reported²⁷ to exhibit a nonzero slope in the emission polarization spectra. This phenomenon was concluded to be intrinsic to dd* emission as was the variation in lifetime across the emission band. The dd* emission of [Ru- $(HDPA)_3]^{2+}$ is of such low intensity that the error in P is estimated at $\sim 2\%$, which may be too large to enable observation of a small monotonic variation across the band, especially since the choices for λ_{ex} were limited to values which produced sufficient emission intensity. Similarly, decay curves could not be obtained over a very wide range of emission energies, and those lifetimes calculated exhibited no significant difference.

Conclusions

The unusual chemical properties of complexes of HDPA and DPA⁻ with Ru(II) have been examined in aqueous and nonaqueous solvents. The fully protonated complex $[Ru(HDPA)_3]^{2+}$ (3-H) has been isolated as a solid, and

 $[Ru(HDPA)_2DPA]^+$ (2-H), $[Ru(HDPA)(DPA)_2]^0$ (1-H), and $[Ru(DPA)_3]^-$ (0-H) have been characterized in solution. A solid of molecular formula Na[Ru(DPA)₃]·H₂O has also been isolated and is believed to be an aquated form of the fully deprotonated complex. The protonated species behave as very weak acids in aqueous or alcoholic solution. The presence of water in solution results in the occurrence of slow equilibrium processes as manifested by changes in optical properties.

The spectroscopic properties are unique as (1) a spinforbidden dd* emission occurs for 3-H, (2) IId* chargetransfer spin-forbbiden emission occurs for the deprotonated tris(dipyridylamine) complexes of Ru(II), (3) spatially isolated (single-ring) emission occurs for 0-H and 2-H in nonaqueous solvents with the chromophore unit a Ru-DPA⁻ fragment, and (4) multiring-type emission is suggested for the 1-H complex in aqueous and nonaqueous solvents.

Multiple Fluorescences. 6. The Case of 1,8-Naphthosultam

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The emission from 1,8-naphthosultam (2H-naphth[1,8-cd]isothiazole 1,1-dioxide) (1a) is composed of two bands, one for the acid ($\lambda_{max} = 480$ nm) and one for the corresponding anion (2, $\lambda_{max} = 600$ nm). The fluorescence of both 1a and 2, as well as that of the N-methyl- and N-ethyl-1,8-naphthosultams (1b and 1c), has a modest sensitivity to solvent polarity. The ground-state pK_a for 1a is 6.2, with pK_a^* of -3.0. The proton transfer rate for 1a to water is $>5 \times 10^{10}$ s⁻¹, from the rise time of anion fluorescence by picosecond pulse techniques. The fluorescence lifetimes for 1a and 2 are 16 ($\phi_F = 0.37$, dioxane) and 1.4 ($\phi_F = 0.005$, H₂O, pH 10) ns, respectively.

Introduction

Examples of multiple fluorescence, as distinct emissions from different electronic states in the same manifold, are very rare. The states are not necessarily coexistent in time. Some aromatic hydrocarbons and molecules like azulene exhibit such multiple fluorescences (cf. summary by Birks²). In fact, most multiple fluorescences appear to arise from multiple species, each following Kasha's "rule" that emission will normally occur from the lowest excited electronic state. Such species may be as closely related as the planar and twisted forms of the charge-transfer state of 4-(N,N-dimethylamino) benzonitrile³ (Grabowski et al.⁴). Lippert has summarized the various processes which can lead to multiple fluorescent species via excited states.⁵ Multiple ground-state species can also give rise to multiple excited-state species as in the examples of methyl salicylate⁶ and 2-hydroxy-1-naphthaleneacetic acid.⁵

Our interest in the subject arose from the discovery of the dual fluorescences from 6-(N-phenylamino)-2naphthalenesulfonate (6,2-ANS).^{8a} In detailed and extensive studies,⁸ we have shown that the fluorescences originate from two emitting states, $S_{1,np}$ (np = nonplanar) and $S_{1,ct}$ (ct = charge transfer) and that these states are responsible for the excited-state behavior of 6-(Nphenylamino)-2-naphthalenesulfonate and 8-(N-phenylamino)-1-naphthalenesulfonate (8,1-ANS). Our results as well as those of Grabowski showed conclusively that a donor group (e.g., phenyl or dimethylamino) which was only weakly conjugated to the acceptor group within an excited molecule stabilized a charge-transfer state sufficiently well for that state to compete as a channel for excited-state decay. In the case of ANS derivatives, a distinct second fluorescence may be readily observed.

