method [7,8]. A large molecule that can absorb visible photons stores part of the absorbed energy in a metastable triplet state; this energy can then be transferred to oxygen molecules, thereby exciting $^1\text{O}_2$. We previously reported a new Raman-based, photosensitizer-free method for $^1\text{O}_2$ photoexcitation [9–12], in which a pumping photon generates a Stokes photon of lower energy, inducing the transition from the ground state to the $^1\text{O}_2$ level. The energy difference between the two photons corresponds to the $^1\text{O}_2$ energy level. We demonstrated that the observed Stokes signal was oxygen-dependent by reducing the oxygen concentration with an oxygen quencher such as sodium bisulfite (NaHSO_3), increasing the sample temperature, or purging the solvent with argon [9]. We also showed that the signal's wavelength was the same across different solvents, demonstrating its solvent independent nature. Furthermore, we assessed the Raman character of the observed



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$^1\text{O}_2$ Stokes signal by measuring its wavelength shift as the pump wavelength was varied, and showing its temporal coincidence with the pump pulse [10]. We reported that the $^1\text{O}_2$ Stokes' signal exhibited a diffraction pattern with a central spot and a system of rings, characteristic of a stimulated Raman process [10,13]. We also reported the $^1\text{O}_2$ phosphorescence at 1270 nm, which is typically observed upon excitation of the $^1\text{O}_2$ state [11]. More recently, we determined the efficiency of the abovementioned $^1\text{O}_2$ Raman photoexcitation process [12].

When performing the previous experiments, we noted that Stokes signals corresponding to the solvent's vibrational modes overlap with the $^1\text{O}_2$ Stokes signal in both parts of the diffraction pattern, making their detection difficult. However, Stokes photons from water typically have lower energy than those from $^1\text{O}_2$, allowing the contributions to be separated using long-pass spectroscopic filters. Furthermore, the oxygen Stokes peaks are of electronic origin and exhibit a spectral width on the order of tens of nanometers, while the solvent Stokes peaks have a spectral width that is an order of magnitude smaller [9]. These differences help to identify peaks and separate them from one another. In this work, we present evidence for two other remarkable characteristics of the $^1\text{O}_2$ Stokes signal that have not been reported previously. First, we provide spectroscopic evidence regarding the contribution of the vibrational structure of the $^1\text{O}_2$ electronic level. Second, we show that the $^1\text{O}_2$ Stokes signal grows exponentially with the pulse energy.

The spectral response of the lowest electronic levels of molecular oxygen has been studied in detail for over a century. Analyzing the atmospheric absorption of solar radiation, Herzberg reported peaks at 1268 and 1067 nm [14,15], which were assigned to absorption bands corresponding to transitions from the ground state to the two lowest vibrational modes of the $^1\text{O}_2$ state. These results were confirmed in Ellis and Kneser's study of the absorption of light by liquid oxygen [16]. Details of molecular oxygen spectra were further discussed in later reviews [17,18], while more recent studies have reported the same spectral absorption peaks for molecular oxygen dissolved in solvents [19–21]. Here, we demonstrate that examining the spectral properties of the Raman diffraction pattern provides insight into the Raman photoexcitation of oxygen molecules. In particular, we observed Stokes components corresponding to excitation of the two lowest vibrational sublevels of the $^1\text{O}_2$ state, which is in agreement with previous absorption studies. This study's novelty lies in the fact that the peaks are Stokes signals in the visible spectrum, generated during the excitation of molecular oxygen via a stimulated Raman process. The presence of both peaks confirms that the reported Stokes signals originate from oxygen, as only the oxygen molecule can induce such a spectral response.

The basic theory of stimulated Raman scattering predicts exponential gain in Stokes signals [22–25], which is the fundamental idea underlying the development of Raman fiber lasers, Raman sensors, and highly sensitive Raman spectroscopy techniques [26–29]. The exponential gain in the Stokes signals due to Raman $^1\text{O}_2$ photoexcitation observed in this study confirms the basic predictions of standard stimulated Raman excitation theory. These results may impact the design of methods and instrumentation to improve $^1\text{O}_2$ photosensitizer-free excitation using the Raman approach.

