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Picosecond photoinduced formation of a radical cation: CARS and transient absorption studies of 1,4-diphenylbutadiene

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Abstract

We report the direct observation of the formation and stabilization of the radical cation of 1,4-diphenylbutadiene (DPB) in polar solvents (acetonitrile, linear alcohols) by picosecond "pump–probe" and polarization-sensitive resonant CARS (Coherent Anti-Stokes Raman Scattering) experiments. For the first time, we have observed the formation and stabilization rate of the DPB radical cation which occurs on a 10–20 ps timescale. We confirm that the formation process is mainly monophotonic. © 1997 Elsevier Science S.A.

Keywords: CARS; Cation formation; Diphenylpolyenes; Excited states; Femtosecond; Non-linear optics; Transient absorption; Vibrational spectroscopy

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1. Introduction

The photophysical properties of diphenylpolyenes on UV excitation have been studied extensively [1] owing to the role of this molecular family as a model for photoisomerization processes or visual transduction. Of the possible processes which can occur after excitation, direct photoionization and the production of ion radicals have been observed at nanosecond time resolution [2]. Although the excitation wavelength is well below the photoionization threshold, it has been shown unambiguously that, in polar solvents, the direct formation of radical ions occurs. It has been demonstrated that this process involves a decrease, by solvent interaction, in the ionization threshold, which allows direct photoionization [2–4]. However, owing to the nanosecond time resolution, the formation rate has not been measured directly. It would be interesting to observe this process directly to obtain information, for example, on the solvent dependence of the formation rate. Indeed, it has been suggested by Hirata and Mataga [5] that, for *p*-phenylenediamine in alcohols, the formation rate is directly correlated with the dielectric relaxation time of the solvent. It is therefore interesting to determine whether this property also holds for diphenylpolyenes.

In this paper, we describe subpicosecond time-resolved degenerate CARS (Coherent Anti-Stokes Raman Scattering) and transient absorption experiments. For the first time, we have observed, on a subpicosecond timescale, a direct monophotonic ionization process on excitation at 300 nm of 1,4-diphenylbutadiene (DPB) in polar solvents.

2. Experimental section

2.1. *Laser sources and "pump–probe" experiments*

Our laser set-up and the "pump–probe" experiments, described previously [6], are based on a hybrid mode-locked dye laser (Coherent 702) associated with an actively mode-locked continuous wave (cw) pumped Nd^{3+}:YAG laser (Coherent "Antares-76"), a dye amplifier (Continuum "PTA 60") and a regenerative amplifier ("Continuum RGA 10"). This system generates 500 fs pulses (1.5 mJ; repetition rate, 10 Hz) at 600 nm.

The "pump–probe" experiments allow for the determination of the transient absorption spectra on a picosecond timescale. Typically, 200 signal shots were accumulated with and without UV excitation of the sample, and the transient optical density was calculated. To ensure kinetics free from rotational reorientation effects, the angle between the polarizations of the pump and probe beams, which were linearly polarized, was set to the "magic angle" of 54.7° [7].

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2.2. *Polarization-sensitive CARS set-up*

In addition to transient absorption experiments, we also used the time-resolved degenerate (two-colour) polarization-sensitive CARS technique. Two pulses are required to generate the CARS signal: one pulse (the so-called "pump beam") at fixed frequency ω_1 and the second pulse (the so-called Stokes beam) at variable frequency ω_2, such that $\omega_1-\omega_2=\Omega$, the molecular vibrational frequency to be observed. The CARS signal is then generated at the frequency $\omega_{CARS}=2\omega_1-\omega_2$ in a well-defined propagation direction fixed by the phase matching conditions. The CARS experimental set-up has been described in detail in Ref. [8].

As described elsewhere [8], to improve the sensitivity of the experiments and to suppress the non-resonant contributions, the polarization directions of the various incoming pulses were carefully controlled and adjusted by means of wave-plates and high-quality Thomson–Glan prisms. The spectral resolution of the detection system was 2 cm^{-1}, well below the experimental spectral resolution imposed by the pulse duration.

The CARS spectra were recorded according to the following procedure. Without UV excitation of the sample, the CARS signal was optimized and recorded by adjusting the propagation directions and delays between ω_1 and ω_2 pulses and by accumulating 200 laser shots. The UV pulse was then sent to the sample and the CARS signal was recorded again with 200 laser shots for a given delay Δt_{uv} between the ω_{uv} pulse and the ω_1, ω_2 pulses. The same procedure was repeated for different delays Δt_{uv} to study the time evolution of the CARS spectrum of the excited sample.

