PARAMETRICALLY GENERATED SPECTRA AND OPTICAL BREAKDOWN IN H_2O AND NaCl

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Picosecond light pulses of high intensity have shown to generate broad light spectra by parametric four photon interaction. The threshold for plasma formation was investigated in order to assess the contribution to the frequency broadening by free electrons in the breakdown and prebreakdown region. It could be confirmed that our previously observed parametric spectra were not effected by prebreakdown processes.

In a recent paper we reported on the generation of a broad frequency spectrum when a single picosecond light pulse passed through an isotropic medium [1]. Stimulated parametric four-photon processes were shown to be responsible for our observations. On account of the resonant structure of the nonlinear susceptibility $\chi^{(3)}$ intense parametric light is produced in spite of large infrared absorption of the idler light and of phase mismatch in certain frequency regions.

It has been suggested that two other nonlinear processes might produce similar broad spectra at high light intensities: *i*) self-phase modulation due to the intensity dependent index of refraction of the medium $n = n_0 + n_2\langle E^2\rangle$ [2–4] and *ii*) self-phase modulation due to the rapid change of the refractive index with electron density when optical breakdown occurs [5].

The first nonlinear process is ruled out for the intensities and materials used in our investigations. For a peak pulse intensity of $I_{0L} = 10^{12}$ W/cm^2 and a pulse duration of $\Delta t_L = 6$ ps a spectral band width of $\Delta\tilde{\nu} = 150$ cm^{-1} and 300 cm^{-1} is estimated for a sample of H_2O (length $z = 5$ cm) and NaCl ($z = 4.4$ cm), respectively*. Note that self-focusing of the light beam is not observed in H_2O and NaCl at the light intensities and probe lengths discussed here.

The second process, the spectral broadening in relation to the optical plasma formation in dielectrics is discussed in this letter. It will be shown below that optical breakdown occurs at sufficiently high light intensities not to effect our previously discussed four-photon parametric processes [1].

Optical breakdown was observed when the incident pulse intensity exceeded a certain threshold value. In NaCl crystals the occurrence of breakdown was readily detected by a permanent microscopic damage spot. In water, however, no permanent damage is observable after plasma formation. Optical breakdown was established in water observing the light flash which is associated with the plasma. In our experiments the light was observed at an angle of 90° to the direction of the laser beam. Care has to be taken in interpreting these observations since scattering of the parametrically generated light and induced fluorescence give a similar light flash. To distinguish the various processes we focused the input light into the sample with a short lens ($f = 5$ cm). In this way the effective interaction length z for parametric light generation was drastically reduced. Up to high light intensities, plasma formation could be investigated without disturbing parametric light.

In our experiments a mode-locked Nd–glass laser was used [9]. One – in some cases two or ten – pulses were selected from the leading part of the pulse train

* $\Delta\tilde{\nu}$ was estimated according to the relation

$$\Delta\tilde{\nu} = 2.04\tilde{\nu}_L z n_2 \langle E^2\rangle/(c\Delta t_L);$$

this equation is valid for gaussian pulses [2, 6]. The values $n_2(H_2O) \simeq 9 \times 10^{-14}$ cm^3/erg and $n_2(NaCl) \simeq 2 \times 10^{-13}$ cm^3/erg are taken from ref. [7] and ref. [8], respectively.

Table 1

Experimental results of water.

Mode of operation		Intensity I_{0L} [W/cm^2]	Parametric light (forward)	Light under 90°			Damage/ plasma light
				With film	With multiplier (S20)	Decay time [ns]	
single pulse	(f = 60 cm)	2×10^{10}	start	no	start	< 3	no
		5×10^{10}	saturation	no	yes	< 3	no
		8×10^{10}	yes	no	yes	< 3	no
		1.2×10^{11}	yes	faint trace	yes	≃ 5	no
	(f = 40 cm)	8×10^{11}	yes	trace	yes	≃ 20	no
ten pulses	(f = 60 cm)	2×10^{10}	start		start	< 3	no
		5×10^{10}	saturation		yes	< 3	no
		8×10^{10}	yes		yes	< 3	no
		1.2×10^{11}	yes		yes	≃ 5	no
single pulse	(f = 5 cm)	1.5×10^{12}	start	no	start	< 3	no
		3×10^{12}	saturation	faint trace	yes	≃ 20	no
		1.4×10^{13}	yes	spot on trace	yes	≃ 40 and ≃ 150	threshold
two pulses	(f = 5 cm)	8×10^{12}	yes	spot on trace	yes		threshold
ten pulses	(f = 5 cm)	1.1×10^{12}	no	blue spot	yes		threshold

Table 2

Experimental results of NaCl.