2. Theoretical Considerations

Figure 1 shows the schematic of the first two vibrational sublevels, $^1\text{O}_2(0)$ and $^1\text{O}_2(1)$, of the $^1\text{O}_2$ electronic state, as established in the studies cited above. $^1\text{O}_2(0)$ lies 0.97 eV from the ground, which corresponds to the energy of a photon with a wavelength of 1270 nm. $^1\text{O}_2(1)$ is at 1.16 eV, which corresponds to the energy of a photon with a wavelength of 1067 nm. Both states have rotational sub-levels that are not indicated in the figure. Raman excitation generates Stokes signals for these two levels; for example, when pumping at

411 nm, Stokes signals at 607 and 668 nm are expected. Anti-Stokes components are also generated in the ultraviolet (UV) region of the spectrum, but this contribution is generally small for the pulse energies used in the present experiments.

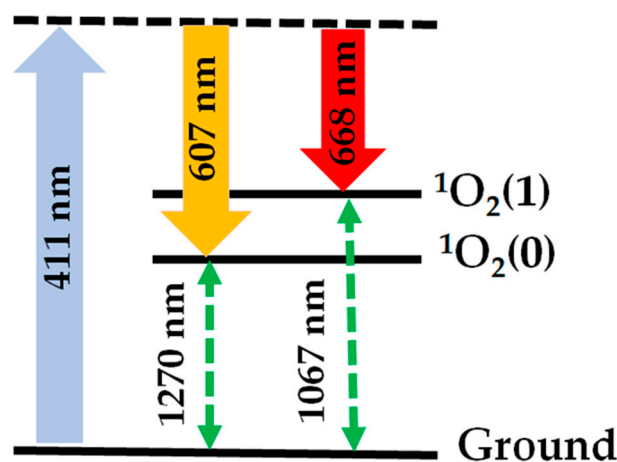


Figure 1. Schematic of Raman excitation of the two lowest vibrational levels of the $^1\text{O}_2$ electronic state. When pumping at 411 nm, Stokes components at 607 nm and 668 nm are generated.

Stimulated Raman scattering refers to the interaction between Stokes and anti-Stokes photons and matter. The basic theory of the effect states that there are two kinds of stimulated Raman scattering signals: one set of signals propagates in the direction of the excitation beam, and another set propagates at an angle with respect to this direction [24,25]. As a result, the stimulated Raman interaction-induced diffraction pattern shows a central spot and concentric rings [14].

As discussed above, theoretical models of stimulated Raman scattering indicate that the Stokes signal experiences exponential gain, whereas the anti-Stokes beam exhibits losses [25]. In Appendix A we present the calculated gain values g_E (see Equation (A5)), which quantify the signal's growth as a function of the pump pulse energy.

The Raman diffraction pattern ring's structure corresponds to the phase-matching condition given by the following equation [13]:

$$\vec{\Delta K} = 2\vec{K}_P - (\vec{K}_S + \vec{K}_a) = \frac{4\pi n_P}{\lambda_P} \vec{e}_P - \frac{2\pi n_a}{\lambda_a} \vec{e}_a - \frac{2\pi n_S}{\lambda_S} \vec{e}_S = 0, \quad (1)$$

where $\vec{K}_P$, $\vec{K}_S$, and $\vec{K}_a$ are the wavevectors of the pump, Stokes, and anti-Stokes fields, respectively, λ_P , λ_S , and λ_a are the pump, Stokes, and anti-Stokes wavelengths, respectively, n_P , n_a , and n_S are the refraction indices at λ_P , λ_a , and λ_S , respectively, and $\vec{e}_P$, $\vec{e}_S$, and $\vec{e}_a$ are the unit wave-vectors of the pump, Stokes and anti-Stokes beams, respectively.

The values of λ_S and λ_a are calculated from their definition $\lambda_S = (1/\lambda_P - 1/\lambda_O)^{-1}$ and $\lambda_a = (1/\lambda_P + 1/\lambda_O)^{-1}$, where λ_O are the wavelengths corresponding to the transitions from the ground to the quantum levels $^1\text{O}_2(0)$ and $^1\text{O}_2(1)$.

