J. Phys. Chem. A 2006, 110, 7375−7385

Two-Photon Photosensitized Production of Singlet Oxygen: Optical and Optoacoustic Characterization of Absolute Two-Photon Absorption Cross Sections for Standard Sensitizers in Different Solvents

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Received: February 16, 2006

Singlet molecular oxygen, $O_2(a^1\Delta_g)$, can be produced upon resonant two-photon excitation of a photosensitizer. In the present study, two molecules that have received recent attention in studies of nonlinear organic materials were characterized for use as standard two-photon sensitizers: 2,5-dicyano-1,4-bis(2-(4-diphenylaminophenyl)-vinyl)-benzene, CNPhVB, and 2,5-dibromo-1,4-bis(2-(4-diphenylaminophenyl)vinyl)-benzene, BrPhVB. Absolute two-photon absorption cross sections, δ, were independently determined for these molecules using two techniques that have heretofore not been applied to this problem: an optical technique (time-resolved detection of $O_2(a^1\Delta_g)$ phosphorescence) and a nonoptical technique (a time-resolved laser-induced optoacoustic experiment). For experiments performed in toluene, a solvent commonly used for such nonlinear optical studies, appreciable absorption by the solvent itself complicates the measurements. In cyclohexane, however, δ values could be obtained without the interfering effects of solvent absorption. On the basis of these results, we discuss key aspects of the respective techniques used to quantify values of δ. The information reported herein provides some explanation for the lack of consensus that is routinely observed in published values of δ, certainly for experiments performed in aromatic solvents such as toluene and benzene.

Introduction

In recent reports, it has been established that singlet molecular oxygen, $O_2(a^1\Delta_g)$, can be produced upon resonant, two-photon excitation of a photosensitizer.[1−5] In this process, a sensitizer excited state, S_n, is populated as a consequence of the simultaneous absorption of two photons (Figure 1). The transition proceeds via a virtual state, $S_0 \rightarrow S_{vir} \rightarrow S_n$ and, for centrosymmetric molecules, follows selection rules that differ from those for a one-photon transition.[6,7] As such, the state initially populated in a two-photon process is different from that initially populated upon one-photon excitation. Irrespective of the excitation method and which state is populated first, however, we make the reasonable assumption that rapid relaxation will ensue and that all subsequent photophysics and photochemistry originate from one common state: the vibrationally relaxed, lowest excited singlet state, S_1.[8]

Although $O_2(a^1\Delta_g)$ can be produced upon quenching of S_1 by $O_2(X^3\Sigma_g^-)$,[9,10] the S_1 lifetime for most molecules is generally so short as to render this bimolecular process improbable. Rather, $O_2(a^1\Delta_g)$ is more efficiently produced upon $O_2(X^3\Sigma_g^-)$ quenching of the longer-lived sensitizer triplet state formed upon intersystem crossing, $S_1 \rightarrow T_1$ (Figure 1).

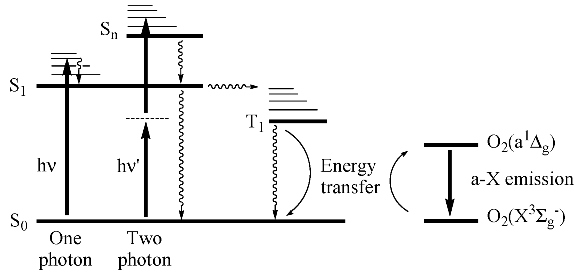

Figure 1. State diagram illustrating the triplet-sensitized production of singlet oxygen in both one- and two-photon excitation schemes.

The two-photon absorption process is inherently improbable and the number of sensitizer excited states produced is generally small, certainly in comparison to sensitizer excitation in a one-photon process. Nevertheless, we have established that, upon two-photon excitation of a sensitizer, the $O_2(a^1\Delta_g)$ produced can still be optically detected via its weak $O_2(a^1\Delta_g) \rightarrow O_2(X^3\Sigma_g^-)$ phosphorescence at ∼1270 nm in time-resolved experiments.[1−3] This result can have significant ramifications, certainly with respect to $O_2(a^1\Delta_g)$ imaging experiments.[11]

A great deal of recent activity has focused on the two-photon excitation of comparatively large organic molecules dissolved in a solvent.[3−5,12−15] Much of this work has been driven by reports of extraordinarily large values for the two-photon absorption cross section, δ.[5b,12,16−19] In this regard, significant efforts are currently being expended to determine values of δ for a plethora of molecules which, in turn, has provided unique challenges for both the experimental as well as computational communities.

Currently, most attempts to experimentally quantify δ rely on the detection of fluorescence as a measure of excited-state production.[19,20] Although such studies can be performed to directly yield an absolute δ value,[21] they are generally performed to yield a value relative to that of a chosen standard.[12,19] Methods

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10.1021/jp0609986 CCC: $33.50

based on monitoring the extent of light transmitted through the sample are also used (e.g., the z-scan technique).[22] We note, however, that any experimental method used to quantify δ is subject to many variables which, in turn, compounds sources of error.[21−25] Thus, it is not surprising that δ values obtained for a given molecule can vary significantly, even for reports from one research group. Nevertheless, as the community becomes more aware of likely pitfalls, inconsistencies in the published data will undoubtedly decrease. The introduction of new methods to quantify δ will likewise play a key role.

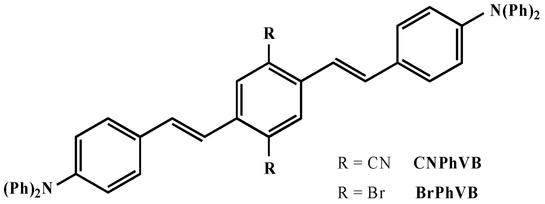
For a molecule that can produce $O_2(a^1\Delta_g)$ in a photosensitized process, the detection of the time-resolved near-IR phosphorescence of $O_2(a^1\Delta_g)$ provides one alternative method by which both relative and absolute values of δ can be determined. In this approach, it is only necessary to know the quantum yield of $O_2(a^1\Delta_g)$ production, Φ_Δ, for the molecule, and this parameter is easily obtained with reasonable accuracy in a one-photon experiment performed against a luminescence standard.[26]

The $O_2(a^1\Delta_g)$ approach has several distinct advantages, certainly in comparison to methods based on the detection of sample fluorescence. One advantage is that the spectral profile of $O_2(a^1\Delta_g)$ phosphorescence does not vary as the sample under study (i.e., the sensitizer) is changed. Specifically, $O_2(a^1\Delta_g)$ has a discrete and narrow emission band centered at ~1270 nm.[27,28] It is thus straightforward to consistently collect emitted light over the entire spectral profile of the probe and to avoid problems of reabsorption that may influence fluorescence studies of molecules with small Stokes shifts (i.e., the inner filter effect). Second, and perhaps most importantly, under all conditions of any practical importance, the solvent-dependent lifetime of singlet oxygen, τ_Δ, will fall in the range ~0.5 to 100 μs.[29] Thus, τ_Δ is sufficiently long that it is easy to temporally discriminate between the signal of interest (i.e., $O_2(a^1\Delta_g)$ phosphorescence) and undesired sources of light that may also be incident on the detector (e.g., scattered laser light). Such temporal discrimination is often difficult to achieve in a fluorescence experiment where lifetimes of the emitting state are typically less than ~5 ns. A final advantage of the $O_2(a^1\Delta_g)$ approach is that experiments performed in different solvents can be compared to each other simply because the effect of solvent on the photophysical properties of $O_2(a^1\Delta_g)$ is now well established.[10,30]