Mode of operation		Intensity I_{0L} [W/cm^2]	Parametric light (forward)	Light under 90°			Damage/ plasma light
				With film	With multiplier (S20)	Decay time [ns]	
single pulse	(f = 60 cm)	1×10^{10}	start	no	start	< 3	no
		4×10^{10}	saturation	no	yes	< 3	no
		7×10^{10}	yes	faint trace	yes	≃ 30	no
ten pulses	(f = 60 cm)	1×10^{10}	start		start	< 3	no
		4×10^{10}	saturation		yes	< 3	no
		7×10^{10}	yes		yes	≃ 50	no
single pulse	(f = 40 cm)	1.5×10^{12}	yes		yes	≃ 200	threshold
two pulses	(f = 40 cm)	4×10^{11}	yes		yes	≃ 200	threshold
ten pulses	(f = 40 cm)	1.5×10^{11}	yes		yes	≃ 200	threshold

by an electro-optic shutter. The pulses were amplified to an energy of approximately 10^{-2} J each; they had a pulse duration of $\Delta t_L \simeq 6$ ps (fwhm) and a spectral width of $\Delta\tilde{\nu} \simeq 3$ cm^{-1} (fwhm). The light beam had a divergence of $2\theta \simeq 7 \times 10^{-4}$ rad. Light generated in the sample in forward direction by parametric four photon interaction was detected at a wavelength of λ = 7000 Å with a double monochromator and a photomultiplier. Light emitted perpendicular to the laser beam was investigated by Polaroid pictures and photomultipliers. The incident laser intensity was monitored with the help of a saturable absorber [10]. The light intensity inside of the specimen was varied with filters and lenses of different focal length. The length of the

samples was 5 cm and 4.4 cm for water (distilled) and a NaCl crystal, respectively.

Our experimental results are summarized in tables 1 and 2. There is substantial similarity between our observations with H_2O and NaCl. In the following brief discussion the data of NaCl are given in parenthesis.

i) At an input peak intensity of $I_{0L} \simeq 2 \times 10^{10}$ W/cm^2 (1×10^{10} W/cm^2) parametric light was detected in the forward direction and at an angle of 90° with photomultipliers. The 90°-light is caused by (spontaneous) scattering of the parametrically generated light. The scattering coefficient [11] of our specimen was measured with an argon laser ($\lambda = 4880$ Å) and found to be $R_{90} \simeq 4 \times 10^{-5}$ cm^{-1} (2.5×10^{-5} cm^{-1}). These values agree with the observed 90°-scattering of parametric light. The cause of the scattered light appears to be impurity scattering. Molecular scattering has published values of $R_{90,m} \simeq 2 \times 10^{-6}$ cm^{-1} (1.8×10^{-7} cm^{-1}) [11] and the Raman scattering coefficients are even smaller $R_{90,R} \simeq 2.7 \times 10^{-8}$ cm^{-1} [12] (6.3×10^{-8} cm^{-1} [11]). The following points give additional support that the 90°-light results from parametric light: the scattered light starts at a definite laser intensity independent whether one or ten pulses are used (for contrast see below) and the time duration of the scattered light is very short, below the resolution of our detection system ($\lesssim 5$ ns).

ii) In the intensity range of 2×10^{10} to 8×10^{10} W/cm^2 (1×10^{10} to 5×10^{10} W/cm^2) the generation of parametric light increases rapidly and finally saturates. The duration of the 90°-scattering is less than the resolution time of the system independent of the number of selected pulses. The observed scattered light flash results from parametric light.

iii) For laser light focused with a lens of 60 cm or 40 cm focal length, at an intensity exceeding 10^{11} W/cm^2 (6×10^{10} W/cm^2) the rise time of the 90°-light remained shorter than the resolution of the detection system ($\lesssim 2$ ns) but the decay time became longer. Now, the spectrum of the parametrically generated light extended to the ultraviolet part of the spectrum ($\lambda \lesssim 2000$ Å). It is felt that photofluorescence occurs from the impurities which absorb short wavelength parametric light. This fluorescence is measured under 90°, it exhibits a decay time of several nanoseconds. The 90°-emission is strong enough that a light trace is readily seen on Polaroid film.

iv) In NaCl the decay time of the 90°-light increased continuously with intensity for $I_{0L} \gtrsim 4 \times 10^{10}$ W/cm^2. The threshold intensity for damage decreased linearly with the number of pulses selected from the mode-locked pulse train.