In Appendix B, we describe the procedure for estimating the deviation angles of the beams that form the ring structure. Notably, nonlinear Raman diffraction effects such as self-focusing are not included in this simplified model, which may affect the final deviation values [13]. As indicated by Equation (1), the radii of the rings depend on the wavelength of each of the fields; thus, the procedure for separating and identifying different Stokes components becomes less cumbersome. In the Experimental Section, we take advantage of this fact, allowing us to identify the Stokes signals corresponding to the Raman transition to the $^1\text{O}_2$ electronic state vibrational sublevels (0) and (1).

3. Materials and Methods

Figure 2 shows a schematic of the experimental setup. An optical parametric oscillator (OPO, OPOTEK, Carlsbad, CA, USA) provided the pump beam. We used a pump wavelength of 411 nm. The device generated 5-nanosecond pulses with a pulse energy of around 20 mJ. A lens with a 20 cm focal length focused the pumping light onto the sample. We estimated a waist beam radius of 5.2 μm and a Rayleigh range of 0.02 cm. The sample was distilled water in a glass cuvette with a path length of 20 cm.

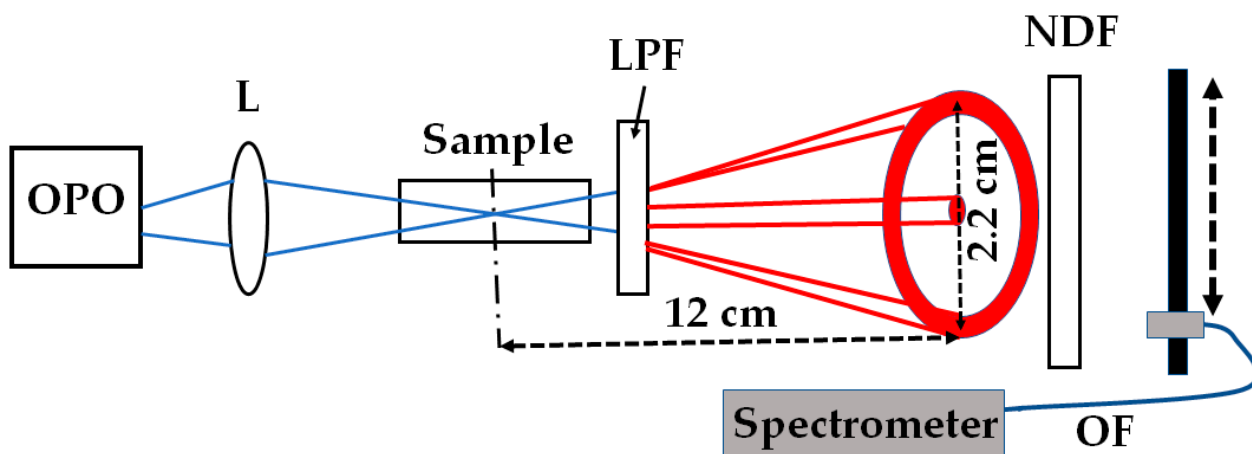


Figure 2. Schematic of experimental setup showing the optical parametric oscillator (OPO), the focusing lens (L), the glass cuvette containing water (Sample), the long-pass filter (LPF), the neutral-density filter (NDF), an optical fiber (OF, dark blue line), and a spectrometer. A schematic of the Raman diffraction pattern is shown in red. The pump beam is shown in blue. The distances between the pump focal plane and the observation plane is indicated, as well as the ring diameter.

A long-pass filter (LPF) with a cut-off wavelength of 600 nm was used to select light matching the $^1\text{O}_2$ Stokes contribution. The filter removed all Stokes contributions from the solvent molecules, leaving only those from dissolved oxygen molecules [9,10]. As a result, a red-colored Raman diffraction pattern with a central spot and a ring appeared at the cuvette's exit. A neutral-density filter (NDF) was used to control the intensity of this light and prevent saturation of the detection system.