In contrast to optical probes of excited-state production (e.g., $O_2(a^1\Delta_g)$ phosphorescence, fluorescence,[21] the z-scan technique[22]), methods based on nonradiative excited-state decay can provide a unique approach by which to quantify δ. Such an approach would certainly complement optical methods, and may likely be the preferred experimental technique for molecules that do not emit light in appreciable yield. It is well established that laser-induced optoacoustic spectroscopy (LIOAS) can be used to accurately quantify excited-state yields.[31] Indeed, this method has been used to determine values of δ in neat liquids[32] and organic crystals,[33] and to quantify the comparatively weak three-photon absorption cross section in thallium halide crystals.[34]

In the present work, we set out to examine two centrosymmetric molecules that have received recent attention in the study of nonlinear optical materials: 2,5-dicyano-1,4-bis(2-(4-diphenylaminophenyl)vinyl)-benzene, CNPhVB, and 2,5-dibromo-1,4-bis(2-(4-diphenyl-aminophenyl)vinyl)-benzene, BrPhVB (Chart 1). Although originally designed for fluorescence experiments,[12] these molecules are not only $O_2(a^1\Delta_g)$ photosensitizers but they also have an appreciable component of nonradiative decay that gives rise to a LIOAS signal. As such, we were particularly interested in characterizing them for use as two-photon standards, at least for $O_2(a^1\Delta_g)$ experiments. For this work, we opted to develop and use two techniques that have heretofore not been applied to characterize the nonlinear properties of a solvated system: a time-resolved $O_2(a^1\Delta_g)$ phosphorescence experiment and a time-resolved LIOAS experiment.

CHART 1



Experimental Section

Femtosecond (fs) Experiments. In attempts to obtain two-photon absorption spectra and values of δ, the accuracy of the data depends critically on how the given experiment is performed and on the characteristics of the excitation source.[21−25] Thus, to establish the credibility of our results, a reasonable amount of instrumental detail must be provided.

Lasers. The heart of our system is a Ti:sapphire laser (Spectra Physics, Tsunami 3941) pumped by a Spectra Physics Millenia Vs Nd:VO_4 laser. The Tsunami operates at a repetition rate of 80 MHz, and can be tuned over the range ~725 to 910 nm. The output of the Tsunami can be amplified (Spectra Physics Spitfire pumped by a Spectra Physics Evolution Nd:YLF laser). Although the process of amplification reduces the range of tunable wavelengths that can be accessed to ~765 to 845 nm, it has the desirable feature of reducing the pulse repetition rate to 1 kHz, or lower. This is important for the time-resolved detection of $O_2(a^1\Delta_g)$ which, under most circumstances of interest, has a lifetime, τ_Δ, in the microsecond domain [i.e., $\tau_\Delta < (1\ \text{kHz})^{-1}$].

The intensity of the laser beam incident on the sample was adjusted by rotating the polarization of the beam with a half-wave plate (Thorlabs model WPH05M-830) and then passing the resultant beam through a fixed polarized optic (Thorlabs model GT-10B Glan-Taylor Polarizer). For the experiments in which the laser output was frequency-doubled, the β-barium borate (BBO) doubling crystal and associated filters were placed after the Glan-Taylor polarizer in the optical path. In some cases, calibrated neutral density filters were added to further reduce the intensity of the beam. Laser powers were measured using a FieldMax-TO digital power meter (Coherent) with a NIST-traceable, calibrated detection head (PS19Q, Molectron) with a specified accuracy of $\leq$1%. Finally, we accounted for the transmittance of the front window of the sample cuvette, thus giving an accurate measure of the power actually incident on the sample.

Spatial Profile of the Laser Beam. Samples were irradiated using a beam that had been focused and then recollimated using two 12 in. lenses. Thus, throughout the sample, the beam diameter was constant, and the volume irradiated was cylindrical.

The spatial profile of the laser beam intensity at the sample was characterized by translating the edge of a razor blade through the beam and monitoring the resultant change in the total beam intensity with a photodiode or a power meter. The details of this procedure and representative data have been published.[3] As outlined in the Supporting Information, these data are used to obtain the so-called spatial coherence factor, g_S.

When determining δ values for CNPhVB and BrPhVB in the $O_2(a^1\Delta_g)$ phosphorescence experiments, the laser beam had a Gaussian waist of 474 ± 11 μm. At a repetition rate of 1 kHz, the incident energy was varied over the ranges 0.8−4.1 μJ/pulse at 400 nm and 14.7−25.9 μJ/pulse at 800 nm.

In the LIOAS experiments, the collimated beam incident on the cuvette had a Gaussian waist of 540 ± 15 μm. Laser energies varied over the ranges 0.5−4.0 μJ/pulse at 400 nm and 10−40 μJ/pulse at 800 nm, both at a 1 kHz repetition rate. Thus, average and peak intensities (the latter typically ~10 GW/cm^2) are similar in the two approaches.

Temporal Profile of the Laser Beam. The temporal profile of our laser beams was characterized using a home-built background-free autocorrelator. The details of this procedure and the pertinent data have likewise been published.[3] As outlined in the Supporting Information, these data are used to obtain the so-called temporal coherence factor, g_T.

Optical Signal Collection and Processing. For the optical experiments, the sample was contained in a 1 cm path length cuvette mounted in a light-tight housing with a small entrance hole for the laser beam. Luminescence from the sample was collected and collimated using a 2.5 cm focal length lens. The collection efficiency was enhanced by placing a parabolic mirror on the backside of the cuvette. The light detected was spectrally isolated with interference filters and was focused with a second lens onto the active area of a photomultiplier tube, PMT (Hamamatsu model R5509-42, operated at −80 °C, rise time of 3 ns). Because the spectral response of the PMT covers the range ~400 to 1500 nm, both $O_2(a^1\Delta_g)$ phosphorescence and sensitizer luminescence could be readily monitored by using different interference filters. The output of the PMT was amplified (Stanford Research Systems model 445 preamplifier) and sent to a photon counter (Stanford Research Systems model 400), operated using a program written in LabView (National Instruments, Inc.).

In the $O_2(a^1\Delta_g)$ phosphorescence intensity experiments used to quantify δ, the width of the photon-counter sampling window was adjusted to encompass the most intense portion of the time-resolved $O_2(a^1\Delta_g)$ profile, thus maximizing the signal-to-noise ratio. A second sampling window of the same width, but temporally displaced by 500 μs to ensure complete decay of the $O_2(a^1\Delta_g)$ phosphorescence, measured the background signal. The latter was then subtracted from the $O_2(a^1\Delta_g)$ data to yield a corrected intensity signal.[35] For a given intensity measurement, data from 10 000 laser pulses were recorded. Results from 8 such measurements were averaged to yield the number reported.

In the time-resolved $O_2(a^1\Delta_g)$ experiments, the sampling period was reduced to 100 ns and counts were accumulated as the signal sampling window was successively delayed relative to the laser pulse. For all experiments, the lifetime of the $O_2(a^1\Delta_g)$ produced was consistent with that expected (e.g., $\tau_\Delta = 29$ μs in toluene and $\tau_\Delta = 23$ μs in cyclohexane).[29]

LIOAS Signal Collection and Processing. For LIOAS detection, a home-built cell holder for a regular 1 cm quartz cuvette was used. The transducer was clamped to the side of the cuvette using a small amount of vacuum grease for better acoustic coupling.[36] Time-resolved LIOAS signals were detected using either a home-built PZT ceramic piezoelectric transducer or a commercially available transducer (Panametrics, A103S) with matched preamplifier (Panametrics 5670). The waveforms detected were amplified, averaged 500 times, and stored (Tektronix TDS754A digital oscilloscope). As in the optical experiments described above, samples were irradiated using the well-characterized output of our fs laser system.