It was thus with considerable concern that we encountered the report by Weber⁹ (quoted by $Woody^{10}$) that

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Figure 1. Emission spectra for 1,8-naphthosultam (1a) in dioxane, in 85% dioxane-water, and in water (excitation at 330 nm).

1,8-naphthosultam (2*H*-naphth[1,8-cd]isothiazole 1,1-dioxide) (1a) exhibited a highly solvent-sensitive emission.



The nitrogen of the sultam must perforce be conjugated to the ring, and it did not seem possible that two different excited-state species could be produced from such a molecule.

We have now reexamined the fluorescence of 1,8-naphthosultam and that of the key N-methyl (1b) and N-ethyl (1c) derivatives. It appears that the "solvent-sensitive" fluorescence is an artifact due to a solvent-induced shift in the equilibrium between the sultam (1a) and its anion (2), the two species exhibiting fluorescences at rather different wavelengths. Neither the fluorescence of the sultam nor that of its anion is particularly sensitive to solvent.

Results

To examine the proposition^{9,10} that the fluorescence parameters for 1,8-naphthosultam were strongly dependent on solvent polarity, we measured both the fluorescence maxima and fluorescence quantum yields for 1,8naphthosultam (1a) in a series of dioxane-water mixtures, using the approach developed previously.⁸ The emission data are summarized in Table I.

Fluorescence spectra for 1a in dioxane, 85% dioxanewater, and water solutions are shown in Figure 1. A short-wavelength emission band (SE) is observed for pure dioxane solutions and for solvent mixtures containing small amounts of water. For solutions containing appreciable water, a sharp decrease of the SE occurs, accompanied by the appearance of a new emission band at longer wavelengths (LE). Both fluorescence emissions are observed for dioxane-water solutions of 1a containing intermediate amounts of water (Figure 1 and Table I). In contrast, the

TABLE I: Emission Maxima and Quantum Yields of Fluorescence ($\phi_{\rm F}$) for 1,8-Naphthosultam Derivatives (1a-c) in Dioxane-Water Mixtures^{a, b}

d

iowono	F_(30) ¢	$\lambda_{\max}, \operatorname{nm}(\phi_{\mathrm{F}})^{e}$		
H ₂ O, ^c %	kcal/mol	H(1a)	CH ₃ (1b)	$C_2H_s(1c)$
100	36.0	449 (0.37)	466 (0.14)	470 (0.14)
99.6	37.0	451 (0.36)		. ,
99.1	38.5	453 (0.31)		
98.1	41.2	454 (0.25)		472 (0.15)
97.2	41.8	$456 (0.18)^{f}$		
96.3	42.8	$457(0.14)^{f}$		473 (0.15)
95.3	43.7	$459(0.10)^{f}$		
94.4	44.2	461, 550		473 (0.15)
		(0.08) ^g		
92.5	45.6	462, 555		473 (0.15)
		(0.06) ^g		
90.5	46.5	465 sh, 564		474 (0.14)
		$(0.05)^{g,h}$		
87.5	47.4	465 sh, 555		
		$(0.04)^{g,h}$		
85.9	47.8	465 sh, 578	470 (0.15)	
		$(0.04)^{g,h}$		
84.3	48.1	465 sh, 580		
		$(0.04)^{g,h}$		
81.2	48.8	465 sh, 580		476 (0.15)
		$(0.04)^{g,h}$		
78.1	49.4	581 (0.03)		
75.0	50.0	582 (0.03)		
71.8	50.6	584 (0.03)	473 (0.14)	478 (0.15)
62.5	51.9		474(0.14)	479 (0.14)
53.1	53.2	586 (0.02)	476 (0.13)	480 (0.13)
43.8	54.9		477 (0.12)	481 (0.12)
34.4	56.5		478 (0.11)	482 (0.12)
25.0	57. 9		480 (0.10)	483 (0.11)
15.6	59.9		483 (0.09)	484 (0.10)
6.2	61.9	596 (0.005)	485 (0.08)	485 (0.09)