The pattern was analyzed using a spectrometer (Ocean Optics USB 2000, Orlando, FL, USA) connected to an optical fiber (OF). The instrument averaged 100 spectra. We placed the optical fiber's entrance coupler 12 cm from the pump waist position. At that distance, the ring's radius was about 11 mm. The coupler's entrance diameter was 1 mm.

We collected spectra from different parts of the diffraction pattern by scanning the fiber's coupler along the center of the pattern in 1 mm steps. We also measured the signals' dependence on pump energy at the central spot and the ring using a diode detector (DET100 A2, Thorlabs, Newton, NJ, USA). The detector sent the signal to a digital oscilloscope (TDS 3052, Tektronix, Beaverton, OR, USA) for averaging and monitoring, with the resulting signal corresponding to an average of 512 pulses. A reference detector (not shown in Figure 2) triggered the oscilloscope. We varied the pump energy by placing neutral-density filters with optical densities from 0.1 to 1.9 in front of the cuvette. The pump pulse energy was calibrated using a pulse energy detector (Pulsar-1, Newport Corporation, Ophir, North Logan, UT, USA), which averaged the energy of 500 pulses, providing a standard deviation of about 10%.

4. Results and Discussion

Figure 3a shows a photograph of the diffraction pattern observed when pumping at 411 nm and using a long-pass filter with a cut-off wavelength of 600 nm, in which the central spot and the ring structure can be seen. Our previous experiments have demonstrated that the observed signal corresponds to the Stokes signal generated by Raman excitation of oxygen toward the $^1\text{O}_2$ level [9–12].

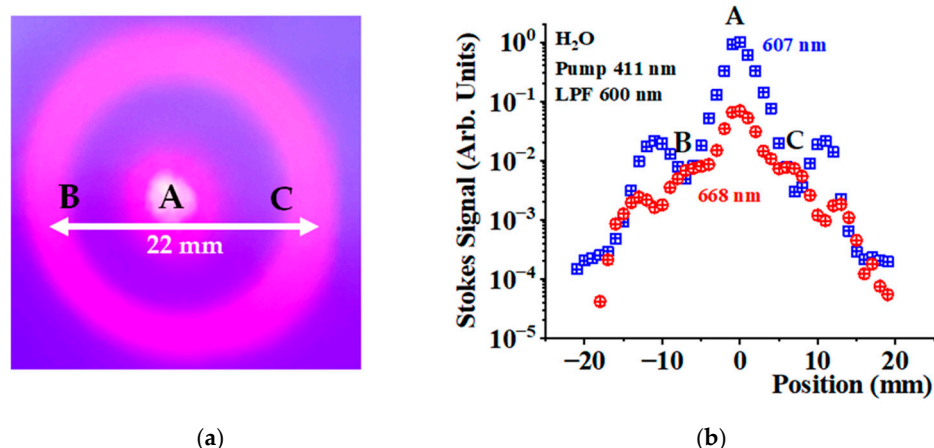


Figure 3. (a). Raman diffraction pattern observed at a distance of 12 cm from the pump waist when pumping at 411 nm and using an LPF with a cut-off wavelength of 600 nm. (b) Stokes signal amplitudes at 607 nm (blue crossed squares) and 668 nm (red crossed circles) as a function of position in the Raman diffraction pattern. The points indicated by the letters A, B, and C are the same in both figures.

Using the spectrometer, we collected spectra along the direction indicated by the white arrow as we scanned the optical fiber coupler with 1 mm steps. For each spectrum, we determined the Stokes signal amplitude as a function of the positions at 607 and 668 nm.

Figure 3b shows this relationship on a semi-logarithmic scale. The blue-crossed squares correspond to the signals at 607 nm, while the red-crossed circles refer to those at 668 nm. The signals at 668 nm are generally smaller than those at 607 nm, particularly for the central spot (point A). At some points on the ring—indicated by B and C—the signals become comparable. From the figure, it can be seen that the ring radii depend slightly on wavelength, allowing for the separation of Stokes components with slightly different wavelengths.

