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### **Nanosecond Time-Resolved Resonance CARS Spectroscopy of Triplet Excited Polycyclic Aromatic Compounds**

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## Nanosecond Time-Resolved Resonance CARS Spectroscopy of Triplet Excited Polycyclic Aromatic Compounds

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### ABSTRACT

We use time-resolved resonance CARS spectroscopy as a diagnostic approach to study the structure and the dynamics of photoinduced transient molecular species. Transient CARS spectra of several highly fluorescent organic molecules in the lowest excited triplet state are reported and discussed. Several fundamentals of anthracene and some monosubstituted derivatives are observed and assigned unambiguously by comparison of the  $S_0$  and  $T_1$  spectral features. Moreover, it is verified that the most intense CC stretching band of anthracene in the lowest excited triplet state exhibits an upward wavenumber shift upon deuteration. Nanosecond time-resolved transient CARS spectroscopy opens up the possibility to study the triplet relaxation process of the sample molecules. Furthermore, it is shown by means of transient

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CARS spectroscopy that the lowest excited triplet state of 9-fluorenone exhibits  $\pi\pi^*$  character. The wavenumbers of the transient CO and CC stretching modes differ considerably from the appropriate Raman wavenumbers of the  $n\pi^*$  triplet state of benzophenone. Moreover, time-resolved CARS spectroscopy is used to demonstrate that the inter-system crossing of 1,2-benzanthracene occurs on a nanosecond time scale in deaerated solutions.

**Key Words:** Transient CARS; Time-resolved CARS; Kinetics; Singlet-to-triplet conversion; Triplet molecules.

## INTRODUCTION

In the last few years, there has been considerable interest in the Raman spectroscopic investigation of photoinduced transient molecular species.<sup>[1–10]</sup> Besides spontaneous linear Raman scattering, non-linear coherent anti-Stokes Raman scattering (CARS) spectroscopy is a well-established technique<sup>[11]</sup> to obtain time-resolved Raman spectra of electronic excited states. In the non-linear Raman method a coherent signal beam is generated in a sample medium through a four-wave mixing process,  $\tilde{\nu}_{CARS} = \tilde{\nu}_p + (\tilde{\nu}_p - \tilde{\nu}_S)$ ,  $\tilde{\nu}_p$  and  $\tilde{\nu}_S$  being the wavenumbers of the pump and Stokes laser, respectively.<sup>[12–26]</sup> The collimated high-intensity signal output in the anti-Stokes spectral region allows vibrational spectroscopic investigation of highly fluorescent molecules. Owing to these unique properties, CARS spectroscopy is particularly useful for obtaining vibrational spectra from short-lived molecular species created by photoexcitation.<sup>[3,7,8,10,27–36]</sup>

Recently, we have reported on a multi-purpose CARS spectrometer that allows one to perform nanosecond time-resolved CARS experiments using either the scanning CARS or the broadband CARS techniques.<sup>[37]</sup> The data acquisition process of broadband CARS spectra is based on the recently developed scanning multichannel technique.<sup>[38–40]</sup> The setup was used to determine the third-order susceptibility parameters of electronic excited state molecules unambiguously.<sup>[41]</sup> In the present paper, we demonstrate the capability of the developed CARS spectrometer to study the vibrational properties and the life-time of the lowest excited triplet state of well-suited test molecules.

At first, we present the CARS spectra of the electronic ground ( $S_0$ ) and the lowest excited triplet ( $T_1$ ) state of anthracene and several monosubstituted derivatives. The vibrational wavenumbers of  $T_1$  anthracene have already been determined by Tripathi and Fisher<sup>[42]</sup> and Van Zeyl et al.<sup>[43]</sup> using spontaneous time-resolved Raman spectroscopy. However, the



observed Raman bands were assigned by each group partly in different ways. In the present work, we show that comparison of the signal intensities of the corresponding resonance CARS bands enables a reasonable correlation between the observed  $S_0$  and  $T_1$  fundamentals of anthracene. Furthermore we verify the observation of Tripathi and Fisher<sup>[42]</sup> that the strongest vibrational band of  $T_1$  anthracene shows an upward wavenumber shift upon deuteration. Subsequently, we present the observation and analysis of the transient resonance CARS spectrum of the  $T_1$  state of 9-fluorenone, a typical aromatic carbonyl compound. The lowest excited triplet states of aromatic ketones show a clear correlation between the electron configuration and the reactivity for hydrogen abstraction:  $n\pi^*$   $T_1$  states are efficiently photoreduced by alcohols and amines, whereas  $\pi\pi^*$   $T_1$  states do not react with hydrogen donors.<sup>[44,45]</sup> Several authors emphasized that the CC and CO stretching wavenumbers of  $T_1$  states of these compounds are a direct indication of changes of the electron density distribution and the molecular structure in going from  $S_0$  to  $T_1$  states, and can thus be directly related to the photochemical reactivity of the triplet excited state.<sup>[46–50]</sup> In this work, we compare the vibrational wavenumbers of  $T_1$  9-fluorenone with the corresponding data of benzophenone, which has been extensively studied by Tahara et al.,<sup>[47,48]</sup> and explain the different photochemical behaviour of both molecules in terms of their  $T_1$  vibrational spectroscopic properties. Finally, we consider the intersystem crossing process of 1,2-benzanthracene into the triplet state in order to demonstrate the performance of time-resolved CARS spectroscopy for the investigation of photoinduced molecular dynamics. We point out that in outgassed solutions the intersystem crossing of 1,2-benzanthracene requires several nanoseconds, whereas in aerated environments the corresponding transition from the singlet into the triplet manifold is accelerated considerably.

The sample molecules mentioned above were chosen for study as their photophysical and photochemical properties are fairly well-known. Especially, several molecules investigated in the present study are highly fluorescent, which is the reason that they have not been observed by means of transient linear Raman spectroscopy up to now. However, CARS spectroscopy provides an excellent means of eliminating luminescence signals by the use of spatial filtering.