^a Temperature, 25 ± 1 °C. ^b Procedures and instrumentation are described in the Experimental Section. ^c Percentage of dioxane by volume mixed with water. ^d Values were either taken from Table 2, p 28, in Reichardt, C. Dimroth, K. Fortsch. Chem. Forsch. 1968, 11, 1 or derived from values in this table by linear interpolation. ^e ±10% or less, according to reproducibility. Quinine sulfate in 0.1 N H₂SO₄, $\phi_{\rm F} = 0.55$. Values are not corrected for refractive index. ^f A contribution of long-wavelength emission to the spectrum is evident. ^g Quantum yield for total emission. ^h sh = shoulder. The short-wavelength emission appears as a shoulder and the position is difficult to determine.

N-alkylated 1,8-naphthosultams, the N-methyl (1b) and N-ethyl (1c) derivatives, in a series of dioxane-water solutions, exhibit only short-wavelength emissions (460 nm). For the N-alkylated 1,8-naphthosultams, the position of the emission maximum moves smoothly to somewhat longer wavelengths and the quantum yield of fluorescence decreases slightly with increasing solvent polarity. Emission data for 1b and 1c are given in Table I.

The effect of solvent polarity on the position of the fluorescence maxima of 1,8-naphthosultams may be evaluated by correlation with $E_{\rm T}(30)$, an empirical solvent polarity parameter.¹¹ Plots of emission energies (fluorescence maxima expressed in kcal/mol) for the *N*-hydrogen and *N*-methyl compounds in dioxane-water mixtures and in pure solvents, against the appropriate $E_{\rm T}(30)$ values, are shown in Figure 2. The emission energies for the *N*-methyl derivative 1b are correlated by a single line with a slope of 0.14. Two lines (slopes 0.14 and 0.12) are required to correlate the emission energies for the sultam 1a.

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Figure 2. Plots of emission energies (in kcal/mol) for 1,8-naphthosultam (1a) and N-methyl-1,8-naphthosultam (1b) against the solvent polarity parameter, $E_{T}(30)$ (in kcal/mol). The emission energies for 1a in solvents other than dioxane-water are indicated by filled squares (III). Emission energies for 1a in dioxane-water mixtures are indicated by empty squares (III). Emission energies for 1b in dioxane-water mixtures are shown as empty triangles (Δ).

Dual emissions for 1a are also observed for solutions in various alcohols (Figure 2). The ratio of LE to SE intensities varies with the solvent (1.9 (methanol), 0.9 (ethanol), 1.6 (1,2-ethanediol), and 0.5 (1,3 propanediol)) but is independent of the exciting wavelength in 1,2-ethanediol. In the protic, viscous solvent glycerol, only SE emission is seen.

Emission and excitation spectra for 1,8-naphthosultam were measured for aqueous solutions of various acidities (Figure 3). The SE emission (at 480 nm) is dominant in concentrated sulfuric acid, but the LE emission (at 600 nm) is favored for dilute acid. Both emissions have the same excitation spectrum, identical with the absorption spectrum (λ_{max} ca. 330 nm). However, the excitation spectrum for the LE emission of sultam in buffer, pH 10, is characterized by a new band at 375 nm, identical with the absorption spectrum of the anion 2 in water. We can therefore assign the SE emission to the neutral species 1a and the LE emission to the corresponding anion, 2.

The variations in the naphthosultam and naphthosultam anion concentrations as a function of pH, determined with absorption and emission spectra, are used for the determination of the ground-state (K_a) and excited-state (K_a^*) dissociation constants. The changes in the UV spectrum of naphthosultam, measured in buffers of different pH, are illustrated in Figure 4. The optical density at 375 nm was plotted against the corresponding pH value, and a pK_a of 6.2 was determined from the inflection point.

The pK_a^* for 1a is derived from a plot of the relative fluorescence intensities I(LE)/I(SE) for sulfuric acid solutions vs. the Hammett acidity function H_0^{12} (Figure 3).



Figure 3. Left: An absorption spectrum for 1,8-naphthosultam (1a) in sulfuric acid (0.001–18 M). The excitation spectra for the emissions of 1a in sulfuric acid at 480 and 600 nm are identical with the absorption spectra. Right: Emission spectra for 1a in H_2SO_4 (7 M) and in H_2SO_4 (1 M), with excitation at 330 nm.