Figure 4 shows the spectra measured at points A, B, and C (Figure 4a, Figure 4b, and Figure 4c, respectively). All signal amplitudes are given in the same arbitrary units. The signal at point A is more than two orders of magnitude larger than those at B and C. The most important feature is that the central spot exhibits a single peak around 607 nm, whereas those at B and C show a double-peak structure with peaks around 607 and 668 nm. These spectra confirm the generation of Stokes signals corresponding to Raman transitions from the ground state to the $^1\text{O}_2(0)$ and $^1\text{O}_2(1)$ levels. Only the oxygen molecule can exhibit the double-peak response in the Stokes signal spectrum shown in Figure 4b,c. For the central spot, the contribution at 668 nm is more than one order of magnitude smaller than the Stokes signal at 607 nm. Some spectral asymmetry toward longer red wavelengths is evident in Figure 4a due to the contribution at 668 nm.

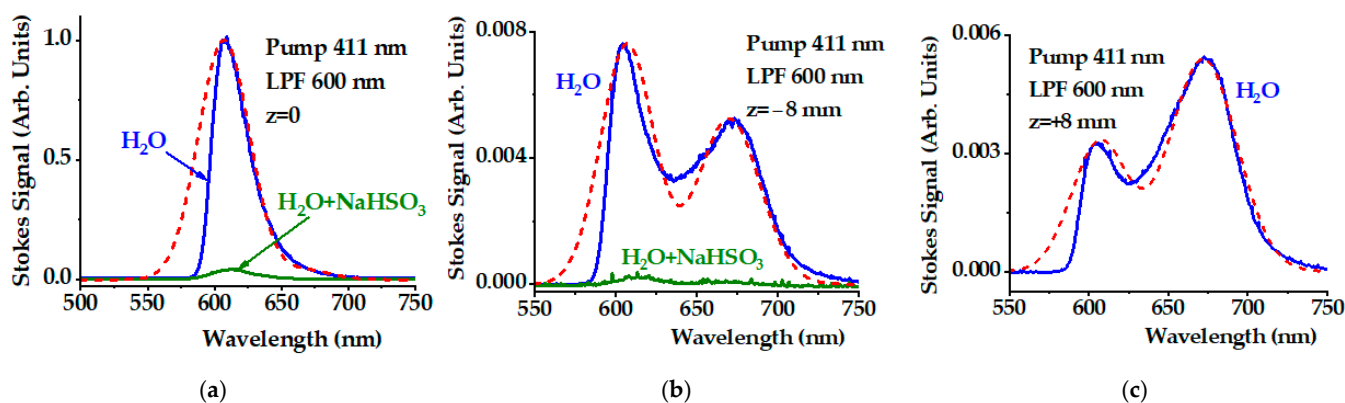


Figure 4. (a) Stokes spectra collected at the central spot at position A ($z = 0$), and those at the ring positions (b) B ($z = -8$ mm), and (c) C ($z = +8$ mm) shown in Figure 3. The green curve in (a,b) is the signal after adding NaHSO_3 at a concentration of 40 mg/mL. The red dashed lines represent the interpretation of the spectra as the sum of two Gaussians centered at 607 nm and 668 nm (see Table 1 for details). We used a pump wavelength of 411 nm and a long-pass filter with a cut-off of 600 nm.

To validate that the observed Stokes signal is oxygen-dependent, we added the oxygen quencher NaHSO_3 to the water sample. The green lines in Figure 4a,b represent the same Stokes signal upon adding NaHSO_3 up to a final concentration of 40 mg/mL. We measured the oxygen concentration using an optical sensor (LabQuest 2, Vernier, Beaverton, OR, USA). Adding NaHSO_3 reduced the oxygen concentration from 8.5 mg/L to 0.6 mg/L. Both Stokes signals at 607 nm and 668 nm were significantly reduced (see Figure 4a,b), confirming that these peaks originate from oxygen.