## EXPERIMENTAL

In our experiments, we used nanosecond time-resolved CARS as a means for the investigation of photoinduced electronic processes. The experimental setup used to obtain the transient resonance CARS spectra has



been described in detail elsewhere.<sup>[37]</sup> Briefly, the 337 nm pulse of a nitrogen laser ( $\tilde{\nu}_{exc}$ , Lambda Physik, M100AS, 5 ns, 150 kW) is used to produce triplet excited molecules which can be probed at different delay times by means of multiplex CARS spectroscopy. The CARS probing radiations are generated in two dye lasers, a narrowband pump laser ( $\tilde{\nu}_p$ , Molelectron DL200, 8 ns, 10 kW) and a broadband Stokes laser ( $\tilde{\nu}_s$ , Spectra Physics PDL3, 8 ns, 40 kW), which are pumped synchronously by the third harmonic (355 nm) of a Q-switched Nd:YAG laser (Spectra Physics Quanta Ray GCR-4, 6 ns). The three  $\tilde{\nu}_p$ ,  $\tilde{\nu}_s$ , and  $\tilde{\nu}_{exc}$  beams are focused into the sample solution ensuring that the beam waist of the slightly focused UV beam was much larger than the focus diameter of the probing dye laser beams. Polarization directions of the  $\tilde{\nu}_p$ ,  $\tilde{\nu}_s$ , and the generated CARS signal ( $\tilde{\nu}_{as}$ ) beams are specified by Glan-Thompson prisms. In the present study, all measurements are performed with parallel polarization directions of the analyzer and the input laser fields so that the displayed spectra indicate the dispersion profiles due to  $\chi_{1111}^{(3)}$ . The polarization-selected signal beam was passed through several apertures, for laser stray light and luminescence rejection, before it was focused on the entrance slit of a double monochromator (Spex 1403) and detected by a CCD camera (Photometrics, model 9000). A home-made synchronization electronic device (10 Hz) was used to trigger the Nd:YAG laser with a variable delay after the nitrogen laser emission in the range of 0 ns  $\rightarrow$  10 ms with a 10 ns step variation. An additional drift control unit automatically compensates continuous temporal drifts between triggering and actual lasing of the nitrogen laser, which would otherwise seriously affect transient CARS measurements. The overall jitter between the nitrogen and Nd:YAG laser pulses is approximately  $\pm 8$  ns. In the case when a short delay time (*ca.* 3 ns) is imposed between sample excitation and CARS generation, the electronic excitation of the molecules is achieved by focusing a part of the third harmonic (355 nm) of the Nd:YAG laser beam into the sample cell. Moreover, nanosecond time-resolved experiments can be performed using the scanning CARS technique. Details of the scanning CARS set-up have been described previously.<sup>[51]</sup>

Intensity calibration is performed by normalizing the resulting multi-channel CARS spectra on the featureless non-Raman-resonant background spectrum of carbon tetrachloride, recorded under the same experimental conditions. Wavenumber calibration is carried out according to a computational method developed by Lindrum and Nickel.<sup>[52]</sup> No data smoothing was applied.

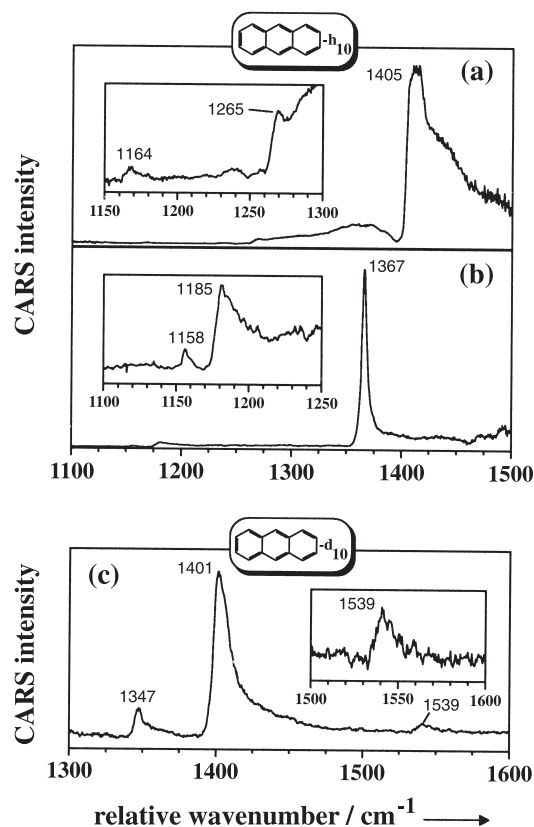
The employed samples and solvents were commercial and used without further purification. If not mentioned otherwise, the sample solutions were not degassed. The sample cell was constructed from two microscope cover glasses with a sealing ring 1 mm thick between them.

## RESULTS AND DISCUSSION

The lowest excited triplet state of anthracene has been investigated several times by means of transient linear Raman spectroscopy.<sup>[42,43,53]</sup> A vibrational analysis of the observed  $T_1$  Raman modes has been performed by Tripathi and Fisher<sup>[42]</sup> and Van Zeyl et al.<sup>[43]</sup> As mentioned above, the proposed vibrational assignments of both groups partly contradict each other. In particular, the transient Raman band at  $1180\text{ cm}^{-1}$  has been related to ground state modes of different symmetry. Whereas Tripathi and Fisher<sup>[42]</sup> assigned this Raman line as the counterpart of the totally symmetric ( $a_g$ )  $S_0$  mode around  $1260\text{ cm}^{-1}$ , Van Zeyl et al.<sup>[43]</sup> expected this triplet band to correspond to a non-totally symmetric  $b_{2g}$  ground state mode of nearly the same vibrational wavenumber. In this study we used transient CARS spectroscopy as a suitable device to clear up this contradiction.

Figure 1(a) depicts the resonance CARS spectrum of anthracene dissolved in n-heptane. For excitation at  $\lambda_p = 385\text{ nm}$ , both pump and anti-Stokes wavelengths are close to the maximum of the  $S_1 \leftarrow S_0$  absorption band of anthracene in the electronic ground state. Hence, apart from the strong CARS band at  $1405\text{ cm}^{-1}$ , two additional weak Raman lines occur around  $1164$  and  $1265\text{ cm}^{-1}$ . These vibrational wavenumbers agree well with the strongest spontaneous Raman bands of  $S_0$  anthracene observed by several authors.<sup>[54–58]</sup> Using simultaneous excitation with the third harmonic ( $355\text{ nm}$ ) of the Nd:YAG laser, the spectrum undergoes significant changes as shown in Figure 1(b). Since the pump laser wavelength  $\lambda_p = 433\text{ nm}$  is close to the transient  $T_n \leftarrow T_1$  absorption maximum at  $421\text{ nm}$ ,<sup>[59]</sup> the plotted CARS signals are most likely attributable to resonance-enhanced modes of anthracene in the lowest excited triplet state. As shown in Figure 1, the resonance CARS spectra of  $S_0$  and  $T_1$  anthracene exhibit similar Raman spectral patterns. Apart from a strong transient Raman band around  $1367\text{ cm}^{-1}$  which exhibits maximum resonance enhancement, two weaker triplet state lines appear in the low wavenumber region at  $1158$  and  $1185\text{ cm}^{-1}$ . On the assumption that the normal motions and the electronic resonance enhancement do not change drastically between the  $S_0$  and  $T_1$  states, it is reasonable to correlate these triplet lines to the corresponding ground state bands according to the relative intensities recognizable in Figure 1. Consequently the triplet line of anthracene at  $1185\text{ cm}^{-1}$  relates to the totally symmetric ground-state band at  $1265\text{ cm}^{-1}$  in agreement with the vibrational assignment proposed by Tripathi and Fisher.<sup>[42]</sup> In going from  $S_0$  to  $S_1$  states, the vibrational wavenumber of this mode exhibits a remarkable drop  $\approx 80\text{ cm}^{-1}$ . This difference can be mainly attributed to the changes in the extent of coupling the CC stretch and CH bending modes in the  $S_0$  and  $T_1$  electronic states.<sup>[42]</sup> The vibrational