Nanosecond (ns) Experiments. Quantum yields of $O_2(a^1\Delta_g)$ production, Φ_Δ, were obtained using techniques and instrumentation described elsewhere.[37,38] Experiments were performed by comparing the magnitude of the integrated time-resolved $O_2(a^1\Delta_g)$ phosphorescence signal produced upon one-photon irradiation of the sensitizer to that obtained upon one-photon irradiation of a standard sensitizer (phenalenone with $\Phi_\Delta = 1.00 \pm 0.05$).[39]

In the LIOAS experiments, fractions of prompt heat release, α, were measured using the same ns laser system. Data were quantified by comparing the peak-to-peak amplitude of the signal (Figure 4) to that of a calorimetric reference, 2-hydroxybenzophenone (2-HBP), which releases all its excitation energy as prompt heat (i.e., $\alpha = 1$).[40] Subsequent analysis of the recorded LIOAS waveforms was performed using a commercially available deconvolution routine (Sound Analysis 1.50D, Quantum Northwest).[41]

Details of the instrumentation and approach used for the time-resolved absorption measurements are likewise published elsewhere.[4b,37]

Materials. The approach used to synthesize and purify CNPhVB and BrPhVB has been published elsewhere.[1,19] The data reported herein were collected under conditions in which there was no photodegradation of the sensitizers. 2-Hydroxybenzophenone (2-HBP, Aldrich, 99%) was used as received. All solvents were purchased from Aldrich (spectroscopic grade) and were also used as received.

Results and Discussion

A. Optical Experiments. *Absolute Two-Photon Absorption Cross Section, δ.* The intensity of $O_2(a^1\Delta_g)$ phosphorescence produced upon fs two-photon excitation of a sensitizer was compared to the intensity of $O_2(a^1\Delta_g)$ phosphorescence produced upon fs one-photon excitation of the same sensitizer.

Although the initial state populated upon two-photon excitation may differ from that populated upon one-photon excitation, both processes should ultimately result in the creation of the lowest excited singlet state, S_1, via internal conversion (Figure 1). This is a reasonable assumption for this type of molecule. Subsequent events such as fluorescence, intersystem crossing, and, most importantly, the production of $O_2(a^1\Delta_g)$ will then be independent of whether one- or two-photon excitation was used. Thus, by monitoring the relative intensities of $O_2(a^1\Delta_g)$ phosphorescence from these respective processes and by knowing exactly how many photons were absorbed in the linear one-photon process, one can determine the number of photons absorbed in the nonlinear two-photon process and, in turn, quantify δ.

Although the general treatment for light absorption outlined below will presently be used in the context of a $O_2(a^1\Delta_g)$ phosphorescence experiment, it is equally applicable to LIOAS and fluorescence experiments. The only caveat is that the excitation beams used in the one- and two-photon cases must be spatially equivalent so that the origin of the signal collected (i.e., light or acoustic wave) will be identical.

The number of excited states initially produced upon light absorption in the one-photon process, N_1, is given by

$$N_1 = \frac{P_1 \lambda_1}{fhc}(1 - 10^{-A}) \qquad (1)$$

where P_1 is the average power of the laser used to irradiate the system at the wavelength λ_1, f is the laser repetition rate, h is

Planck's constant, c is the speed of light, and A is the sample absorbance at λ_1.

From Appendix 1 (Supporting Information), the number of excited states initially produced upon two-photon excitation, N_2, is

$$N_2 = \frac{\delta P_2^{\,2} \lambda_2^{\,2} C}{2 f^2 h^2 c^2} g_T g_S \tag{2}$$

where P_2 is the average power of the excitation laser at the irradiation wavelength λ_2, C is the sensitizer concentration, and g_T and g_S are the temporal and spatial coherence factors for the irradiating laser beam, respectively. From eq 1 and eq 2, an expression for the two-photon absorption cross section at the wavelength λ_2, δ, is easily obtained.

Quantum yields of $O_2(a^1\Delta_g)$ production, Φ_Δ, for both BrPhVB and CNPhVB are appreciable, but not particularly large. In toluene, $\Phi_\Delta(\mathrm{BrPhVB}) = 0.46 \pm 0.05$ and $\Phi_\Delta(\mathrm{CNPhVB}) = 0.11 \pm 0.02$ and, in cyclohexane, $\Phi_\Delta(\mathrm{BrPhVB}) = 0.37 \pm 0.05$ and $\Phi_\Delta(\mathrm{CNPhVB}) = 0.06 \pm 0.01$. Most importantly, these molecules generate a measurable two-photon sensitized $O_2(a^1\Delta_g)$ phosphorescence signal upon irradiation at 800 nm.[1] Moreover, they also generate a measurable one-photon sensitized $O_2(a^1\Delta_g)$ phosphorescence signal upon irradiation at 400 nm, a wavelength readily obtained by frequency-doubling the 800 nm beam used to pump the two-photon transition.

Cyclohexane as Solvent. Cyclohexane solutions of BrPhVB and CNPhVB were irradiated at 800 nm using a fs laser for which the temporal and spatial coherence factors had been determined. The intensities of the $O_2(a^1\Delta_g)$ emission signals observed scaled quadratically with an increase in the power used to irradiate the sample (Figure 2b), as expected for a two-photon excitation process.

In a separate experiment, the 800 nm beam used in the two-photon experiment was directed into a BBO crystal to generate 400 nm light. Filters were subsequently used to eliminate wavelengths other than the desired 400 nm light and to attenuate the power. It is important to note that these manipulations did not alter the spatial properties of the beam. Thus, we were able to irradiate samples under one-photon conditions with a beam that had the same spatial profile as the beam used for the two-photon experiment, and the collection efficiency of $O_2(a^1\Delta_g)$ phosphorescence was identical in the one- and two-photon cases. Any subtle optics-induced changes that may have occurred in the temporal profile of the beam will not influence the one-photon transition. For the one-photon experiments, samples were prepared to have an absorbance at λ_1 of ≤ 0.3 to ensure negligible depletion of the beam in the 1 cm cuvette. Thus, the excitation profile through the cuvette was similar to that in the two-photon experiments. The intensities of the $O_2(a^1\Delta_g)$ signals observed upon 400 nm irradiation scaled linearly with an increase in the laser power used to irradiate the sample (Figure 2a), as expected for a one-photon excitation process.

By comparing the intensities of the $O_2(a^1\Delta_g)$ phosphorescence signals produced upon one- and two-photon excitation, and through the use of eqs 1 and 2, the following two-photon absorption cross sections were obtained in cyclohexane at 800 nm: $\delta(\mathrm{BrPhVB}) = 460 \pm 70$ GM and $\delta(\mathrm{CNPhVB}) = 1090 \pm 165$ GM (1 GM $= 10^{-50}$ cm^4 s photon^{-1} molecule^{-1}, see Supporting Information).

Toluene as Solvent. Toluene has been the solvent of choice for many previous studies of both absolute and relative δ values.[12,19,42,43] Under our experimental conditions, we observed that neat toluene absorbs light at 400 nm in a process that scales quadratically with the incident laser power.[44] Moreover, the light thus absorbed results in the production of $O_2(a^1\Delta_g)$ which is easily detected with our instrumentation (Figure 3). A single-exponential fit to the time-resolved phosphorescence decay trace recorded upon 400 nm irradiation of neat toluene yielded a lifetime of 28.7 ± 0.3 μs, in excellent agreement with the established value of τ_Δ in toluene.[29,45] With neat cyclohexane, however, a $O_2(a^1\Delta_g)$ signal could not be observed upon irradiation under the same conditions (Figure 3).