The red dashed lines in Figure 4a–c correspond to the interpretation of the spectra as the sum of two Gaussians centered at 607 nm and 668 nm. These lines were calculated using the equation

$$I_S(\lambda) = a_1 \exp \left[- \left(\frac{\lambda - 607}{\delta_1} \right)^2 \right] + a_2 \exp \left[- \left(\frac{\lambda - 668}{\delta_2} \right)^2 \right], \quad (2)$$

where $I_S(\lambda)$ represents the predicted spectrum and λ is the signal's wavelength (in nm). The values of the parameters $a_{1,2}$ and $\delta_{1,2}$ are given in Table 1.

Table 1. Parameters used in the calculations of Equation (2).

Figure	a_1	a_2	δ_1 (nm)	δ_2 (nm)
Figure 4a	1	0.04	27	27
Figure 4b	0.0076	0.0052	23	27
Figure 4c	0.0033	0.0054	25	27

The values of a_1 and a_2 are provided in the same arbitrary units. The values for the spectral widths δ_1 and δ_2 varied slightly. The signals shown in Figure 4b,c correspond to beams propagating at an angle with respect to the pump beam. As this angle depends on the wavelength, small changes in the spectral width may be expected. The lines are broad with an average full spectral width of 55 ± 8 nm. The width reflects the rotational structure of the electronic-vibrational lines, which are broadened by interactions with solvent molecules. The real spectra disagree with the model spectra at wavelengths below 600 nm. As the LPF partially depleted the signal below 600 nm, yielding the asymmetric spectra shown in Figure 4.

We calculated the angle of deviation following the procedure described in Appendix B using the parameters presented in Table 2; in particular, the wavelengths λ_O corresponding

to the transition from the ground state to $^1\text{O}_2(0)$ and $^1\text{O}_2(1)$ predicted from the literature, the wavelengths of the Stokes λ_S and anti-Stokes λ_a components, and the expected angle of deviation α_S of the Stokes components at 607 nm and 668 nm when pumping at 411 nm. We used Equation (A8) in Appendix B to calculate α_S . The final column shows the actual deviations measured in the experiments. For the calculation, we used the refractive index values available from the literature [30].

Table 2. Wavelength values corresponding to the transition from ground toward $^1\text{O}_2(0)$ and $^1\text{O}_2(1)$, λ_O , Stokes λ_S , anti-Stokes λ_a wavelengths, and predicted and measured values for the deviation of the $^1\text{O}_2$ Stokes components at 607 nm and 668 nm (α_S).

λ_O (nm)	λ_S (nm)	λ_a (nm)	Expected α_S (°)	Measured α_S (°)
1270 [14–18]	607	310	8.8	4.8
1068 [14–18]	668	296	10.6	6

Although the model predicted a larger deviation angle for larger Stokes wavelengths, the measured deviation values were smaller than the predicted ones. As nonlinear Raman diffraction induces beam self-focusing, thereby reducing the deviation a more precise model that includes these effects is required to better validate the measured values.

We also studied the dependence of the Stokes signal on the pump energy using a set of neutral-density filters to change the pump energy. Figure 5 shows this dependence on a semi-logarithmic scale measured for the central spot (Figure 5a) and the ring structure (Figure 5b). Both dependencies are similar: when the pulse energy changes by a factor of 20, the Stokes signal changes by 5 orders of magnitude, indicating exponential growth.