**Figure 1.** Resonance CARS spectra of the (a) electronic  $S_0$  ground state of anthracene in  $n$ -heptane acquired with a pump laser wavelength  $\lambda_p = 385$  nm. Resonance CARS spectra of the lowest excited triplet  $T_1$  state of (b) anthracene and (c) deca-deuteroanthracene in  $n$ -heptane obtained with a pump laser wavelength of  $\lambda_p = 433$  nm. The electronic excitation was performed by simultaneous irradiation by the third harmonic of the Nd:YAG laser (355 nm). The insets show parts of the spectra on an expanded scale.

attribution reported by Van Zeyl et al.<sup>[43]</sup> may also be excluded on the basis of symmetry considerations. As a general rule, the high intensity of the triplet absorption band around 421 nm,<sup>[59]</sup> and the strong enhancement of the CARS signals excited in resonance with this absorption, denote a Franck-Condon (Albrecht's A term)<sup>[60]</sup> scattering process. Accordingly, only the totally symmetric modes, along which the potential minimum is displaced with the electronic transition, give rise to notable resonance

CARS activity. Hence, it is concluded that no  $b_{2g}$  modes are observed in the resonance CARS spectrum of  $T_1$  anthracene depicted in Figure 1(b).

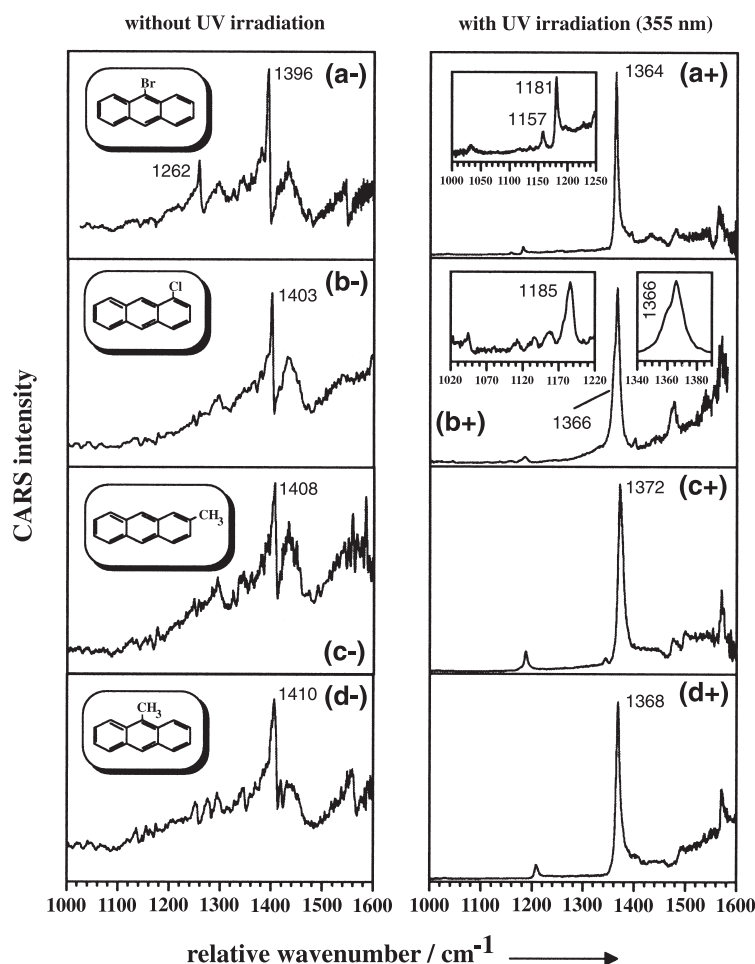
Tripathi and Fisher<sup>[42]</sup> also characterized the lowest excited triplet state of deca-deuteroanthracene by means of transient spontaneous Raman spectroscopy. These authors correlated the strong totally symmetric CC stretching mode of  $T_1$  anthracene- $h_{10}$  at  $1365\text{ cm}^{-1}$  with the transient mode of anthracene- $d_{10}$  around  $1399\text{ cm}^{-1}$ . This would mean an increase in the wavenumber of the most resonance enhanced Raman line in  $T_1$  anthracene upon deuteration, which is opposite to that expected from simple considerations of the isotopic substitution effect. Hence, we tried to reproduce the experimental results of these authors by means of transient resonance CARS spectroscopy. The CARS spectrum of  $T_1$  anthracene- $d_{10}$  obtained by pump laser excitation at  $\lambda_p = 433\text{ nm}$  is shown in Figure 1(c). As can be seen from this figure, the transient CARS spectrum of triplet anthracene- $d_{10}$  consists of two weak Raman lines around  $1347$  and  $1539\text{ cm}^{-1}$  and an intense CARS band at  $1401\text{ cm}^{-1}$ . Assuming that the same vibrational mode in anthracene- $h_{10}$  and anthracene- $d_{10}$  appears with maximum resonance enhancement from the same electronic transition in resonance, the most prominent Raman bands in (b) and (c) of Figure 1 can be reasonably correlated to each other. Hence, the CARS spectra plotted in Figure 1 provide an obvious verification of the upward direction of the deuterium shift in  $T_1$  anthracene reported by Tripathi and Fisher.<sup>[42]</sup> It is interesting to note that a similar observation has been made by Takemura et al.<sup>[61]</sup> in triplet naphthalene- $h_8$  and naphthalene- $d_8$ .