v) In water the investigations of plasma formation required a lens of $f = 5$ cm. With this tight focusing, parametric light was observed at $I_{0L} \gtrsim 1.5 \times 10^{12}$ W/cm^2. The plasma formation was detected at a considerably higher laser intensity of $I_{0L} \gtrsim 1.4 \times 10^{13}$ W/cm^2 and 8×10^{12} W/cm^2 for one and two pulses, respectively. A bright light spot in the focal region superimposed on a weak light trace was seen under 90° on a Polaroid picture. We take this observation as evidence of optical breakdown. In the case where 10 pulses were incident on the sample, the threshold for breakdown decreased below the threshold of parametric light. One blue spot in the focal region indicated clearly the plasma formation. Note that threshold for plasma formation decreased linearly with the number of selected pulses. The 90°-light of a single pulse showed two decay times when plasma formation occured. The shorter time of approximately 40 ns might be due to the photofluorescence of the parametric light while the longer time of $\simeq 150$ ns might correspond to the plasma recombination time.

There are three mechanisms which generate free electrons and cause optical breakdown in dielectrics at high light intensities: *a*) multiphoton ionization, *b*) avalanche ionization, and *c*) inclusion heating.

a) The electron density produced by multiphoton ionization is estimated to be [13]:

$$N_{el} \simeq N_A \Delta t_L \omega_L n^{3/2} \left(\frac{\pi e^2 I_{0L}}{m_{el} c \omega_L^2 \Phi} \right)^n \exp(n). \qquad (1)$$

$\omega_L = 1.78 \times 10^{15}$ s^{-1} is the laser frequency, Φ is the ionization potential (H_2O: $\Phi \simeq 12.6$ eV [14]; NaCl: $\Phi \simeq 8.6$ eV [15]). n is the smallest number of photons necessary to exceed the effective ionization energy

$$\tilde{\Phi} = \Phi + \frac{2\pi e^2 I_{0L}}{mc\omega^2}, \quad ((n-1)\hbar\omega_L < \tilde{\Phi} \leq n\hbar\omega_L)$$

N_A is the number of atoms per unit volume (H_2O: $N_{\hat{A}} \simeq 10^{23}$ cm^{-3}; NaCl: $N_{\hat{A}} \simeq 2.2 \times 10^{22}$ cm^{-3}). With our experimental values for breakdown of single light pulses we calculate an electron density of $N_{el} \simeq 10^{14}$ cm^{-3} for H_2O ($n = 12$) and NaCl ($n = 8$). This electron density is too small to explain the observed optical break-

down [16]. The linear decrease of the damage threshold intensity with the number of selected pulses is also at variance with a picture of multiphoton ionization.

b) The electron density produced by avalanche ionization is estimated from eq. (2) as long as losses are neglected [16]

$$N_{el} = N_0 \exp\left(\int_{-\infty}^{\infty} \eta(E(t'))\, dt' \right). \quad (2)$$

η is the avalanche ionization rate. N_0 is an initial density of free electrons. Damage and plasma light occur when [16]

$$N_{el} \simeq N_0 \exp(\eta \Delta t_L) \simeq 10^{18}\ \mathrm{cm}^{-3}.$$

Avalanche ionization can start with at least one free electron in the focal region. In NaCl at room temperature ionized impurities give N_0 values of the order of 10^7 to 10^8 cm^{-3} [16]. While the damage threshold of single pulses is in agreement with the data for avalanche ionization [17] the reduced damage threshold for ten pulses can not be explained by this process. (A possible explanation of our experimental data is given below).

In water there are no free electrons present. In our experiments on water ($f = 5$ cm) the focal volume is of the order of 10^{-7} cm^3 and therefore N_0 must be of the order of 10^7 cm^{-3}. The first free electrons may be generated by multiphoton ionization of impurity particles and of water itself. The linear decrease of threshold intensity with the number of selected pulses is not understood by avalanche ionization.

c) The linear decrease of the damage threshold intensity with the number of selected pulses can be explained by inclusion heating. Heating of inclusions up to 10^3 K to 10^4 K causes sample damage and generates light spots [18–20]. The following short estimate shows that temperature values necessary for damage can be reached in our experiments. We consider small dielectric particles of radius a and absorption coefficient β_I that obey the relation $a\beta_I \ll 1$. The thermal time constant $\tau_H = C_H a^2/(4K_H)$ should be larger than 100 ns and therefore $a \gtrsim 2.5 \times 10^{-5}$ cm for water (volume heat capacity $C_H \simeq 4.2$ J/cm^3 K, thermal conductivity $K_H \simeq 6 \times 10^{-3}$ W/cm K) and $a \gtrsim 1 \times 10^{-4}$ cm for NaCl ($C_H \simeq 1.9$ J/cm^3 K, $K_H \simeq 6 \times 10^{-2}$ W/cm K; the subscripts H and I stand for host material and inclusion, respectively). Under these conditions the temperature at the center of the inclusion is given by eq. (3) [19]:

