Enhancement of ultrafast supercontinuum generation in water by the addition of Zn^{2+} and K^+ cations

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Nonlinear-optical properties of various salts and water solutions were measured using an 8-psec laser pulse at 530 nm. It was found that the optical Kerr effect and supercontinuum signals were several times larger in saline water than in pure water. The optical Kerr effect signals from saturated aqueous solutions of $ZnCl_2$ were about 35 times greater, and the self-phase-modulation signals from saturated aqueous solutions of K_2ZnCl_4 were about 10 times greater.

The ultrafast supercontinuum[1] laser source (USL) has been used as a spectroscopic tool for measuring a number of nonlinear optical effects,[2] time-resolved absorption spectroscopy,[3] and ultrashort-light-pulse compression.[4] It has simplified experiments that measure time delay and relative intensity for different wavelengths simultaneously. New technological uses for the USL have been established in ranging, atmospheric remote sensing, imaging, and optical-fiber measurements. For these applications it will be necessary to increase the conversion efficiency from the exciting laser pulse to the USL pulse. One method to accomplish this is based on induced phase modulation[5] and uses multiple-excitation laser beams of different wavelengths. In this Letter we report a tenfold enhancement of the USL pulse from water by the addition of cations. The enhancement arises from the increase in the aqueous solutions' nonlinear refractive index and involves both self-phase modulation (SPM) and four-photon parametric generation (FPPG).

A schematic of the apparatus used to measure the USL phase enhancement is shown in Fig. 1. The laser system consisted of a mode-locked Nd^+:glass laser with an amplifier, a single-pulse selector, and a KDP second-harmonic generator. The 1.06-μm primary light was blocked with filter F_1; the 530-nm laser pulse emitted from the KDP crystal then weakly focused into a 15-cm-long cell containing aqueous salt solutions. At the front face of the sample cell the 530-nm pulse energy, duration, and beam size were measured to be about 80 μJ, 8 psec, and 1.2 mm^2, respectively. Filters F_3 and F_4 after the sample cell were used to remove the 530-nm laser pulse. A set of neutral-density filters was used to adjust the light intensity before it entered the detection system. The USL was measured with a 0.25-m grating spectrometer in combination with a one-dimensional optical multichannel analyzer (OMA1). The former recording method measures both the on-axis SPM and the off-axis FPPG processes. The latter spectral method quantitatively detects the on-axis SPM component.

The optical Kerr gate[6] (OKG) was used to measure the nonlinear refractive index of the salt solutions.

The primary and second-harmonic light beams were separated by a dichroic mirror and then focused into a 1-cm-long sample cell filled with the same salt solutions that produced the USL pulse enhancements. The size of the nonlinear index of refraction, n_2, was determined from the transmittivity of the probe beam through the OKG.

Three different two-component salt solutions of various concentrations were tested. The solutes were KCl, $ZnCl_2$, and K_2ZnCl_4. All measurements were performed at 20 ± 1°C. Typical spectra of USL pulses exhibited both SPM and FPPG features.[1] The collinear profile arising from SPM has nearly the same spatial distribution as the incident 530-nm laser pulse. The two wings correspond to FPPG pulse propagation. The angle arises from the phase-matching condition of the generated wavelength emitted at different angles from the incident laser beam direction. FPPG spectra sometimes appear as multiple cones and sometimes show modulated features. SPM spectra also show modulated patterns. These features can be explained by multiple filaments. The formation of filaments is a stochastic process. The resultant modulation patterns were not reproducible.