Van Zeyl et al.<sup>[43]</sup> mentioned that the detection of spontaneous Raman spectra of  $T_1$  anthracene was superimposed by a strong fluorescence background, in spite of using a gated optical multichannel analyzer. Several derivatives of anthracene are even much more fluorescent. Therefore, transient CARS spectroscopy provides a valuable means of obtaining vibrational spectra of the triplet excited states of these molecules. Furthermore, substituted anthracene derivatives are well suited for nanosecond time-resolved resonance CARS studies, since these sample molecules are transferred in the triplet excited state with high quantum efficiency upon excitation either with the third harmonic of a Nd:YAG laser ( $355\text{ nm}$ ) or with a nitrogen laser ( $337\text{ nm}$ ). Moreover, all these substances exhibit a transient  $T_n \leftarrow T_1$  absorption maximum around  $430\text{ nm}$ .<sup>[62]</sup> Therefore, transient resonance CARS spectra of the lowest excited triplet states of different anthracene derivatives can be obtained using the same pump laser excitation and compared with each other.

The CARS spectra of 9-bromoanthracene (panels a), 1-chloroanthracene (panels b), 2-methylanthracene (panels c), and 9-methylanthracene (panels d) in the electronic  $S_0$  ground state (left panels, marked by “-”) and in the lowest excited triplet  $T_1$  state (right panels, marked by “+”) are shown in Figure 2. Since the employed sample molecules are non-absorbing substances







**Figure 2.** CARS spectra of 9-bromoanthracene (panels a), 1-chloroanthracene (panels b), 2-methylantracene (panels c), and 9-methylantracene (panels d) in n-heptane without (left panels, marked by “–”) and with irradiation (right panels, marked by “+”) by the third harmonic of the Nd:YAG laser (355 nm). The measurements were performed at a pump laser wavelength of  $\lambda_p = 433$  nm. The insets display parts of the spectra on an expanded scale.

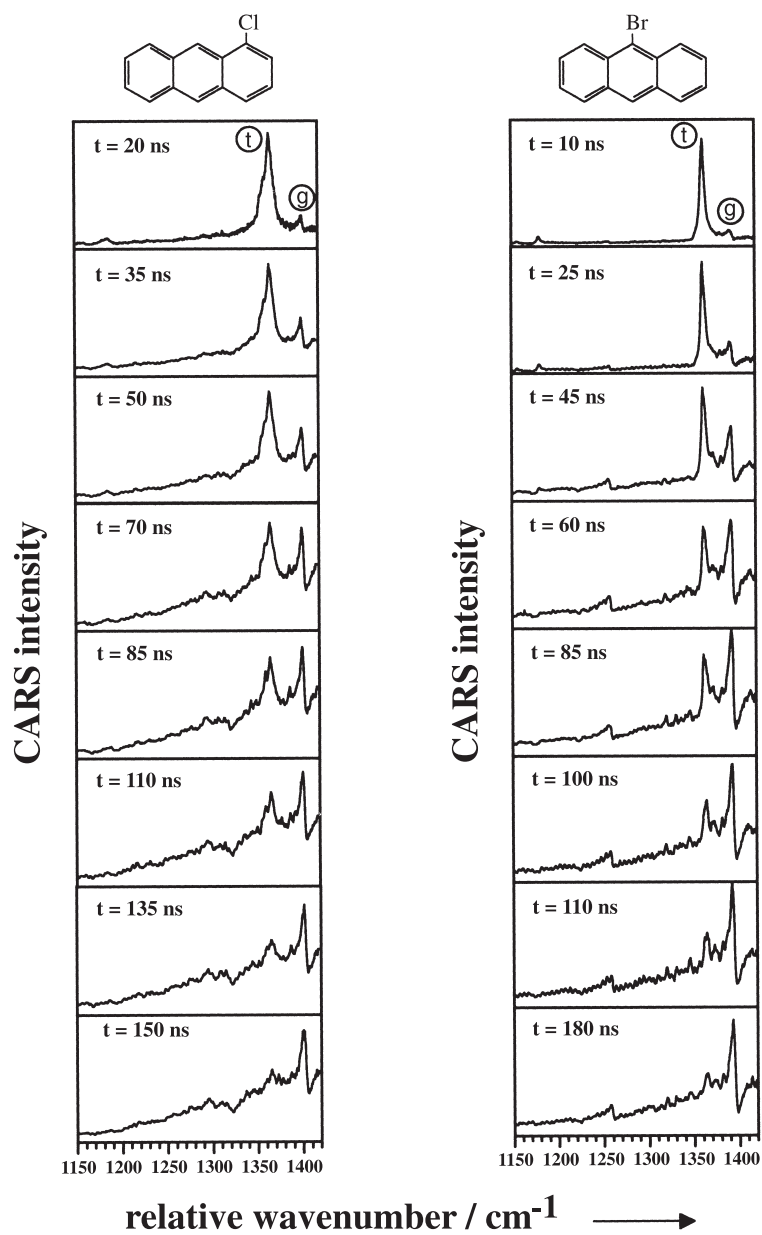
in the visible spectral region, a resonance Raman effect does not appear for these molecules in the ground state. Dispersive, sometimes negative, band-shapes are consequently observed in the CARS spectra of the  $S_0$  states which are partly difficult to distinguish from mode structures in the spectral profile of the broadband Stokes laser emission. These line shapes arise from the

interference of the Raman-resonant CARS signals with the non-Raman resonant background of the solvent. Recognition of the electronic ground state bands was performed by means of literature data.<sup>[63,64]</sup> Using simultaneous excitation of the third harmonic (355 nm) of the Nd:YAG laser, the observed Raman spectral features of the spectra change drastically as can be seen in the right panels of Figure 2. 9-Bromoanthracene shows a similar UV-induced decomposition as we already have reported for 9,10-dibromoanthracene.<sup>[37]</sup> With continuous UV illumination the transient CARS line intensity at 1364  $\text{cm}^{-1}$  (shown in panel a( + )) of Figure 2) decreases gradually, whereas at the same time a new transient Raman line around 1368  $\text{cm}^{-1}$  rises continuously

**Table 1.** Comparison and assignments of the  $S_0$  and  $T_1$  fundamental wavenumbers ( $\text{cm}^{-1}$ ) of anthracene, deca-deuteroanthracene, 1-chloroanthracene, 2-methylanthracene, and 9-methylanthracene. Additionally, the wavenumber shifts ( $\text{cm}^{-1}$ ) of the corresponding modes upon going from  $S_0$  to  $T_1$  states are listed.