$$T \simeq 3\beta_I I_{0L} \Delta t_L m/(4C_I). \quad (3)$$

$m \lesssim 10$ describes the number of selected picosecond light pulses. With our measured values for the damage threshold a temperature of $\simeq 10^4$ K is obtained for reasonable absorption coefficients of $\beta_I \simeq 3 \times 10^2$ cm^{-1} and 3×10^3 cm^{-1} for H_2O and NaCl, respectively. Eq. (3) indicates that a certain damage temperature depends on the total energy supplied to the system. The critical laser intensity decreases proportional to the number of pulses as experimentally observed★.

In our experiments with single and double pulses inclusion heating and avalanche ionization may act together in the formation of plasmas [23]. The damage threshold for ten pulses may be determined mainly by inclusion heating.

Now, we wish to discuss the influence of plasma formation on the spectral broadening of picosecond light pulses. The spectral broadening is given by

$$\Delta\tilde{\nu}_{br} \simeq \frac{\tilde{\nu}_L}{c} z_{eff} \left(\left.\frac{\partial \mathrm{Re}(\Delta n)}{\partial t}\right|_{max} - \left.\frac{\partial\, \mathrm{Re}(\Delta n)}{\partial t}\right|_{min} \right). \quad (4)$$

z_{eff} is the length over which the change of refractive index occurs.

In the case of inclusion heating [$\Delta n = (\partial n/\partial T)\Delta T$] we consider the most unfavorable case, where all the laser energy is absorbed. In this case eq. (4) reduces to

$$\Delta\tilde{\nu}_{br} \simeq \frac{\tilde{\nu}_L}{c} \frac{\partial n}{\partial T} \frac{I_{0L}}{C}. \quad (5)$$

With common values of $\partial n/\partial T$ ($\simeq 5 \times 10^{-5}$ K^{-1}) and C in condensed matter we calculate $\Delta\tilde{\nu}_{br} \simeq 5$ cm^{-1} at $I_{0L} = 10^{12}$ W/cm^2. This estimate shows clearly that spectral broadening by inclusion heating can be neglected.

When free electrons are generated in the dielectrics the change of refractive index is given by

$$\Delta n_{PL} = \frac{2}{n_0} N_{el} \frac{e^2 \tau}{m\omega_L} \frac{i - \omega_L \tau}{1 + \omega_L^2 \tau^2}. \quad (6)$$

★ It is shown in ref. [21] that purification of samples increases the damage threshold considerably (less and smaller impurity particles). In ref. [22] the same damage threshold of $I_{0L} \simeq 5 \times 10^{12}$ W/cm^2 ($\Delta t_L \simeq 3$ ps) for water was found independent of the fact whether one or ten pulses were selected. This results would be expected for very pure substances.

τ is the collision time. Using eq. (2) we obtain $\partial \Delta n_{PL}/\partial t = \Delta n_{PL}\,\eta(E)$ and the spectral broadening is given by

$$\Delta\tilde{\nu}_{br} \simeq (\tilde{\nu}/c) z_{eff}\,\mathrm{Re}\,(\Delta n_{PL})\eta. \qquad (7)$$

z_{eff} is the length where the high electron density N_{el} is present. z_{eff} is determined by the focal region and is smaller than the length of the sample. For water we estimate a spectral broadening of $\Delta\tilde{\nu}_{br} \simeq 8\ \mathrm{cm}^{-1}$ at a free electron density of $N_{el} = 10^{18}\ \mathrm{cm}^{-3}$ when we assume an effective length of $z_{eff} = 1$ cm (too long in the case of focusing with $f = 5$ cm) and a collision time $\tau = 1.3 \times 10^{-16}$ s†. For NaCl we calculate a spectral broadening of $\Delta\tilde{\nu}_{br} \simeq 120\ \mathrm{cm}^{-1}$ ($N_{el} = 10^{18}\ \mathrm{cm}^{-3}$, $z_{eff} = 1$ cm, $n_0 = 1.54$, $\tau = 3 \times 10^{-15}$ s [5]). This spectral broadening at the electron density of breakdown is very small compared to the observed parametric spectra which extent over approximately 50 000 cm^{-1}.

At intensity values slightly below the threshold intensity the free electron density reduces very rapidly and the spectral broadening becomes very small. Using the experimentally verified curve in ref. [17] we estimate a reduction of $\Delta\tilde{\nu}_{br}$ by a factor of 10^5 for picosecond light pulses when the laser intensity is reduced by a factor of two below the threshold value.