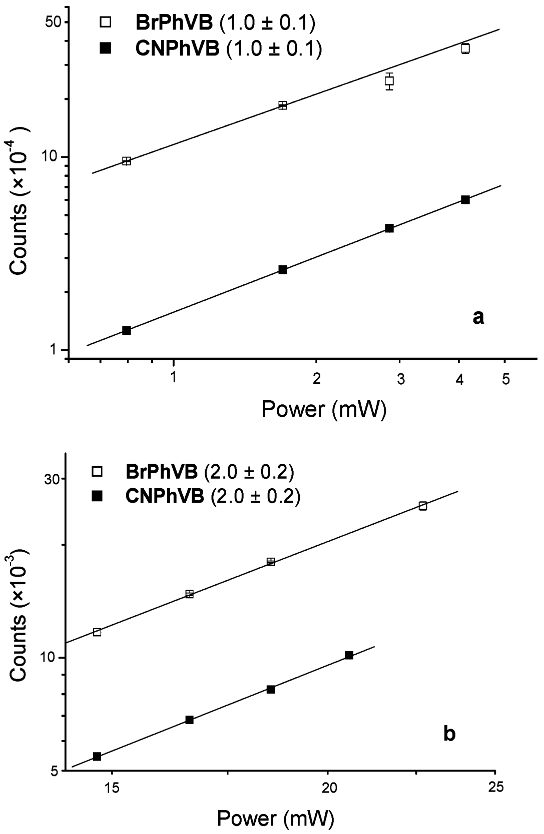


Figure 2. Representative double logarithmic plots of the $O_2(a^1\Delta_g)$ phosphorescence intensities against the incident fs laser power for irradiation of BrPhVB and CNPhVB in cyclohexane at both 400 (panel a) and 800 nm (panel b). The numbers shown in parentheses reflect average values of the slopes obtained from several independent experiments, and the errors reflect the standard deviation. For a given experiment, the error on a given data point is generally incorporated within the symbol in the plot. There was no signal observed from the neat solvent at either wavelength.

As clearly seen in Figure 3, for a given irradiation power, the magnitude of the $O_2(a^1\Delta_g)$ phosphorescence signal observed upon 400 nm irradiation of neat toluene is approximately half that obtained upon 400 nm irradiation of CNPhVB in toluene. For this reason, we opted not to proceed any further with the determination of δ values for CNPhVB and BrPhVB in toluene with this technique.

Other Solvents. Identical experiments, as described above, performed with two other neat aromatic solvents, benzene and *p*-xylene, yielded similar results to those in toluene. Specifically, upon 400 nm irradiation of neat benzene and *p*-xylene, $O_2(a^1\Delta_g)$ phosphorescence signals were observed whose intensity scaled quadratically with an increase in laser power. The time-resolved signals obtained decayed single-exponentially with lifetimes of 31.6 ± 2.6 and 19.4 ± 0.3 μs in benzene and *p*-xylene, respectively. These values are likewise in excellent agreement with the literature values for τ_Δ in these solvents.[29]

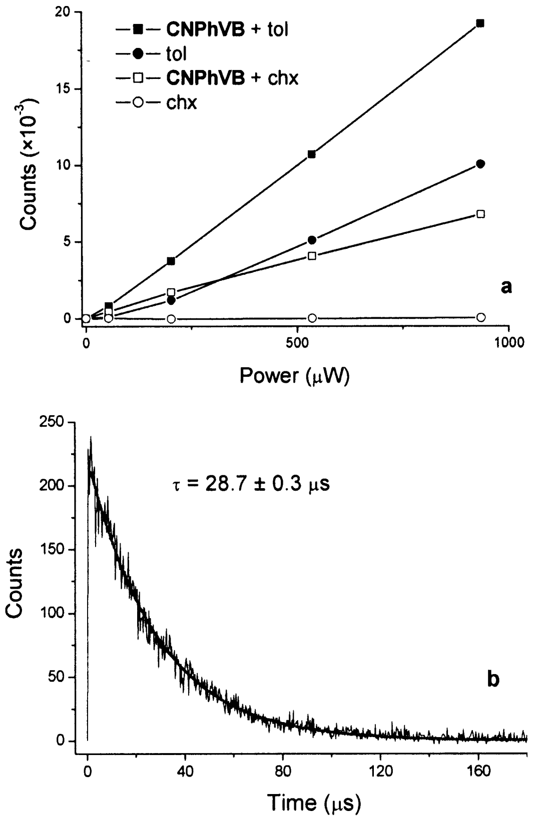


Figure 3. (a) Plots of the $O_2(a^1\Delta_g)$ phosphorescence intensity against the incident laser power for irradiation at 400 nm with a fs laser: tol = toluene and chx = cyclohexane; (b) time-resolved decay of the signal observed upon irradiation of neat toluene at 400 nm.

The data in Figure 3 also show that upon irradiation of neat cyclohexane at 400 nm, no $O_2(a^1\Delta_g)$ emission signal was observed for irradiation powers up to ~1 mW. When neat tetrahydrofuran was irradiated at 400 nm, a $O_2(a^1\Delta_g)$ signal was likewise not observed.

The $O_2(a^1\Delta_g)$ phosphorescence signal observed upon irradiation of the neat solvent at 400 nm appears to arise as a consequence of two-photon absorption by the solvent itself, followed by energy transfer from an excited-state solvent molecule to ground-state oxygen.[44] The data do not appear to reflect the phenomenon in which light is absorbed by a weakly bound contact complex between a solvent molecule and oxygen to produce the oxygen-organic molecule charge-transfer state; a process known to likewise result in the production of $O_2(a^1\Delta_g)$.[46-48] Upon irradiation into the oxygen-organic molecule charge-transfer absorption band, the $O_2(a^1\Delta_g)$ emission signal scales linearly with the irradiation power.[46-48]

In summary, considering the peak intensities used in these fs pulsed experiments, one must clearly exercise caution when using this particular approach to quantify values of δ for organic molecules dissolved in certain aromatic solvents.

B. LIOAS Experiments. In a time-resolved LIOAS experiment performed against a calorimetric reference, one can accurately quantify the amount of heat released by a given compound as a consequence of nonradiative excited-state decay.[31] With particular reference to our photosystem (Figure 1), one obtains the fraction, α, of heat promptly released by a given compound. Such "prompt" heat is distinguished from heat released over longer periods within the time window of experimental observation (i.e., "slow" heat), or heat stored by the system for periods longer than the experiment time window.[31]

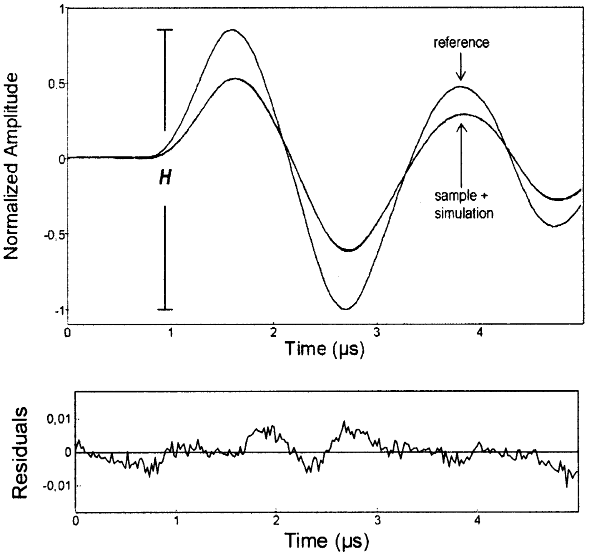


Figure 4. (top) LIOAS signals obtained after 355 nm ns laser irradiation of BrPhVB and of 2-HBP in toluene. Superimposed on, and indistinguishable from, the signal from BrPhVB is a fitted waveform obtained by convoluting the signal for 2-HBP with a sum of two exponential terms with time constants of 10 ns and 170 ns. (bottom) Residuals plot for the difference between the fitted and experimental data for BrPhVB. Data were recorded in air-saturated toluene, and the traces are an average of signals obtained after 100 independent laser pulses.