TABLE II: Fluorescence Lifetimes of 1,8-Naphthosultam in Various Solvents at 25 $^\circ C$

$\tau_{\rm F}(1a),^{a,b}$ ns	$\tau_{\mathbf{F}}(2),^{a,c}$ ns	
16.8		
	4.2	
	1.5	
0.6^{d}		
	1.4	
1.3	5.7	
	$ au_{\rm F}(1a),^{a,b}$ ns 16.8 0.6^{d} 1.3	$\begin{array}{c} \tau_{\rm F}(1{\rm a}),^{a,b} & \tau_{\rm F}(2),^{a,c} \\ {\rm ns} & {\rm ns} \\ \\ 16.8 & \\ & 4.2 \\ 1.5 \\ 0.6^d & \\ & \\ 1.4 \\ 1.3 & 5.7 \end{array}$

^a $\pm 5\%$. ^b Lifetime of the neutral sultam 1a measured at 460 nm. ^c Lifetime of the sultam anion 2 measured at 580 nm. ^d As noted in ref 12, protonation of the excited state, probably on the aromatic ring (cf.: Lau, Y. K.; Nishizawa, K.; Tse, A.; Brown, R. S.; Kebarle, P. J. Am. Chem. Soc. 1981, 103, 6291-5, for data concerning ring protonation of aniline derivatives in the gas phase) competes with NH proton dissociation and emission as channels for the decay of the sultam excited state.

The pK_a^* was observed from the inflection point (at H_0 = -2.46) and corrected for the fluorescence lifetimes as described by Weller¹³ and Schulman.¹⁴ Since the

⁽¹²⁾ According to Weller,¹³ the relative fluorescence quantum yields should be used. However, the 480-nm band is quenched in concentrated sulfuric acid (fluorescence intensity decreases in acid of concentrations greater than 7 M) so that the exact quantum yields of each band (at 480 and 600 nm) are not available. We have therefore plotted the ratio of the fluorescence intensities. The fluorescence of the N-methyl and N-ethyl sultam derivatives are also quenched in concentrated sulfuric acid, probably because of protonation which should occur more easily than that reported for aromatic sulfonamides, $pK_a = -7$ (Olavi, P.; Virtanen, I; Heinamaki, K. Suom. Kemistil. B 1969, 42, 142-6).

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fluorescence lifetime of 1a in alkaline solutions is longer than in acid solutions (Table II), the pK_a^* is shifted by 0.41 log unit with respect to the inflection point, yielding a pK_* value of -2.87. Fluorescence lifetimes for the neutral species and the anion in various solvents are given in Table II.

The rate of deprotonation of 1a in the excited state is estimated by following the rate of formation of the anion 2 in the picosecond time scale at 580 nm, in HCl solution of pH 3. Under these conditions, the initial concentration of 2 is minimal (<0.001[1a]) and [H₃O⁺] low enough so that reprotonation $(k < 10^7 \text{ s}^{-1})$ does not decrease the rate of appearance of the anion fluorescence. (When the rate of recombination is comparable to that of dissociation, the rate of appearance of the anion emission is shortened.¹³) The rise time of anion fluorescence was comparable to or less than the time resolution of the apparatus, implying a rate constant for proton dissociation of 10¹⁰ s⁻¹ or more.

Phosphorescence emission was not detected for any of the sultam derivatives (1a-c), in EPA at 77 K.

Discussion

Fluorescence spectra of 1,8-naphthosultam (1a) do not represent a single band highly sensitive to solvent but comprise two distinct broad bands. Our results demonstrate that the short-wavelength band is due to emission from the first electronically excited state of the neutral species, 1a, while the band at longer wavelength, with a maximum shifted with respect to the former band by 4400 cm^{-1} , is the emission from the excited state of the anion 2, formed by proton loss from 1a in either the ground or excited states.

One of the most effective and practical ways of evaluating the effects of solvents on emission processes is that of comparison of fluorescence data with empirical solvent polarity parameters (Z value, $E_{\rm T}(30)$ value).^{11,15} The solvent sensitivity is reflected in a plot of emission energies against the appropriate parameter; slopes greater than 0.5 suggest that a charge-transfer process is under examination. Decisions on the number of different emitting states are also simplified through such plots; different states decay with different solvent sensitivities or occur in different energy ranges.