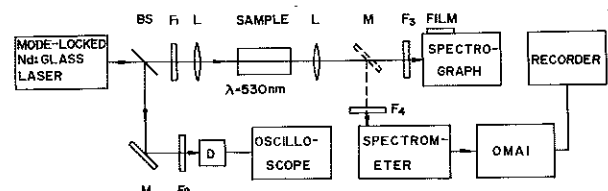Typical USL pulse spectra (USP's), on the Stokes side for different aqueous solutions and neat water,

Fig. 1. Schematic diagram for USP measurements. The USP is measured with both a spectrograph and a spectrometer. Filter sets consisted of F_1, 2 Corning 1-75; F_2, Corning 1-75, a 530-nm narrow-band filter, and neutral-density filters; F_3,F_4, Corning 1-75 and 3-3-67 for Stokes side measurements and Corning 1-75 and 2-5-57 for anti-Stokes side measurements. Neutral-density filters are also used to adjust light intensity. L's, lenses; M's, mirrors; D, photodetector.
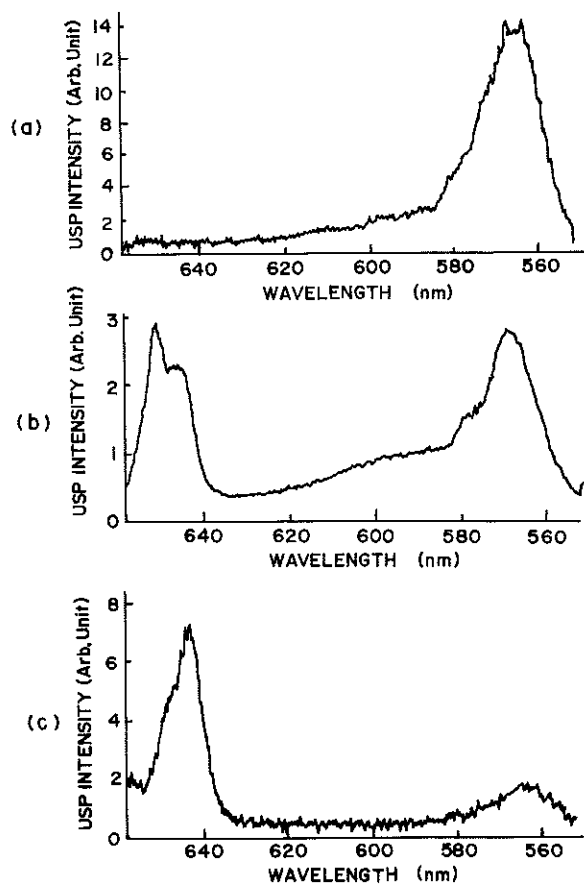
Fig. 2.   SPM spectrum of a (a) saturated K_2ZnCl_4 solution, (b) 0.6-M K_2ZnCl_4, and (c) pure water. The SRS signal (645 nm) is stronger in pure water, and it disappears in high-concentration solution.

measured with the OMA are shown in Fig. 2.   The salient features displayed in Fig. 2 are a wideband SPM spectrum together with the stimulated Raman scattering (SRS) of the OH stretching vibration around 645 nm.   The addition of salts causes the SRS signal to shift toward the longer-wavelength region and sometimes causes the SRS to be weak [Fig. 2(a)]. The SRS signals of pure water and dilute solution appear in the hydrogen-bonded OH stretching region (~3400 cm^{-1}).   In a high-concentration solution, it appears in the nonhydrogen-bonded OH stretching region (~3600 cm^{-1}).   This is the same phenomenon that was observed in an aqueous solution of $NaClO_4$ by Walrafen.[7]