Prompt heat is attributed to heat released on time scales shorter than the effective acoustic transit time, τ_a. The latter is defined in the expression $\tau_a = d/v_a$, where d is the diameter of the laser beam, as determined by the Gaussian waist at $1/e$ of the intensity maximum, and v_a is the velocity of sound in the given medium.[31] In an independent experiment (see Supporting Information), we determined v_a in toluene and obtained a value identical to the accepted standard. For our spatial beam profiles, τ_a is approximately 0.41−0.65 μs. Thus, with reference to experiments performed in the presence of oxygen, prompt heat derives from S_n and T_n deactivation of the sensitizer,[49] whereas any $O_2(a^1\Delta_g)$ that is produced will store energy for a time period that is much longer.

Values of α can also be readily calculated using an expression derived from the law of energy conservation:

$$E_{laser}(1 - \alpha) = \Phi_f E_f + \Phi_\Delta E_\Delta \exp(-\tau_a/\tau_\Delta) \qquad (3)$$

where E_{laser} is the molar energy of the laser pulse, Φ_f is the quantum yield of fluorescence, E_f is the molar energy of the fluorescent state obtained from the band maximum of the fluorescence spectrum, and E_Δ is the molar energy content of $O_2(a^1\Delta_g)$, i.e., 94 kJ/mol.[50] Because $\tau_\Delta \gg \tau_a$ in our systems, the exponential function in eq 3 reduces to a value of ca. 1.0.

Absolute Two-Photon Absorption Cross Section, δ. In a LIOAS experiment (see representative data in Figure 4), the initial peak-to-peak amplitude of the acoustic signal, H, is given by

$$H = \kappa \alpha E_{abs} \qquad (4)$$

where κ is an instrumental constant that depends on the specific transducer and beam geometry used as well as on the thermoelastic properties of the solvent, and E_{abs} is the molar energy absorbed by the molecule from the incident laser pulse. E_{abs} can be equated to the number of excited states, N, initially produced upon light absorption. Thus, in a one-photon experiment, eq 5 holds,

$$H_1 = \kappa\alpha N_1 \tag{5}$$

and in a two-photon experiment, using the same spatial excitation profile, transducer and solvent, eq 6 holds,

$$H_2 = \kappa\alpha N_2 \tag{6}$$

where N_1 and N_2 are as shown in eqs 1 and 2, respectively. In this way, using a procedure that is totally analogous to that used in the $O_2(a^1\Delta_g)$ phosphorescence experiments, experimentally determined values of H_1 and H_2 afford absolute δ values.

A key aspect of using eqs 5 and 6 to determine δ is that the two-photon irradiation wavelength must be exactly twice the one-photon irradiation wavelength such that α is the same in the one- and two-photon experiments, and thus cancels when comparing signals. Moreover, we must ensure that the instrumental constant κ for the two-photon experiment (eq 6) is likewise identical to that for the one-photon experiment (eq 5). The most likely source for any differences in κ would be a wavelength-dependent change in the spatial profile of the laser beam that derives from the process of frequency doubling (i.e., 800 → 400 nm). By using the technique of translating a sharp edge through the laser beam,[3] however, we ascertained that the spatial profiles of the respective beams were identical within experimental error.

Moreover, for experiments performed in cyclohexane (vide infra), the LIOAS signal obtained from the one-photon experiment was similar to the signal obtained from the two-photon experiment when these signals were scaled to the same amplitude (Figure 5a). This indicates that all pertinent parameters, including the decay kinetics responsible for the fast heat release, are equivalent in these systems, and thus validate the cancellation of κ. For experiments in toluene, however, the similarity between the LIOAS signals from the one- and two-photon experiments is not quite as good (Figure 5b). These data likely reflect complications arising from solvent absorption as discussed previously with respect to our $O_2(a^1\Delta_g)$ experiments. We will return to this point again later.

By extension, it also follows from eqs 2 and 6 that, for a relative two-photon experiment in which LIOAS data from molecule A are compared to those from molecule B, eq 7 is obtained when the experiments are performed under identical conditions (i.e., identical spatial and temporal coherence factors, two-photon irradiation wavelength, solvent, sensitizer concentration, and laser power).

$$\frac{H_{2,B}\delta_A}{H_{2,A}\delta_B} = \frac{\alpha_B}{\alpha_A} \tag{7}$$

Cyclohexane as Solvent. Upon fs irradiation of BrPhVB and CNPhVB at 800 nm in aerated cyclohexane, the amplitudes of the LIOAS signals, H_2, increased quadratically with an increase in laser power indicating that we are indeed recording data after two-photon excitation. Upon irradiation at 400 nm, the corresponding LIOAS amplitudes, H_1, increased linearly with power which is consistent with one-photon excitation.

Just as observed in the $O_2(a^1\Delta_g)$ phosphorescence experiments (vide supra), the LIOAS data indicate that neat cyclohexane does not absorb light under the conditions of our experiments (i.e., irradiation of neat cyclohexane at either 400 or 800 nm does not give rise to a LIOAS signal). The data thus obtained in aerated cyclohexane yield absolute two-photon absorption cross sections for BrPhVB and CNPhVB at 800 nm of $\delta = 785 \pm 120$ and 1430 ± 215 GM, respectively. Identical results were obtained with the two different acoustic transducers used.

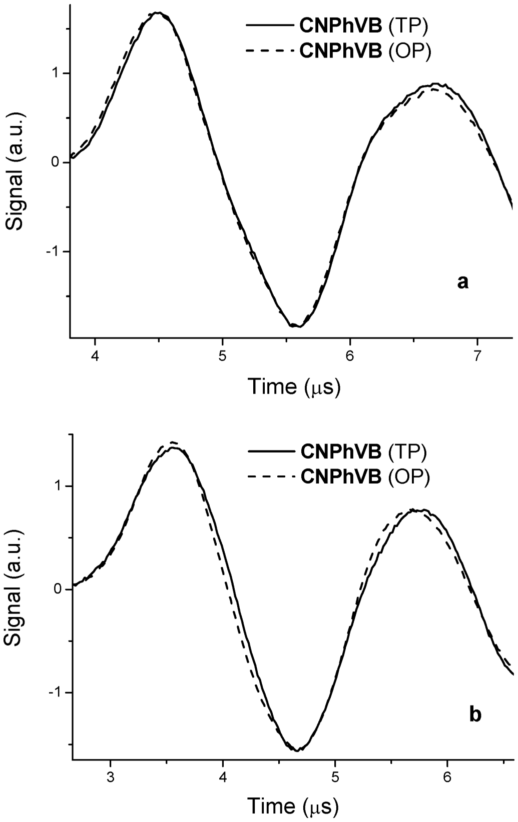


Figure 5. LIOAS signals from CNPhVB after fs laser irradiation in (a) cyclohexane and (b) toluene: OP = one-photon and TP = two-photon.

In an independent ns pulsed laser experiment with irradiation at 355 nm and using 2-HBP as the calorimetric reference ($\alpha = 1$),[40] we ascertained that, for BrPhVB and CNPhVB in cyclohexane, $\alpha_{355} = 0.55 \pm 0.02$ and 0.47 ± 0.02, respectively. These values of α were obtained by quantifying the magnitudes, relative to the standard, of the initial peak-to-peak amplitudes, H, in the acoustic waveforms (Figure 4). Using simple energy conservation in the form of

$$E_{400}(1 - \alpha_{400}) = E_{355}(1 - \alpha_{355}) \tag{8}$$

the α values obtained at 355 nm were then converted to values at 400 nm. For BrPhVB and CNPhVB this yields $\alpha_{400} = 0.49 \pm 0.02$ and $\alpha_{400} = 0.40 \pm 0.02$, respectively.

Under the reasonable assumption that α_{400}(one-photon) = α_{800}(two-photon), values of α_{400} obtained in a one-photon ns laser experiment can, in turn, be used to independently verify the δ values recorded in the corresponding two-photon fs experiment performed at 800 nm. Using eq 7 with δ values and photoacoustic amplitudes, H_2, recorded in the fs cyclohexane experiments, we obtain a ratio $\alpha_{CNPhVB}/\alpha_{BrPhVB} = 0.81 \pm 0.12$. This is in excellent agreement with the ratio independently obtained using the ns values of α_{400}, that is $\alpha_{CNPhVB}/\alpha_{BrPhVB} = 0.82 \pm 0.05$.