		Wavenumber/cm <sup>-1</sup>					
Sample molecule		CH-bend	CH-bend	CC-stretch + CH-bend	CC-stretch	CC-stretch	CC-stretch
anthracene	S <sub>0</sub>		1164	1265	1405		
	T <sub>1</sub>		1158	1185	1367		
	T <sub>1</sub> -S <sub>0</sub>		-6	-80	-38		
anthracene -d <sub>10</sub>	S <sub>0</sub>				1388	1402	1534
	T <sub>1</sub>				1399	1348	1539
	T <sub>1</sub> -S <sub>0</sub>				+11	-54	+5
9-bromo- anthracene	S <sub>0</sub>			1262	1396	1476	1548
	T <sub>1</sub>	1033	1157	1181	1364	1482	1565
	T <sub>1</sub> -S <sub>0</sub>			-81	-32	+6	+17
1-chloro- anthracene	S <sub>0</sub>		1159	1263	1403		
	T <sub>1</sub>	1044	1159	1185	1366	1477	
			(1136, 1112)		(1360)		
2-methyl- anthracene	T <sub>1</sub> -S <sub>0</sub>		±0	-78	-37		
	S <sub>0</sub>			1262	1408		
	T <sub>1</sub>			1188	1372		
9-methyl- anthracene					(1343)		
	T <sub>1</sub> -S <sub>0</sub>			-74	-36		
	S <sub>0</sub>			1257	1410	1453	1563
				(1283)	(1422)		
	T <sub>1</sub>			1210	1368	1492	1572
	T <sub>1</sub> -S <sub>0</sub>			-47	-42	+39	+9



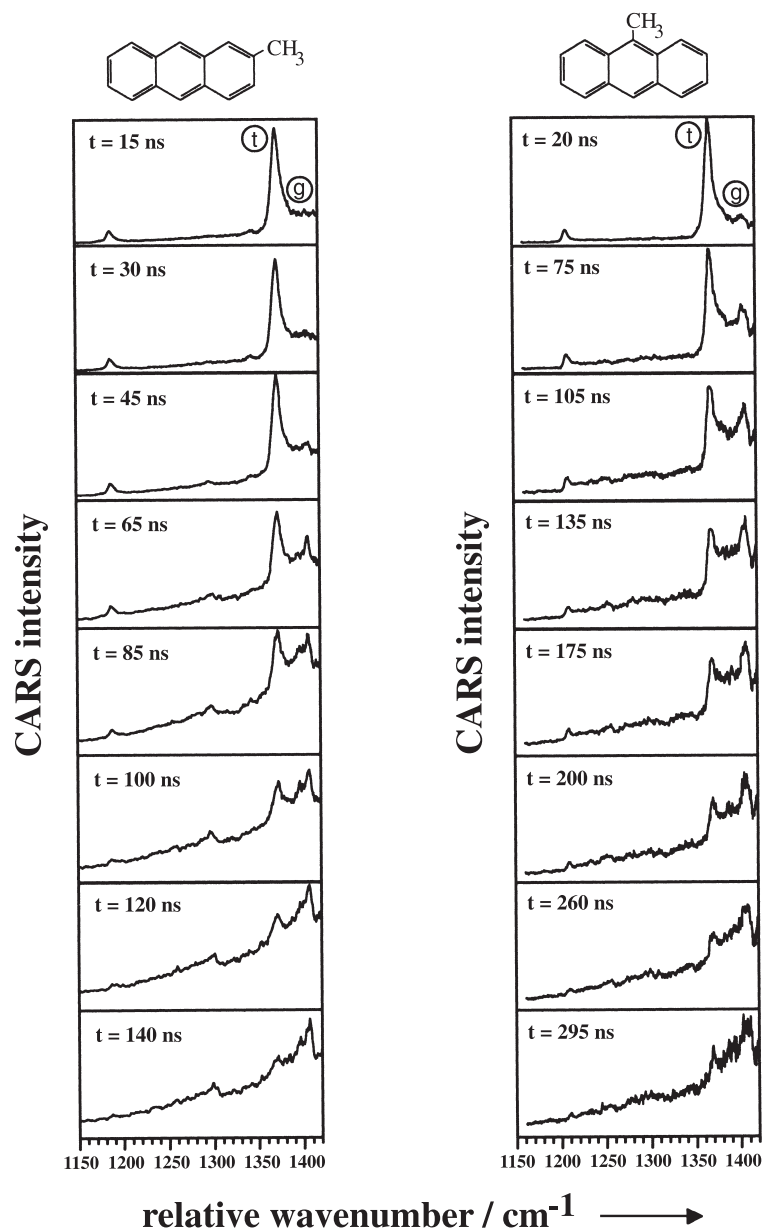


(not shown here). After approximately 4 h, the original transient Raman band has nearly vanished. However, circulating the sample solution by a peristaltic pump (ISMATEC, MS 2/8) through a square-shaped borosilicate glass capillary (inner pathlength 400  $\mu\text{m}$ ) allows efficient avoidance of the sample degradation. Since the pump laser wavelength  $\lambda_p = 433 \text{ nm}$  is close to the transient  $T_n \leftarrow T_1$  absorption maximum around 430 nm,<sup>[62]</sup> the transient CARS signals plotted in the right panels of Figure 2 are attributed to resonance enhanced vibrations of the employed sample molecules in the lowest excited triplet state. With a pump laser excitation close to the triplet absorption maximum, the positive and Lorentzian-shaped contributions to the transient CARS bandshape become dominant and, in consequence, positive and nearly symmetric bandshapes are observed in the transient CARS spectra, facilitating spectral interpretation. One to one correlation between the  $S_0$  and  $T_1$  Raman wavenumbers of the investigated anthracene derivatives was attempted. As outlined above, intensity considerations provide a reasonable basis for assigning the triplet Raman wavenumbers. A comparison and a possible correlation of the  $S_0$  and  $T_1$  Raman wavenumbers of anthracene, deca-deuteroanthracene, 9-bromoanthracene, 1-chloroanthracene, 2-methylanthracene and 9-methylanthracene determined in the present study are listed in Table 1. As can be seen in Figure 2 the chemical structure of the employed sample molecules seems to have an influence on the intensity spectral pattern of the observed resonance CARS spectra. Nevertheless, further systematic experiments are necessary to achieve unambiguous results.