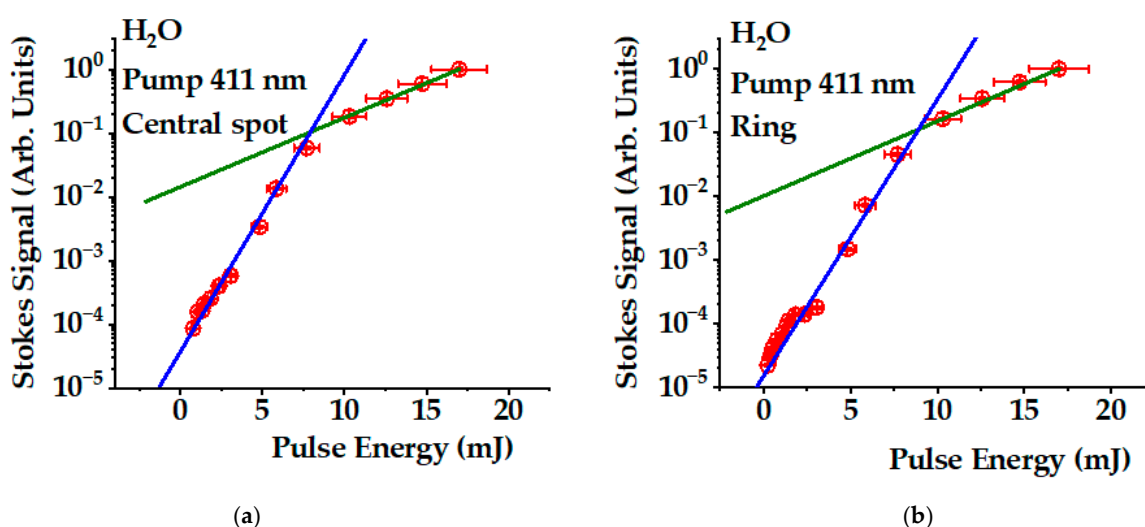


Figure 5. Pump pulse energy dependence of Stokes signals in (a) the central spot and (b) the ring (red dots). We used a pump wavelength of 411 nm and a long-pass filter with a cut-off wavelength of 600 nm. The blue solid lines correspond to a simulation with an exponential gain of 1 mJ^{-1} . The green solid line is a simulation with a gain of 0.25 mJ^{-1} .

A reduction in exponential growth was observed for energies above 8 mJ. The blue solid lines in both, Figure 5a,b, correspond to an energy exponential gain of 1 mJ^{-1} , while the green lines correspond to a gain of 0.25 mJ^{-1} . At high intensity, the coupling between Stokes and anti-Stokes components increases. As the anti-Stokes components exhibit absorption, an additional loss channel for the Stokes component limits the gain. Furthermore, the pump field induces significant Stokes components from the solvent's stretching modes [12]. At high intensity, pump depletion occurs mostly due to these losses.

The interactions between the Stokes and anti-Stokes components have been discussed in detail in the literature [25]. Using Equation (A5), we determined the imaginary component of the $^1\text{O}_2$ Raman susceptibility to be of $(6.0 \pm 0.5) \times 10^{-23} \text{ m}^2 \text{ V}^{-2}$ under the conditions of the present experiment.

5. Conclusions

We measured the Raman $^1\text{O}_2$ photoexcitation spectra upon 411 nm pumping. As predicted by basic stimulated Raman excitation theory, we observed two kinds of Stokes signals. The first propagates in the direction of the pumping beam, forming a central spot in the Raman diffraction pattern, while the second contribution forms an angle with respect to the pump direction, thus creating a ring structure. We analyzed the spectral properties of the Raman diffraction pattern. The central spot exhibits a single-peak structure centered around 607 nm, corresponding to the transition from the ground to the $^1\text{O}_2(0)$ state. At some points of the ring structure, it becomes possible to detect a two-peak structure containing contributions at 607 nm and 668 nm, with the latter corresponding to the transition toward the $^1\text{O}_2(1)$ state. These results confirm the electronic vibrational structure of molecular oxygen predicted in previous studies [14–18]. The findings also demonstrate that studying the spectral properties of the Stokes ring structure is a suitable method for separating different Stokes contributions. This strategy represents a new approach for spectroscopic studies of complex Raman interactions.

We have provided evidence for the exponential growth in the Stokes signals, as predicted by early theoretical models of the stimulated Raman process. This result opens the possibility for designing new methods and Raman instrumentation to improve the efficiency of photosensitizer-free $^1\text{O}_2$ Raman photoexcitation with intrinsic applications in photobiology, photochemistry, and photomedicine. We have previously demonstrated that it is possible to deactivate viruses using only blue light [31]. As the Raman effect is a fundamental physical phenomenon arising from the interaction of light with matter, the approach may have universal applicability for the possible deactivation of any kind of viruses, bacteria, or fungi.