Toluene as Solvent. Upon fs irradiation of BrPhVB and CNPhVB at 800 nm in aerated toluene, the amplitudes of the LIOAS signals, H_2, increase quadratically with an increase in laser power indicating that we are recording data after two-photon excitation (Figure 6c,d). Upon irradiation at 400 nm, the corresponding LIOAS amplitudes, H_1, increase linearly with power which is consistent with one-photon excitation (Figure 6a, b).

Just as in the optical experiments described in the previous section, the LIOAS signal amplitudes also clearly show that

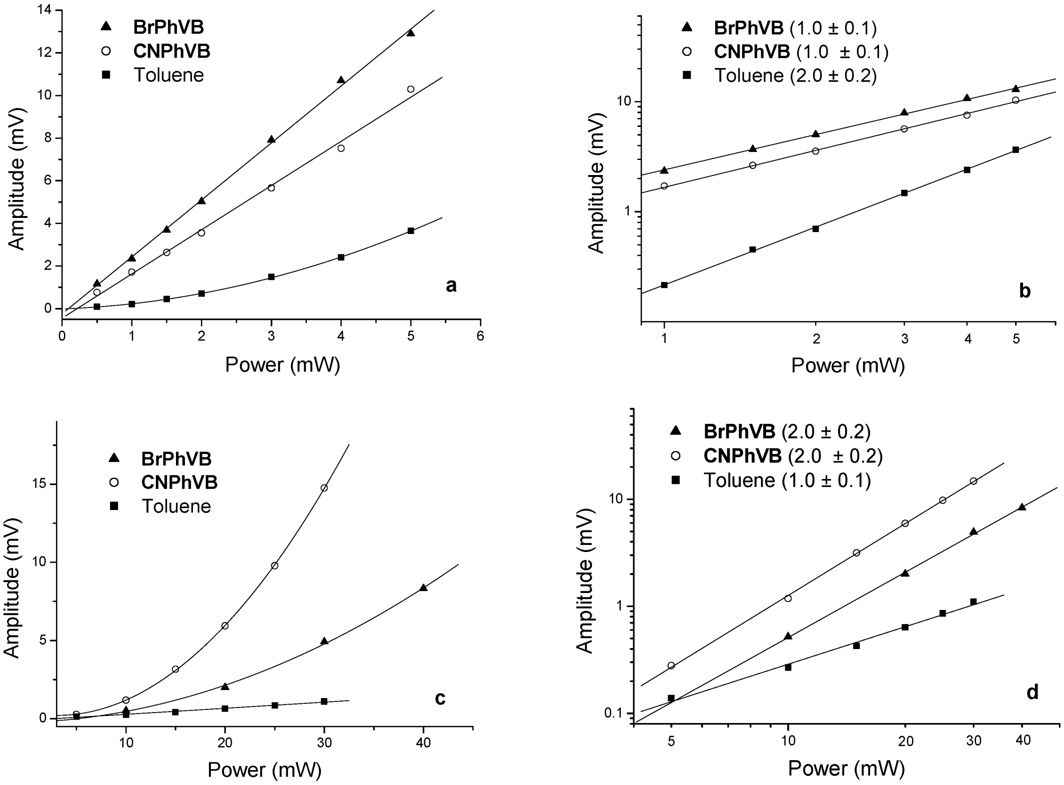


Figure 6. Plots of the LIOAS peak-to-peak amplitudes against the incident laser power for irradiation of BrPhVB and CNPhVB at both 400 nm (a and b) and 800 nm (c and d) in toluene. As with the data shown in Figure 2, the numbers in the parentheses reflect an average slope for the linear fit based on data recorded from several experiments. The errors reflect the standard deviation.

toluene plays a nonnegligible role in the process of light absorption (Figure 6). Upon fs irradiation of neat toluene at 400 nm, a LIOAS signal whose intensity increases quadratically with the incident laser power is observed. This phenomenon again likely reflects two-photon absorption to produce an excited electronic state of toluene.[44] Upon 800 nm fs irradiation of neat toluene, the intensity of the LIOAS signal increases linearly with incident laser power. It is likely that the latter data simply reflect one-photon absorption by vibrational overtones and combination bands in the system.[51,52] This absorption by the solvent itself will contribute in a nontrivial way to the observed LIOAS waveforms. On this basis, measured values of H_1 and H_2 (eqs 5 and 6) will likely reflect different values of α and, as such, cannot be directly compared.

Nevertheless, because the data in Figure 6 clearly show the contribution of the solvent to light absorption, we decided to correct the data for this competing absorption and thereby obtain values of δ for BrPhVB and CNPhVB in toluene that, presumably, would be reasonably accurate. In this regard, it should be apparent from the data in Figure 6 that it is advantageous to use results obtained at comparatively low irradiation powers for excitation at 400 nm, where the ratio of sensitizer-to-solvent signal amplitudes is high. Conversely, upon 800 nm irradiation, it is advantageous to use data obtained at comparatively high irradiation powers. Using results from these power regimes, we corrected for the solvent absorption by subtracting the amplitudes of the signals observed in the neat solvent from the amplitudes observed from the solutions containing the sensitizer. This approach is only reasonable when the contribution from the neat solvent is much smaller than the signal from the sensitizer.

These corrected data were then used, as described above, to obtain absolute two-photon absorption cross sections for BrPhVB and CNPhVB in toluene at 800 nm of $\delta = 990 \pm 150$ and 1365 ± 205 GM, respectively. Identical results were obtained with the two different acoustic transducers.

Once again, eq 7 can be used to independently check whether our corrections for solvent absorption yield accurate data. To proceed with this test, we therefore again need to independently obtain values of α_{400} from both BrPhVB and CNPhVB. In this regard, and with respect to our previous discussion about light absorption by neat toluene upon fs irradiation at 400 nm, we note that the experimental determinations of α_{355} are performed using ns laser pulses that have significantly smaller peak intensities than our fs laser pulses. Under our present conditions, air-saturated neat toluene does not absorb light upon 355 nm irradiation with ns pulses. With fs pulses that have higher peak intensities, however, nonlinear two-photon absorption by toluene becomes evident upon irradiation in this same wavelength domain.

Using the same approach as in cyclohexane, and with 2-HBP as a calorimetric reference, $\alpha_{355} = 0.59 \pm 0.02$ was experimentally obtained for BrPhVB in toluene. Using eq 3, a value of $\alpha_{355} = 0.58 \pm 0.03$ was independently calculated using the following parameters: $\Phi_f = 0.41 \pm 0.04$,[12] $E_f = 244.1 \pm 0.5$ kJ/mol, $\Phi_\Delta = 0.46 \pm 0.05$, and $E_\Delta = 94$ kJ/mol. In a third independent approach, we ascertained that BrPhVB in aerated toluene has a triplet lifetime of $\tau_T = 170 \pm 10$ ns. The latter was recorded in a time-resolved triplet absorption experiment. On this basis, the signal fitting in Figure 4 was performed using a sum of two exponential terms with fixed time constants of 10 ns (prompt heat delivery from S_n, T_n and S_1 deactivation) and 170 ns (T_1 deactivation). From the convolution routine,[41] $\alpha_{355} = 0.62 \pm 0.02$ was obtained, in good agreement with the two values found above. That these three independent values of α are equivalent provides reassuring verification of the various methods used. As before, eq 8 allows calculation of $\alpha_{400} = 0.54 \pm 0.02$ for BrPhVB in toluene.