Nanosecond time-resolved CARS spectroscopy opens up the possibility of determining the lifetime of photoinduced short-lived molecular species and electronic excited states. In order to obtain further information on the temporal behaviour of the observed  $T_1$  states, we thus carried out nanosecond time-resolved CARS experiments. In Figures 3 and 4 we show the nanosecond time-resolved resonance CARS spectra of 1-chloroanthracene, 9-bromoanthracene, 2-methylanthracene, and 9-methylanthracene in n-heptane. As outlined above, the electronic excitation of the employed sample molecules was achieved by irradiation of nitrogen laser pulses (337 nm) preceeding the CARS probe pulses by a defined, adjustable delay time  $t$ .

**Figure 3.** Nanosecond time-resolved CARS spectra of  $ca. 10^{-2} \text{ mol dm}^{-3}$  1-chloroanthracene (left panels) and 9-bromoanthracene (right panels) in n-heptane taken for different delay times  $t$  between the exciting nitrogen laser pulses and the CARS probing process at a pump laser wavelength of  $\lambda_p = 433 \text{ nm}$ . In the first panels, the ground state and triplet excited state lines are marked by “g” and “t”, respectively.



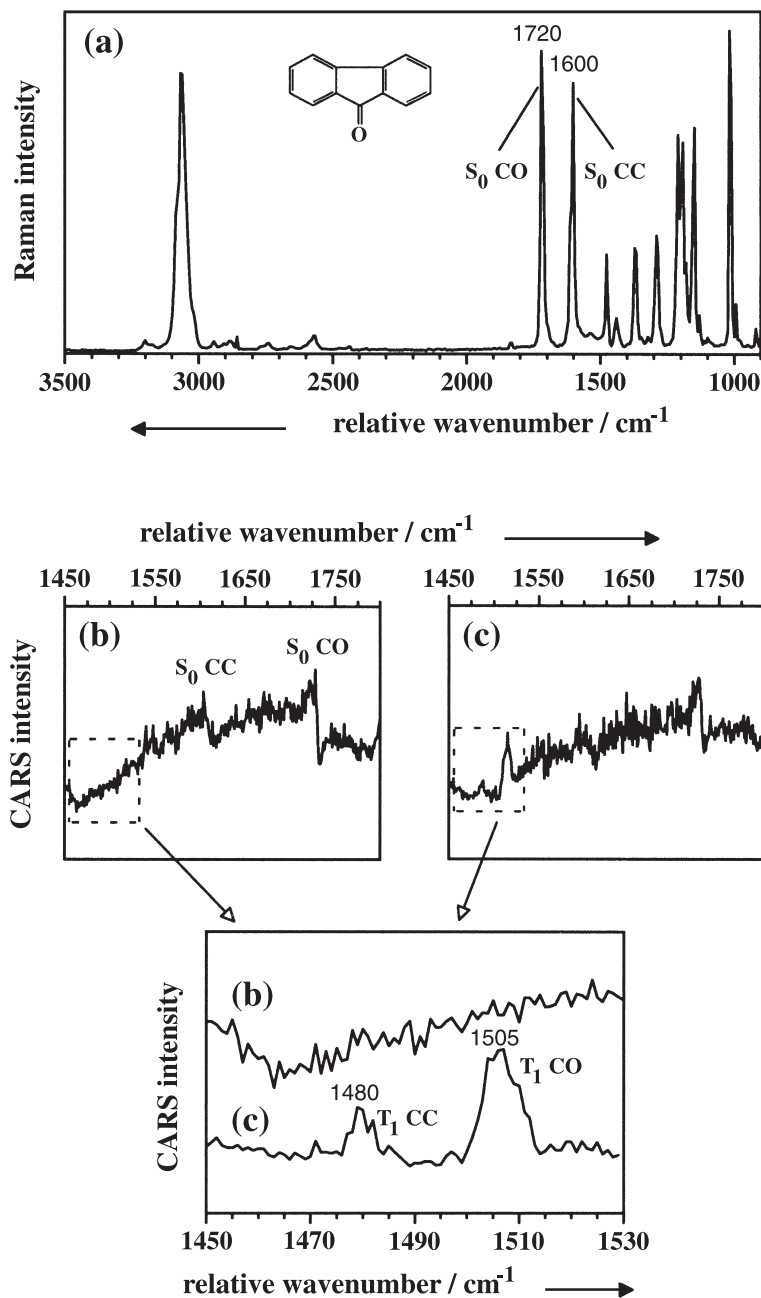


In order to overcome the photochemical sample degradation mentioned above, the solution of 9-bromoanthracene was circulated by a peristaltic pump, whereas the other solutions were filled in static sample cells. It should be mentioned that the intensities of the various spectra are plotted with different scales. After photoexcitation, the overall CARS intensity immediately decreases and then increases gradually. This is because of transient absorption by the excited triplet states, the scattering due to thermal turbulence in the sample cell, and the formation of a negative thermal lens around the waist of the exciting UV beam, which slightly defocuses the CARS probe beams leaving the sample.<sup>[35,65,66]</sup> Owing to these effects the time-resolved CARS spectra shown in Figures 3 and 4 exhibit different overall signal levels at various delay times. The various panels in Figures 3 and 4 clearly illustrate the temporal evolution of the triplet relaxation process, which can be easily followed by the decrease of the  $T_1$  Raman bands and the increase of the corresponding ground state signals. In our experiments the sample solutions employed were not deaerated. Hence, the lifetime of the studied triplet excited states is relatively short due to oxygen quenching. Nevertheless, the lifetime of about 100 ns is consistent with the triplet nature of the investigated transient species. At any delay time no trace of transient Raman bands owing to other electronic excited species was observed.