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Abbreviations

The following abbreviations are used in this manuscript:

$^1\text{O}_2$	Singlet oxygen electronic level
$^1\text{O}_2(0)$	Singlet oxygen lowest vibration sublevel
$^1\text{O}_2(1)$	Singlet oxygen first excited vibration sublevel
LPF	Long-pass filter
NDF	Neutral density filter
OPO	Optical parametric oscillator
OF	Optical fiber

Appendix A

In this appendix, we describe the relationship between the exponential gain and the pump pulse energy shown in Figure 5. We start with the propagation equation for the Stokes intensity [25]:

$$\frac{dI_S}{dx} = g_S I_S, \quad (\text{A1})$$

where x is the coordinate in the direction of the pump beam propagation and

$$g_S = \frac{12\pi}{n_S^2 n_p c \lambda_S \epsilon_0} \text{Im}(\chi_S^{(3)}) I_P, \quad (\text{A2})$$

is the Stokes gain coefficient, where $\text{Im}(\chi_S^{(3)})$ is the imaginary part of the third-order nonlinear susceptibility, I_P is the pump field intensity, c is the speed of light, and ϵ_0 is the permittivity of vacuum. Considering the pump field Gaussian focused on the sample's geometric center, we can write

$$I_P = \frac{E_P}{\tau \pi r_0^2} \frac{1}{1 + x^2/x_0^2}, \quad (\text{A3})$$

where E_P is the pump pulse energy, τ is the pulse duration, r_0 is the pump beam radius at the waist, and $x_0 = \pi r_0^2 / \lambda_P$ is the pump Rayleigh range. Integration of Equation (A1) over the length of the sample yields

$$I_S = I_{S0} \exp(g_E E_P), \quad (\text{A4})$$

where I_{S0} is the initial Stokes signal, and the gain g_E is given by

$$g_E = \frac{12\pi^2 \text{Im}(\chi_S^{(3)})}{n_S^2 n_p c \lambda_S \lambda_P \epsilon_0 \tau}. \quad (\text{A5})$$

In the calculation of Equation (A5), we considered the sample's length to be much larger than the pump field Rayleigh range.

Appendix B

This appendix describes how the deviation angles of the Stokes and anti-Stokes components that form the Raman diffraction ring structure were estimated. Figure A1 shows the geometry of the beams forming the ring structure. The pump beam direction was chosen as the x-axis. The Stokes signal forms an angle α_S with respect to this direction, whereas the anti-Stokes component forms an angle α_a . Equation (1) written for the x- and y-components yields

$$\frac{n_S}{\lambda_S} \cos \alpha_S + \frac{n_a}{\lambda_a} \cos \lambda_a = \frac{2n_P}{\lambda_P}, \quad (\text{A6})$$

$$\frac{n_S}{\lambda_S} \sin \alpha_S - \frac{n_a}{\lambda_a} \sin \lambda_a = 0, \quad (\text{A7})$$

From these equations, we obtain the equation for determination of α_S as

$$\frac{n_a}{\lambda_a} \sqrt{1 - \left(\frac{n_S \lambda_a}{n_a \lambda_S} \right)^2} \sin^2(\alpha_S) = \frac{2n_P}{\lambda_P} - \frac{n_S}{\lambda_S} \sqrt{1 - \sin^2(\lambda_S)}, \quad (\text{A8})$$

Equation (A8) can be solved using the graphical method. We plot the left and right expressions of Equation (A8) as functions of λ_S . The solution is obtained at the intersection of the lines defined by these expressions.

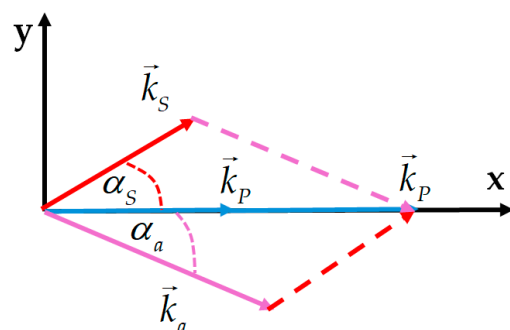


Figure A1. Schematic of the Stokes (red arrow), anti-Stokes (purple arrow), and pump wave (blue arrows) vectors that form the ring-shaped structure.

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