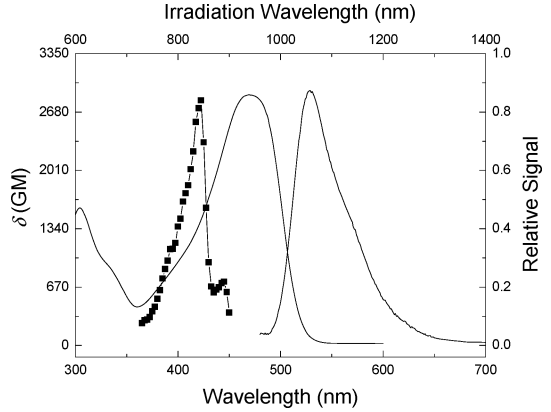


Figure 7. One-photon absorption and fluorescence spectra of CNPhVB in toluene (solid lines, bottom and right axes). The two-photon excitation spectrum of CNPhVB is also shown (■, top and left axes). The scale for δ was established using data from the LIOAS experiment.

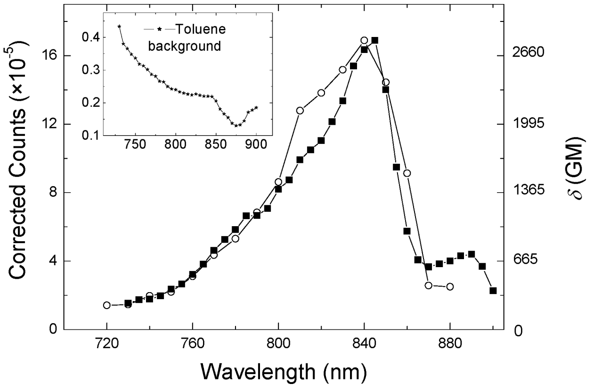


Figure 8. Two-photon fluorescence excitation spectrum of CNPhVB in toluene (relative accuracy of ±4% on each point). The background signal obtained from a CNPhVB-free solution of toluene is shown as an inset (*y*-axis in corrected counts). A spectrum reported by Pond et al.,[19] multiplied by an appropriate scaling factor, is shown with open circles (i.e., the δ axis refers only to our data, ■).

In a corresponding experiment with CNPhVB in aerated toluene, we determined that $\alpha_{355} = 0.43 \pm 0.02$. Using eq 3, a value for $\alpha_{355} = 0.39 \pm 0.04$ was independently calculated using the following parameters: $\Phi_f = 0.86 \pm 0.07$,[12] $E_f = 226.5 \pm 0.5$ kJ/mol, $\Phi_\Delta = 0.11 \pm 0.02$, and $E_\Delta = 94$ kJ/mol. These data yield $\alpha_{400} = 0.37 \pm 0.02$.

Thus, to ascertain whether our corrections for solvent absorption in the fs toluene experiments are valid, we use eq 7 along with the corrected LIOAS amplitudes, H_2, and corrected values of δ, to yield a ratio, $\alpha_{\mathrm{CNPhVB}}/\alpha_{\mathrm{BrPhVB}} = 0.76 \pm 0.12$. The corresponding ratio using the independently determined values of α_{400} is $\alpha_{\mathrm{CNPhVB}}/\alpha_{\mathrm{BrPhVB}} = 0.69 \pm 0.04$. Again note that this latter ratio reflects data obtained in a ns experiment where there was no absorption by neat toluene. The fact that the α-ratio obtained using the corrected fs data agrees with that obtained using the ns data suggests that our adjustments for solvent absorption are indeed reasonable. Note, however, that the agreement between these independently determined α-ratios is not as good as in the case of cyclohexane, where there was no complications arising from solvent absorption.

C. Excitation Spectra and Relative Cross Sections. Having determined an absolute δ value for a given molecule in a given solvent at a given wavelength, one can now use this compound as a standard to determine δ values for other molecules. When measuring relative signals against a standard at a given wavelength, problems related to the temporal and spatial profiles of the laser beam, so crucial for absolute measurements of nonlinear excitation, are now eliminated. On the other hand, for experiments performed over a range of wavelengths, (e.g., when recording excitation spectra), wavelength-dependent variations in both the spatial and temporal coherence factors must be considered. With this in mind, we set out to record two-photon excitation spectra of our compounds, correcting for wavelength-dependent variations in the excitation pulse.

CNPhVB. In toluene, CNPhVB has a one-photon absorption maximum at 470 nm, does not absorb light in a one-photon process at $\lambda > 530$ nm, and has a fluorescence $\lambda_{\max}$ at 529 nm (Figure 7). Upon irradiation of a 2×10^{-4} M solution of CNPhVB over the range 730−900 nm using the output of the Tsunami, CNPhVB fluorescence was observed in a single-photon-counting experiment. At all irradiation wavelengths, the signal intensity scaled quadratically with changes in the laser power demonstrating that the signal derives from two-photon excitation and could thus be used to record a two-photon excitation spectrum. The principal rationale to use fluorescence as a probe for CNPhVB in these experiments was that, with the comparatively short fluorescence lifetime, the output of the Tsunami at 80 MHz could be used. The temporal profile of this beam is readily measured, and its wavelength can be tuned over a large range.

The fluorescence signals detected upon CNPhVB irradiation were corrected for wavelength-dependent changes in (1) the spatial and temporal pulse profile of the laser, (2) the background signal recorded from a CNPhVB-free solution of toluene, (3) the group velocity dispersion of the optics used,[53] and (4) the photon flux (all of the data and correction factors are presented in tabular form in the Supporting Information). An excitation spectrum corresponding to the two-photon absorption profile of CNPhVB (Figures 7 and 8) was obtained. Independent of any discussion about the absolute magnitude of δ, our spectrum of CNPhVB is consistent with that previously reported by Pond, et al. (Figure 8).[19]

The CNPhVB excitation spectrum can now be used as a multiple-wavelength standard against which two-photon spectra of other molecules can be determined. Specifically, at a given wavelength, relative $O_2(a^1\Delta_g)$, LIOAS or fluorescence signals can be recorded from the standard, CNPhVB, as well as from the molecule under study without special concern for the temporal and spatial properties of the irradiating beam (as long as the irradiating beam used for both molecules is identical). In such experiments, it will only be necessary to account for the overall spectral profile of CNPhVB shown in Figure 8.

BrPhVB. With the preceding perspective in mind, we recorded the two-photon excitation spectrum of BrPhVB in toluene using $O_2(a^1\Delta_g)$ phosphorescence as a spectroscopic probe and the spectrum of CNPhVB shown in Figure 8 as a wavelength-dependent calibration standard. The spectrum thus obtained (Figure 9) is consistent with a corresponding spectrum we recorded in an independent ns study.[1]

When considering the data shown in Figures 7−9, it is important to remember that, with a fs laser system, the spectral bandwidth at a specified wavelength is quite broad (ca. 15 nm, fwhm). As shown in Appendix 2 (Supporting Information), the fwhm depends on the excitation wavelength but, in general, is larger than the incremental wavelength step size used to generate the excitation spectra (e.g., 5 nm in the CNPhVB spectrum). Thus, the data reported correspond to δ values that are an average over the spectral width of the pulse at the given wavelength.

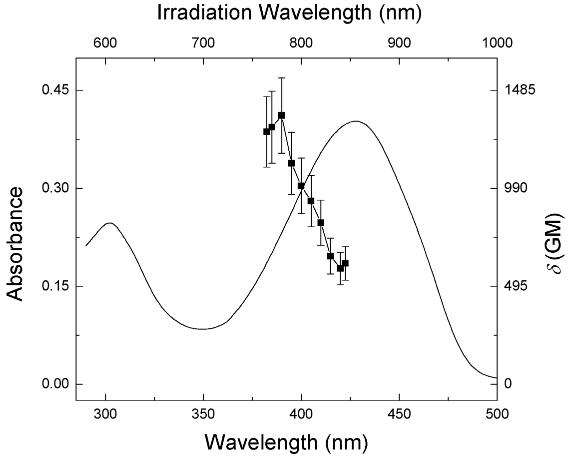


Figure 9. Two-photon excitation spectrum (■, top and right axes), derived from a $O_2(a^1\Delta_g)$ phosphorescence experiment, and one-photon absorption spectrum (solid line, bottom and left axes) of BrPhVB in toluene. The scale for the δ values was established using data from a LIOAS experiment.