The triplet excited states of aromatic carbonyls exhibit an inherent correlation between the electron configuration, the molecular structure, and the photochemical reactivity.<sup>[44–50]</sup> Depending on the employed sample molecule and the solvent, the lowest excited triplet state of these substances can either have  $n\pi^*$  or  $\pi\pi^*$  character. The  $\pi\pi^*$  state shows a marked delocalization of the electronic excitation into the aromatic ring fragment, and the carbonyl group thus retains a significant double bonding order. In contrast, the excitation of an electron from the  $n$  orbital to  $\pi^*$  weakens the CO bonding appreciably, and hence the  $n\pi^*$ -type excited electronic state of an aromatic carbonyl compound shows a single-bond-like structure of the CO group, whereas the ring geometry remains only weakly affected. The photochemical hydrogen abstraction by aromatic carbonyls has been studied extensively as an organic photochemical reaction of fundamental

**Figure 4.** Nanosecond time-resolved CARS spectra of  $ca. 10^{-2} \text{ mol dm}^{-3}$  2-methylanthracene (left panels) and 9-methylanthracene (right panels) in *n*-heptane taken for different delay times  $t$  between the exciting nitrogen laser pulses and the CARS probing process at a pump laser wavelength of  $\lambda_p = 433 \text{ nm}$ . In the first panels, the ground state and triplet excited state lines are marked by “g” and “t”, respectively.





importance. It is well known that this reaction proceeds through the lowest excited triplet state, and that the chemical reactivity can be discussed in terms of the electron density distribution of this key intermediate. The unfilled  $n$  orbital of  $n\pi^*$   $T_1$  states results in a high electron affinity and hence a high reactivity for the hydrogen abstraction and photoreduction. In contrast, the  $\pi\pi^*$   $T_1$  states show much less or no reactivity. Transient Raman spectra of aromatic carbonyls have been studied several times, and it is widely accepted that the CO and CC stretching wavenumbers are good indicators of the structure of the carbonyl group and the aromatic rings in the  $T_1$  state.<sup>[46–50]</sup> Determination of the transient CO and CC stretching wavenumbers is thus critically important in understanding the photochemical reactivity of aromatic carbonyls in terms of their structure.

We have studied the vibrational spectroscopic properties of 9-fluorenone, which is a prototypical aromatic carbonyl compound. Figure 5a depicts the Fourier transform Raman spectrum of 9-fluorenone dissolved in carbon tetrachloride obtained with laser excitation at 1064 nm. The vibrational analysis of 9-fluorenone based upon Raman and infrared spectra has been reported several times in literature.<sup>[67,69]</sup> In this work, only the most intensive Raman bands around 1600 and 1720  $\text{cm}^{-1}$  are of interest, which can be attributed to the CC and the CO stretching wavenumbers of 9-fluorenone in the electronic ground state (Figure 5a). In Figure 5b we show the scanning CARS spectrum of *ca.*  $5 \times 10^{-3}$  mol  $\text{dm}^{-3}$  9-fluorenone in *n*-hexane. For excitation with  $\lambda_P = 445$  nm the pump laser wavelength lies far away from the  $S_n \leftarrow S_0$  absorption maximum of the sample molecules. Hence, the Raman bands of 9-fluorenone in the electronic ground state are not resonance enhanced and accordingly the CARS spectrum plotted in panel b of Figure 5 only shows the CC and CO stretching mode as weak dispersive Raman lines which are imposed significantly by the non-Raman-resonant background of the solvent. With simultaneous excitation with the third harmonic (355 nm) of the Nd:YAG laser, two new Lorentzian Raman lines appear around 1480 and 1505  $\text{cm}^{-1}$  as shown in Figure 5c. As the transient CARS intensity is unusually weak and markedly imposed by a luminescent background, we were, up to now, not able to observe any transient CARS lines of 9-fluorenone using the multiplex CARS technique.<sup>[37]</sup> Since the CARS spectrum displayed in panel c of Figure 5 has been acquired at a pump laser wavelength

**Figure 5.** (a) Fourier transform Raman spectrum (Raman excitation at 1064 nm) of 9-fluorenone in carbon tetrachloride. Scanning CARS spectrum of 9-fluorenone in *n*-hexane ( $5 \times 10^{-3}$  mol  $\text{dm}^{-3}$ ,  $\lambda_P = 445$  nm) (b) without and (c) with irradiation by the third harmonic of the Nd:YAG laser (355 nm).





$\lambda_p = 445$  nm, which is close to the transient  $T_n \leftarrow T_1$  absorption maximum of 9-fluorenone at 460 nm,<sup>[70]</sup> the new Raman lines can be explained by resonance-enhanced vibrations of 9-fluorenone in the lowest excited triplet state. Taking into account the spectral pattern of the ground state CARS spectrum of 9-fluorenone (panel b of Figure 5), we can assign the observed transient CARS lines to the CC and the CO stretching modes of the triplet excited molecules with confidence. In Table 2 we compare the CC and CO stretching wavenumbers of  $S_0$  and  $T_1$  9-fluorenone with the corresponding counterparts of benzophenone, which have been determined by Tahara et al..<sup>[47,48]</sup> While the CC and CO stretching wavenumbers of both molecules are very similar in the  $S_0$  state, they are quite different in the  $T_1$  state. It is concluded that both triplet states differ from each other by a very different distribution of the electronic excitation in the molecule. As can be seen from Table 2 the vibrational wavenumber of the CO stretching mode of benzophenone decreases drastically in going from  $S_0$  to  $T_1$  state, whereas the wavenumber of the CC stretching mode is only slightly downshifted. The marked downshift of the CO stretching wavenumber of  $T_1$  relative to  $S_0$  ( $\Delta\tilde{\nu} = -443$  cm<sup>-1</sup>) indicates a considerable weakening of the  $\pi$  character of the CO bonds, which unambiguously reveals the  $\pi\pi^*$  nature of the  $T_1$  state of benzophenone.<sup>[47,48]</sup> In contrast, the carbonyl group of  $T_1$  9-fluorenone exhibits a notable double-bond-like structure whereas the wavenumber decrease of the CC stretching mode is much higher than in the case of benzophenone. The considerable downshift of the CC stretch wavenumber is consistent with the lowering of the ring CC bond order due to the filling of the  $\pi^*$  orbital. Hence, these results clearly imply the  $\pi\pi^*$  character of  $T_1$  9-fluorenone in accordance with literature data.<sup>[71,72]</sup> The discussed vibrational spectroscopic properties of benzophenone and 9-fluorenone reflect the different photochemical reactivities of both molecules. The lowest excited triplet state of benzophenone is known to be highly electrophilic, and very active in the photochemical hydrogen

**Table 2.** CC and CO stretching wavenumbers (cm<sup>-1</sup>) of the  $S_0$  and the  $T_1$  states of benzophenone and 9-fluorenone. Additionally, the wavenumber shifts (cm<sup>-1</sup>) of the corresponding modes upon going from  $S_0$  to  $T_1$  states are listed. The vibrational wavenumbers of benzophenone have been determined by Tahara et al..<sup>[47,48]</sup>

	Benzophenone			9-Fluorenone		
	$S_0$	$T_1$	$T_1-S_0$	$S_0$	$T_1$	$T_1-S_0$
CO stretch	1665	1222	- 443	1720	1505	- 215
CC stretch	1600	1540	- 60	1600	1480	- 120