To evaluate quantitatively the effect of cations on USL generation, the USL signal intensity for various samples at a fixed wavelength were measured and compared.   Figure 3 shows the dependence of the USL (mainly from the SPM contribution) signal intensity on salt concentration for aqueous solutions of K_2ZnCl_4, $ZnCl_2$, and KCl at 570 nm [Fig. 3(a)] and 500 nm [Fig. 3(b)].   Each data point was averaged over 10 laser shots.   The data were normalized with respect to the averaged USL signal intensity obtained from neat water.   These data indicate that the USL pulse intensity was highly dependent on salt concentration and that both the Stokes and the anti-Stokes sides of the
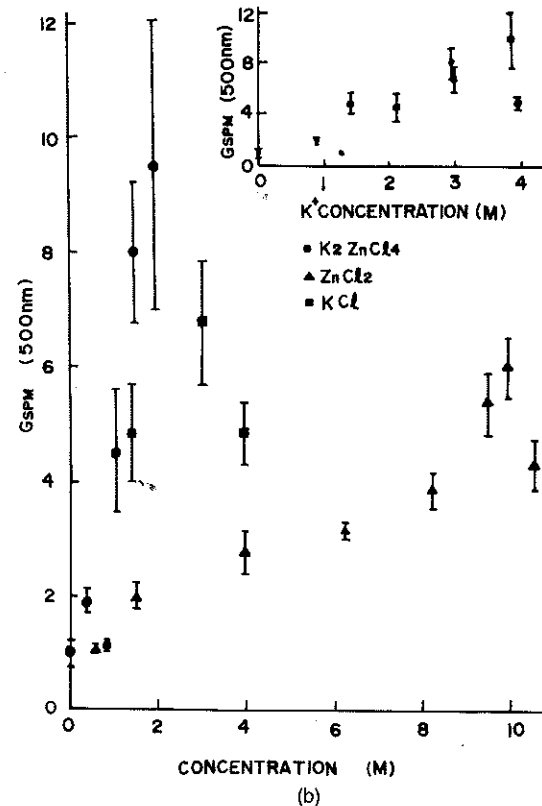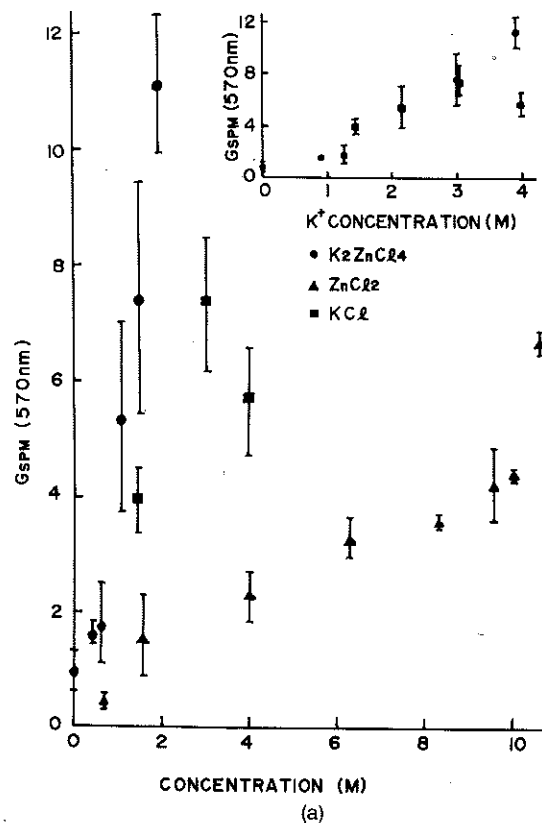
Fig. 3.   The salt concentration dependence of the SPM signal (a) on the Stokes side and (b) on the anti-Stokes side at 20°C.   Each datum point is the average of about 10 laser shots.   The insets are the same data plotted as a function of K^+-ion concentration for KCl and K_2ZnCl_4 aqueous solutions, where N is Avogadro's number.

Table 1. Enhancement of the USL and Optical Kerr Effect Signals in Saturated Aqueous Solutions at 20°C[a]

Signal	K_2ZnCl_4 (1.9 M)	KCl (4.0 M)	$ZnCl_2$ (10.6 M)
G_{SPM} (570 nm)	11 ± 1	5.6 ± 0.9	6.6 ± 0.4
G_{SPM} (500 nm)	9.5 ± 2.5	4.9 ± 0.2	4.3 ± 0.5
G_{Kerr}	16 ± 1	6.1 ± 1.4	35 ± 9

[a] $G_{SPM}(\lambda) = \langle I_{SPM}(\lambda)/I_{laser}(530 \text{ nm})\rangle_{solution}/\langle I_{SPM}(\lambda)/I_{laser}(530 \text{ nm})\rangle_{water}$ and $G_{Kerr} = \langle I_{Kerr}(\text{solution})\rangle/\langle I_{Kerr}(\text{water})\rangle$.