In conclusion we wish to say that up to 10^{12} W/cm^2 in NaCl and up to 10^{13} W/cm^2 in water no breakdown occurs for pulses of approximately 6 ps duration. Up to these intensity values spectral broadening due to the nonlinear refractive index n_2 is small. Spectral broadening due to plasma formation is negligible at intensity values a factor of two below damage threshold. The broad-band light emitted in forward direction is generated by parametric four photon interactions. The detected visible light under an angle of 90° to the laser beam originates from spontaneous scattering and induced photofluorescence of the parametrically generated light.

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† τ is calculated from the relation $\tau = 1/(N_M \sigma \bar{v})$ [24] with $N_M = 3 \times 10^{22}\ \mathrm{cm}^{-3}$ density of water molecules, $\sigma = \pi\langle r^2\rangle = 1.7 \times 10^{-15}\ \mathrm{cm}^2$ [25] scattering cross-section, and $\bar{v} = 0.5\sqrt{2\Phi/m_{el}} = 1.1 \times 10^8$ cm/s free electron velocity.

References

[1] A. Penzkofer, A. Laubereau, and W. Kaiser, Phys. Rev. Lett. 14 (1973) 863.
[2] R.R. Alfano and S.L. Shapiro, Phys. Rev. Lett. 24 (1970) 592;
R.R. Alfano, L.L. Hope, and S.L. Shapiro, Phys. Rev. A6 (1972) 433.
[3] N.N. Il'ichev, V.V. Korobkin, V.A. Korshunov, A.A. Malyutin, T.G. Okroashvili and P.P. Pashinin, JETP Lett. 15 (1972) 133.
[4] G.E. Busch, R.P. Jones and P.M. Rentzepis, Chem. Phys. Lett. 18 (1973) 178.
[5] N. Bloembergen, Opt. Commun. 8 (1973) 285.
[6] A. Laubereau and D. von der Linde, Z. Naturf. 25a (1970) 1626.
[7] M. Paillette, Ann. Phys. (Paris) 4 (1969) 671.
[8] C.C. Wang, Phys. Rev. B2 (1970) 2045.
[9] D. von der Linde, O. Bernecker, and W. Kaiser, Opt. Commun. 2 (1970) 149.
D. von der Linde, IEEE J. Quant. Electron. QE-6 (1970) 725.
[10] A. Penzkofer, D. von der Linde, and A. Laubereau, Opt. Commun. 4 (1972) 377.
[11] I.L. Fabelinskii, Molecular scattering of light (Plenum Press, New York, 1968).
[12] G. Bret and G. Mayer, in Physics of quantum electronics, eds. P.L. Kelley, B. Lax, and P.E. Tannenwald (Mc Graw-Hill, New York, 1966).
[13] L.V. Keldysh, Sov. Phys. - JETP 20 (1965) 1307.
[14] G. Herzberg, Molecular Spectra and molecular structure II Infrared and Raman Spectra of polyatomic molecules (D. van Nostrand, Princeton, New Jersey, 1968).
[15] American Institute of Physics Handbook, ed. by D.E. Gray, (Mc Graw-Hill, New York, 1963).
[16] N. Bloembergen, to be published;
E. Yablonovitch and N. Bloembergen, Phys. Rev. Lett. 29 (1972) 907.
[17] D.W. Fradin, N. Bloembergen, and I.P. Letellier, Appl. Phys. Lett. 22 (1973) 635.
[18] R.W. Hopper and D.R. Uhlmann, J. Appl. Phys. 41 (1970) 4023.
[19] M. Sparks and C.J. Duthler, J. Appl. Phys. 44 (1973) 3038.
[20] Yu. K. Danileiko, A.A. Manenkov, A.M. Prokhorov, and V.Ya. Khaimov-Mal'kov, Sov. Phys. -JETP 31 (1970) 18.
[21] A.V. Butenin and B. Ya. Kogan, Sov. J. Quant. Electron. 1 (1972) 561.
[22] R. Yu. Orlov, I.B. Skidan, and L.S. Telegin, Sov. Phys. -JETP 34 (1972) 418.
[23] Yu. K. Danileiko, A.A. Manenkov, V.S. Nechitailo, A.M. Prokhorov, and V.Ya. Khaimov-Mal'kov, Sov. Phys. -JETP 36 (1973) 541.
[24] H. Opower, W. Kaiser, H. Puell, and W. Heinicke, Z. Naturf. 22a (1967) 1392.
[25] D. Eisenberg and Kauzmann, The structure and properties of water (Clarendon Press, Oxford, 1969).