The existence of two different emitting states for the 1,8-naphthosultam is immediately apparent from the plot of emission energies for 1a vs. $E_{\rm T}(30)$ (Figure 2). It is clear that two correlation lines, both having low slopes, rather than one correlation line with high slope, fit the experimental data. The upper correlation line for the emission energies from 1a is similar in position (i.e., the emission energies are comparable) and slope (solvent sensitivity) to that for the emissions from 1b. The emission maxima corresponding to the energies which are thus correlated must then arise from the neutral species. The lower line correlates the emission energies from the anion, 2. That there are two different correlation lines for the emission energies from 1a confirms the conclusion that two different emitting states are involved.

The low slopes of all of the correlation lines (i.e., low solvent sensitivity of the emission maxima) imply that there is only a modest change in charge separation for the transition from the excited states to the ground states, with the excited states being more polar.

The radiative, nonradiative, and proton-transfer processes for 1,8-naphthosultam in the ground state and in Scheme I



Figure 4. Spectra of the 1,8-naphthosultam (1a) in aqueous solutions of various pH values. A clear isosbestic point for the interconversion of the acid and the anion is visible in the spectra. The solutions used are as follows: carbonate buffer, pH 10.8 (1), pH 9.3 (2); phosphate buffer, pH 7.9 (3), pH 7.1 (4), pH 6.7 (5), pH 6.4 (6), pH 5.9 (7); acetate buffer, pH 5.6 (8), pH 5.2 (9), pH 4.9 (10), pH 4.0 (11).

the excited state are shown in Scheme I. The symbols used are as follows: GH = ground-state neutral sultam, G^- = ground-state anion, EH = excited-state neutral sultam, E^- = excited-state anion, r = subscript for radiative rate constants, nr = subscript for the nonradiative rate constants, i.e., $k_{r,EH}$, k_{r,E^-} , $k_{nr,EH}$, k_{nr,E^-} , the radiative and nonradiative rate constants for the excited-state neutral and anionic species, respectively, k_1 is the pseudo-firstorder rate constant of deprotonation, and k_2 is the bimolecular rate constant for reprotonation.

The ground-state pK_a is 6.2 (determined spectrophotometrically, cf. Figure 4), moderately high for a sulfonamide. The change in the pK_a resulting from the absorption of a photon can be estimated from a Förster cycle¹⁶ (for limitations of the approach^{17,18}). The average of the absorption and fluorescence maxima was used to estimate the transition energies, yielding a pK_* value of -3.0, the system resembling thereby a large group of aromatic phenols or protonated amines for which the pK_a^* is as much as -7 different from the p K_a .¹⁹ The p K_a * obtained by using the Förster cycle is similar to that obtained by fluorimetric titration ($pK_a^* = -2.9$), and, as expected for a strong acid, the anion is also formed in organic solvents like ethanol and methanol.

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The equilibrium position for acid dissociation depends on the strength of the acid and the basicity of the solvent. Strong acids $(pK_a^* < 0)$ dissociate in protic solvents such as alcohols as shown by Urban and Weller²⁰ for 4-aminopyrene. The effect of the alcohol (through solvent viscosity, solvent relaxation, or solvent molecular rotation) on the proton-transfer reaction is seen in the relative importance of the acid (EH) and anion (E⁻) emissions in various solvents: 1,2-ethanediol (mainly E⁻) and in 1,3propanediol or in glycerol (mainly EH).

Acid dissociation of 1,8-naphthosultam in 1,2-ethanediol occurs from the vibrationally relaxed S_1 state, as shown by the lack of excitation wavelength dependence of the emission maximum. Urban and Weller²⁰ have suggested a relationship between the proton-transfer rate and dielectric relaxation time of the solvent. The rate constant (k_1) for proton transfer from 1,8-naphthosultam to water is very high and is estimated to be $>5 \times 10^{10}$ s⁻¹ from the rate of appearance of the anion emission, observed by picosecond techniques. This rate constant is even higher than the deprotonation rate constants reported for 2naphthol-3,6-disulfonate and 8-hydroxy-1,3,6-pyrenetrisulfonate in water, $^{21} 2 \times 10^{10}$ and 1×10^{10} s⁻¹, respectively, thought to be the highest rates yet measured for proton transfer in water. Intramolecular proton transfer in methyl salicylate²² and substituted triazines²³ can occur on the picosecond time scale. The high proton-transfer rate in water and the ease of proton dissociation in different alcohols suggest that the sultam might be a convenient compound for studies of the dynamics of proton transfer in different solvents.