USL signals from a saturated K_2ZnCl_4 solution were about 10 times larger than from neat water. The insets in Fig. 3 are the same data plotted as a function of K^+-ion concentration for KCl and K_2ZnCl_4 aqueous solutions. Solutions of KCl and K_2ZnCl_4 generate almost the same amount of USL if the K^+ cation concentration is same even though they contain different amounts of Cl^- anions. This indicates that Cl^- anion has little effect on generation of USL. The Zn^{2+} cation also enhanced USL, though to a lesser extent than the K_+ cations.

Our measurements of the optical Kerr effect and the ultrafast supercontinuum in salt-saturated aqueous solutions are summarized in Table 1. The measured n_2 (pure H_2O) is about 220 times smaller than n_2 (CS_2). The value $G_{SPM}(\lambda)$ represents the ratio of the SPM signal intensity from a particular salt solution to that from neat water at wavelength λ. G_{Kerr} is defined as the ratio of the transmitted intensity caused by a polarization change of the probe beam in a particular salt solution to that in neat water. G_{Kerr} is equal to $[n_2(\text{particular solution})/n_2(\text{water})]^2$. Table 1 shows that, at saturation, K_2ZnCl_4 produced the greatest increase in USL. Although $ZnCl_2$ generated the largest enhancement of the optical Kerr effect, it did not play an important role in the enhancement of USL (the possible reasons for this will be discussed below). The optical Kerr effect signal from saturated solutions of $ZnCl_2$ was about 2 to 3 times greater than that from saturated solutions of K_2ZnCl_4.

The enhancement of the optical nonlinearity of water by the addition of cations can be explained by the cations' disruption of the tetrahedral hydrogen-bonded water structures and their formation of hydrated units.[8] Since the nonlinear index n_2 is proportional to the number density of molecules,[9] hydration increases the number density of water molecules and thereby increases n_2. The ratio between the hydration numbers of Zn^{2+} and K^+ has been estimated from the measurements of G_{Kerr} and compared with their values based on ionic mobility measurements.[10] At the same concentration of KCl and $ZnCl_2$ aqueous solutions, $(G_{Kerr}$ generated by $ZnCl_2$ solution$)/(G_{Kerr}$ generated by KCl solution $= [N(Zn^{2+})/N(K^+)]^2 \sim 2.6$, where $N(Zn^{2+}) \sim 11.2 \pm 1.3$ and $N(K^+) \sim 7 \pm 1$ represent the hydration number for the Zn^{2+} and K^+ cations, respectively. The calculation of the hydration number of $N(Zn^{2+})/N(K^+) \sim 1.5$ is in good agreement with the Kerr nonlinearity measurements displayed in Table 1.

In addition, from our previous measurements and discussions of nonlinear processes in mixed binary lip-

ids,[11] the total optical nonlinearity of a mixture modeled from a generalized Langevin equation was determined by the coupled interactions of solute–solute, solute–solvent, and solvent–solvent molecules. In the research reported in this Letter, for example, the molar ratio of K_2ZnCl_4 to water was ~0.2. The high-salt solute concentration may contribute additional optical nonlinearity to the water owing to the distortion from the salt ions and the salt–water molecular interactions.

The finding that Zn^{2+} cations increased G_{Kerr} more than G_{SPM} is consistent with the hydration picture. The transmitted signal of the OKG depends on Δn, while the USL signal is determined by $\partial n/\partial t$, i.e., the USL also depends on the response time of the hydrated units. Since the Zn^{2+} hydrated units are larger than those of K^+, the response time will likewise be longer. Two additional factors may contribute to part of the small discrepancy between G_{SPM} and G_{Kerr} for $ZnCl_2$. The first one is related to the mechanism of δn generation in which χ_{1111} is involved in the generation of SPM while the difference $\chi_{1111} - \chi_{1122}$ is responsible for the optical Kerr effect. The second is the possible dispersion of n_2 because of the difference in wavelength between the exciting beams of USL and the optical Kerr effects.

In conclusion, the optical Kerr effect is enhanced 35 times by using a solute of $ZnCl_2$, and the USL is enhanced about 10 times by using a solute of K_2ZnCl_4. The enhancement of the optical nonlinearity has been attributed to an increase in the number density of water molecules owing to hydration and the coupled interactions of solute and solvent molecules.

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