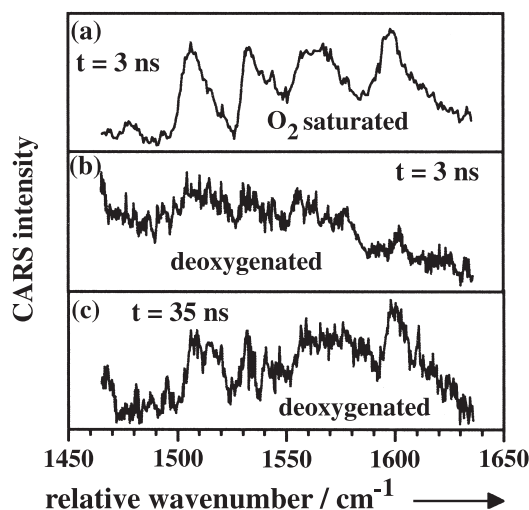


abstraction.<sup>[47,48]</sup> The photoreduction by alcohols and formation of the benzophenone ketyl radical is a typical example of such reactions. In contrast,  $T_1$  9-fluorenone does not react with alcohols under ordinary conditions.<sup>[73]</sup>

The investigation of photophysical and photochemical properties of polycyclic aromatic hydrocarbons and their derivatives has received considerable attention from both experimental and theoretical points of view.<sup>[74]</sup> In particular, quantitative information on quantum yields and lifetimes of the lowest excited triplet states of these compounds have become available by means of transient absorption spectroscopy.<sup>[62,75]</sup> A special feature in the photophysics of polynuclear aromatic compounds is the relatively long time duration of several nanoseconds required for intersystem crossing into the triplet manifold in deoxygenated solutions.<sup>[75]</sup> Hence, nanosecond time-resolved CARS spectroscopy is a suitable tool for the investigation of the photodynamics of these compounds. During the last two decades, transient resonance CARS spectroscopy has been applied to the investigation of  $S_1$  and  $T_1$  states of pyrene,<sup>[3,76,77]</sup> chrysene,<sup>[3,78,79]</sup> phenanthrene,<sup>[3]</sup> and perylene.<sup>[80]</sup> In the present work, we consider the intersystem crossing process of 1,2-benzanthracene into the lowest excited triplet state using nanosecond time-resolved resonance CARS spectroscopy. The obtained time-resolved resonance CARS spectra of  $T_1$  1,2-benzanthracene clearly demonstrate the influence of the concentration of oxygen in the solution on the quantum yield of triplet state formation.

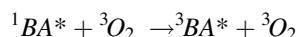
The transient CARS spectrum of aerated *ca.*  $5 \times 10^{-3}$  mol dm<sup>-3</sup> 1,2-benzanthracene in *n*-heptane acquired with a short delay time  $t = 3$  ns between UV excitation and CARS generation is shown in Figure 6a. In order to achieve a very high concentration of oxygen, the employed sample solution was treated for one hour with an ultrasonic bath in an open vessel. From Figure 6a it can be clearly seen that in air-saturated solutions a CARS spectrum of the triplet excited state can be readily obtained even with a short delay time,  $t = 3$  ns, imposed between the exciting pulses of the Nd:YAG laser and the CARS probing process. In contrast to this, no apparent transient CARS signals can be obtained at short delay times of  $t = 3$  ns from an appropriate deoxygenated sample solution which has been filled in argon atmosphere (Figure 6b). At a delay time of *ca.*  $t = 35$  ns, a low population of the triplet excited state becomes detectable (Figure 6c). However, in this case the signal intensities and the signal-to-noise ratios are much lower in comparison with the transient CARS spectrum acquired in an aerated solution at short delay times (Figure 6a). The reason for these observations is well-known in the literature. Since molecular oxygen exhibits a paramagnetic electronic ground state with two unpaired electrons, its presence in the solution accelerates the intersystem crossing rate of





**Figure 6.** CARS spectra with simultaneous irradiation of a (a) air-saturated and (b) deoxygenated solution of 1,2-benzanthracene in *n*-heptane ( $ca. 5 \times 10^{-3} \text{ mol dm}^{-3}$ ) by the third harmonic of the Nd:YAG laser (355 nm). Panel (c) depicts the transient CARS spectrum of a deoxygenated solution of 1,2-benzanthracene in *n*-heptane ( $ca. 5 \times 10^{-3} \text{ mol dm}^{-3}$ ) acquired with irradiation by the nitrogen laser (337 nm); the CARS probing was delayed by 30 to 40 ns. The measurements were performed at a pump laser wavelength of  $\lambda_P = 499 \text{ nm}$ .

1,2-benzanthracene (BA) by bimolecular quenching of the singlet  $S_1$  state according to



simultaneously increasing the triplet quantum yield.<sup>[74]</sup> Hence, the observations mentioned above clearly demonstrate that the observed transient CARS spectrum can be unambiguously assigned to the triplet  $T_1$  state and not the singlet  $S_1$  state. Moreover, the nanosecond time-resolved CARS spectra given in Figure 6 provide an indirect proof that in degassed solutions the intersystem crossing process of 1,2-benzanthracene takes place on a nanosecond time scale. Taking advantage of selective resonance conditions by means of pump laser excitation in the spectral range of the  $S_n \leftarrow S_0$  transition, it should be thus also possible to detect the singlet  $S_1$  state of 1,2-benzanthracene in degassed solutions using transient CARS spectroscopy.

## CONCLUSION

Nanosecond time-resolved resonance CARS spectroscopy is a powerful tool for the Raman spectroscopic investigation of electronic excited states of highly fluorescent molecules. The goal of the present work was to demonstrate the capability of this method to study the vibrational wavenumbers, the electronic configuration and the lifetime of several triplet excited molecules. Future experiments may give further insight into the relations between vibronic structure and the physical and chemical properties of photoinduced transient species.

Besides vibrational spectroscopic information, nanosecond time-resolved CARS spectroscopy is well suited for the unambiguous determination of the third-order susceptibility parameters of triplet excited states, as we showed previously.<sup>[41]</sup> This application has formed the basis for further investigations of the lowest excited triplet state of anthracene in our laboratories. In particular, the dispersion of the complex-valued CARS amplitude of the most intense CC stretch vibration of T<sub>1</sub> anthracene around 1365 cm<sup>-1</sup> is part of an ongoing study, and shows interesting results that were published elsewhere.<sup>[81]</sup>

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