In conclusion, we have shown that the emission from 1,8-naphthosultam is composed of two bands, one for the neutral species, the acid, and the second for the conjugate base, the anion. The 1,8-naphthosultam is a weak acid in the ground state and a rather strong acid in the excited state.

Experimental Section

Syntheses. 1,8-Naphthosultam (1a) (2*H*-naphth[1,8cd]isothiazole 1,1-dioxide) was prepared from 8-amino-1naphthalenesulfonic acid by treatment with POCl₃ (Dannerth²⁴) and recrystallized from benzene, mp 177 °C (lit.²⁴ 178 °C).

Treatment of 1a with NaOH/ethanol yields a precipitate of the sodium salt of 1,8-naphthosultam (Na⁺2), mp >280 °C.

Solutions of the sodium salt of 2 in 0.1 N NaOH were refluxed with 30 equiv of methyl or ethyl iodide (two phases) for 2 days, and the reaction mixtures were extracted with chloroform. The residue remaining after evaporation of the chloroform was chromatographed on alumina (eluant: chloroform). The products were crystallized from methanol, yielding the N-methyl-1,8naphthosultam (1b), mp 123 °C (lit.²⁴ 125 °C), and Nethyl-1,8-naphthosultam (1c), mp 83 °C (lit.²⁴ 85 °C). TLC showed only one spot for each derivative (1a-c): ¹H NMR, 1a (Me₂SO- d_6), δ 11.35 (broad s, removed with D₂O), 6.90-8.30 (m); 1b (CDCl₃), δ 3.35 (s, 3 H), 6.6-8.2 (m, 6 H); 1c (CDCl₃), δ 1.50 (t, 3 H), 3.90 (q, 2 H), 6.6–8.1 (m, 6 H); UV, 1a (dioxane), 335 nm (ϵ 3300), 255 (10000); 1b (dioxane), λ_{max} 342 nm (ϵ 2800), 245 (13000); Na⁺2 (H₂O), λ_{max} 375 nm (ϵ 2900), 338 (2300), 265 (10300), 245 (13100).

The solvents used were spectroquality (Merck-Darmstadt or Fluka). Dioxane-water solutions were prepared as previously described.⁸

Fluorescence Titration. The acidity (H_0) of sulfuric acid solutions (dilution of a known weight of standardized concentrated sulfuric acid with known weight of tripledistilled water) was taken from the reported values.²⁵ Acid solutions covered the H_0 range of -0.5 to -7.0 (10-80%sulfuric acid) with intervals of $0.5 H_0$ units. A solution of 1a in methanol (0.01 mL) was mixed with 3 mL of a sulfuric acid solution (final concentration of 10^{-5} M), and emission spectra of these solutions were recorded. The ratios of the long to the short wavelength emission intensities (600 and 480 nm) were plotted against H_0 .

Absorption Titration. Aliquots of 1a in methanol (6.21 mg/25 mL) (0.5 mL) were diluted with buffer solutions (24.5 mL) (final concentration, 2.4×10^{-4} M). Optical densities at 375 nm (Figure 4) were plotted against pH.

Instruments. A Cary Model 17 spectrophotometer (absorption spectra), a Hitachi-Perkin-Elmer MPF-4 spectrofluorimeter with a corrected spectra attachment, and a digital integrator were used. Quantum yields were determined by using quinine sulfate in 0.1 N H₂SO₄ as the reference standard ($\phi_{\rm F} = 0.55$).

The system used for fluorescence lifetimes in the picosecond domain has been previously described.²¹ Fluorescence lifetimes were measured by using the single-photon system used previously^{8e} or by following the decay rate of molecules excited by a 1-ns pulsed nitrogen laser.^{8f}

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