In preliminary experiments performed in cyclohexane, we ascertained that the two-photon spectral profile of CNPhVB and BrPhVB do not differ significantly from those obtained in toluene.

D. Summary of the $O_2(a^1\Delta_g)$ and LIOAS Data. With the two-photon spectral profiles of CNPhVB and BrPhVB recorded in toluene (Figures 8 and 9), and the corresponding spectra recorded in cyclohexane, we used the data obtained at 800 nm to determine values for δ at the respective band maxima (Table 1).

The two independent experimental approaches, that is, $O_2(a^1\Delta_g)$ phosphorescence and LIOAS, are self-contained and each yield an absolute δ value. We first focus on data recorded in cyclohexane, which are arguably most accurate because it was not necessary to correct for solvent absorption. In this case, we find that, within experimental error, the δ value obtained for CNPhVB in the LIOAS experiment is equivalent to that obtained in the $O_2(a^1\Delta_g)$ experiment. For BrPhVB in cyclohexane, the LIOAS δ value is slightly larger than that obtained from the $O_2(a^1\Delta_g)$ experiment. Considering the variables involved, we find this agreement satisfying. Indeed, as we have stressed throughout this article, the δ value is very sensitive to experimental parameters. Thus, for example, even though we have included the spatial coherence factor of the laser beam in the treatment of the data, the slight differences between the excitation beams in these respective experiments could nevertheless still contribute to differences in the values obtained.

For the two molecules examined, the data also indicate that the change from cyclohexane to toluene does not have an appreciable effect on the δ value. However, the effect of solvent on two-photon transitions is a topic that exceeds the scope of this present report, certainly with the limited data currently available.

E. Comparison to Previously-Published δ Values. The two-photon behavior of CNPhVB and BrPhVB has previously been examined, and it is thus important to compare our current results with those that have been published. In presenting these results (Table 1), we have explicitly distinguished data obtained using fs pulses from those obtained using ns pulses. Implicit in this distinction is the understanding that it is often more difficult to characterize the temporal and spatial profiles of a ns laser and that the longer pulse width may contribute to undesired photophysics (e.g., excited-state absorption)[25] that, in turn, could adversely influence the magnitude of the measured δ values. Moreover, in a fs experiment, the spectral bandwidth of the irradiation source is much larger than that in a ns experiment (vide supra). Thus, whereas a ns laser can be regarded as a monochromatic source with a spectral bandwidth of ≤1 nm, a fs pulse may have a spectral width of ca. 15 nm (see Supporting Information). As such, δ values obtained with the latter pulses reflect an average over a larger bandwidth.

In addition, all of the previously published results (Table 1) were obtained in relative experiments by comparing the two-photon excited fluorescence intensity of the molecule under study to that obtained upon two-photon excitation of an alkaline

TABLE 1: Two-Photon Absorption Cross Sections, δ^a

		δ ($\times 10^{50}$ cm^4 s photon^{-1} molecule^{-1})	
molecule	solvent	present work[b]	literature[c]
CNPhVB	toluene	2815 ± 420 at 845 nm (fs−oa)	6250 ± 940 at 845 nm (3670 ± 550 at 810 nm (fs−fl)[e]) 1950 ± 340 at 845 nm (1890 ± 280 at 840 nm (fs−fl)[d]) 2075 ± 420 at 845 nm (1640 ± 250 at 830 nm (ns−fl)[d]) 2205 ± 330 at 845 nm (1940 ± 290 at 835 nm (ns−fl)[e]) 1385 at 845 nm (1370 at 840 nm (ns−fl)[f]) 1450 at 845 nm (851 at 810 nm (ns−fl)[g])
	cyclohexane	2910 ± 440 at 845 nm (fs−oa) 2250 ± 340 at 845 nm (fs−so)	
BrPhVB	toluene	1310 ± 200 at 780 nm (fs−oa)	595 ± 90 at ~ 780 nm (450 ± 68 at ~800 nm (ns−fl)[d])
	cyclohexane	1040 ± 160 at 780 nm (fs-oa) 610 ± 90 at 780 nm (fs-so)	

[a] The kind of experiment performed is indicated in parentheses; fs = femtosecond excitation, ns = nanosecond excitation, so = singlet oxygen phosphorescence, oa = LIOAS, fl = fluorescence. [b] The values reported are at the two-photon absorption maximum and were obtained using values recorded at 800 nm and scaled according to the spectral profiles in Figures 8 and 9. [c] The values given were obtained by rescaling the published δ value according to the spectral profiles in Figures 8 and 9 to yield a value for δ at the two-photon absorption maximum. The data actually published are shown in parentheses immediately below the corresponding rescaled value. [d] From Pond et al.[19] [e] From Albota et al.[12] [f] From Yoo et al.[43] [g] From Zhang et al.[42]

solution of fluorescein in water, for which $\delta = 38.0 \pm 9.7$ GM has been reported at 782 nm.[20] Thus, any systematic error inherent to this system and/or approach will be propagated in all studies.

For CNPhVB dissolved in toluene, previously published values for δ cover a large range. Such differences could derive from a number of sources, including light absorption by the solvent itself. In any event, our δ value for CNPhVB at its band maximum of 845 nm, $\delta = 2815 \pm 420$ GM, falls within the range of published values.

To our knowledge, only one value of δ (BrPhVB) has been published, and this was from a ns experiment. The δ values we present are slightly larger than this value.

Conclusions

In a search to identify molecular standards against which the two-photon photosensitized production of $O_2(a^1\Delta_g)$ could be calibrated, we selected two molecules that have received a great deal of recent attention in the study of organic nonlinear optical materials, CNPhVB and BrPhVB. Extensive optical and laser-induced optoacoustic experiments were performed to characterize pertinent properties of these molecules in a number of solvents.

We propose that both CNPhVB and BrPhVB can now be used as standard molecules in the determination of δ values. However, our data also reaffirm the need to exercise caution when trying to accurately determine δ values. In addition to carefully characterizing both the spatial and temporal profiles of the excitation source, it is also important to choose a solvent that does not interfere with the experiment. In particular, we have demonstrated that a solvent commonly used for these experiments, toluene, may absorb a significant amount of light under the experimental conditions employed and, as such, introduce serious errors to the measurement.

Acknowledgment. This work was funded by the Danish National Research Foundation through a block grant for The Center for Oxygen Microscopy and Imaging, the Danish Natural Science Research Council, and the Villum Kann Rasmussen Foundation. The authors thank Christian B. Nielsen (University of Aarhus) for synthesizing and purifying the CNPhVB and BrPhVB used in this study and Alberto Rizzi and Simone Moellenbeck (Mülheim) for assistance in the early stages of the LIOAS experiments.

Supporting Information Available: Derivation of expressions used to quantify two-photon excitation, tabulated data for the two-photon-pumped fluorescence of CNPhVB, and LIOAS experiments to determine the speed of sound in toluene. This information is available free of charge via the Internet at http://pubs.acs.org.

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electronic states. The two-photon absorption cross sections have been quantified, and they are generally quite small (e.g., <0.1 GM for benzene). Nevertheless, for experiments performed under our conditions where the aromatic hydrocarbons are used as a solvent, such absorption can be appreciable because the solvent concentration is several orders of magnitude larger than the concentration of the dissolved sensitizer. ((a) Chen, C. H.; McCann, M. P. *J. Chem. Phys.* **1988**, *88*, 4671−4677. (b) Monson, P. R.; McClain, W. M. *J. Chem. Phys.* **1970**, *53*, 29−37.)

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