The calculation of the CARS spectral parameters was made using a CARS fitting program which optimizes the vibrational wavenumber, bandwidth and amplitude for each Raman band [9,10].

2.3. *Materials*

DPB was used as received from Aldrich Chemical Company. UV spectrophotometric grade solvents (Aldrich Chemical Company) were employed. The DPB solutions were prepared in various polar (linear alcohols, acetonitrile, propylene carbonate) and non-polar (heptane) solvents with concentrations near 10^{-3} M.

3. Results and discussion

3.1. *Transient absorption*

The general shape of the absorption spectrum of excited DPB in the non-polar solvent heptane is a strong and broad absorption band (centred near 650 nm) corresponding to $S_1\rightarrow S_n$ absorption, as observed previously [11]. Fig. 1(a) shows the typical transient absorption spectra of excited DPB in *n*-heptane solution obtained by the "pump–probe" method at different delays Δt_{uv} after UV excitation at 300 nm. No strong spectral changes are observed under these experimental conditions. Fig. 2(a) shows the transient absorption kinetics at the maximum of the absorption band. The data are well reproduced with a simple exponential decay convoluted with a gaussian function simulating the excitation pulse. An excited state lifetime τ_{S1} of 575 ± 25 ps can be deduced, well within the range of other measurements in non-polar solvents [12].

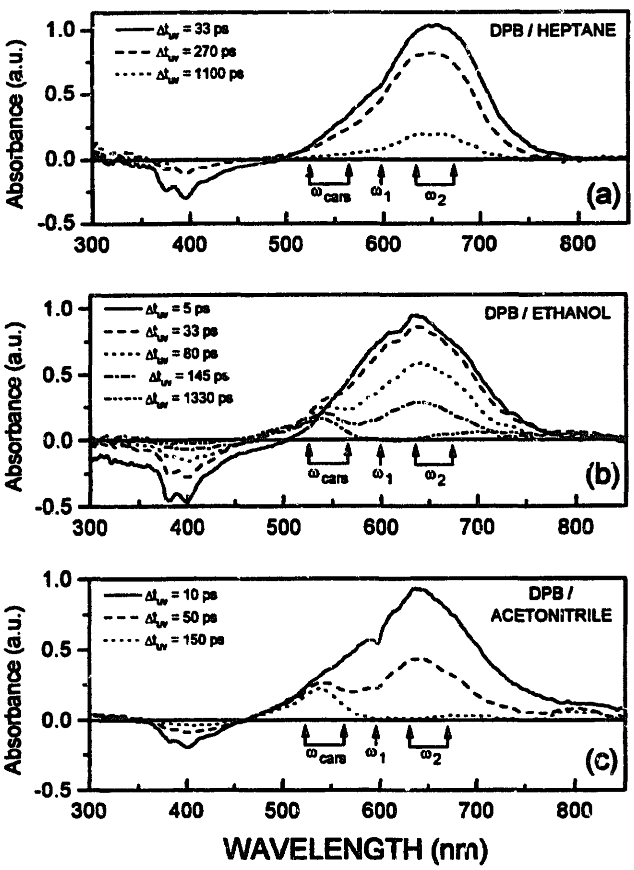

Fig. 1. Transient $S_1\rightarrow S_n$ absorption spectra of DPB obtained by "pump–probe" experiments for different delays (Δt_{uv}) after UV excitation. Wavelengths used for CARS experiments are indicated by arrows. (a) In *n*-heptane (10^{-3} M). (b) In ethanol (10^{-3} M). (c) In acetonitrile (10^{-3} M).

In polar solvents, the behaviour is different (see Fig. 1(b), Fig. 1(c) and Fig. 2(b), Fig. 2(c)). As previously observed [13,14], lifetimes are shorter than in non-polar solvents (see Table 1). This shortening has been attributed to a lowering of the isomerization barrier in polar solvents which opens up a non-radiative decay channel.

The S_1 excited state lifetime was calculated at the maximum of the strong $S_1\rightarrow S_n$ absorption band centred near 650 nm (see Table 1) as shown in Fig. 2(b) ($\tau_{S1}=80\pm10$ ps in ethanol) and Fig. 2(c) ($\tau_{S1}=25\pm5$ ps in acetonitrile). In addition to the shortening of the S_1 lifetime near 650 nm, transient absorption experiments reveal a new behaviour which is apparent for long periods after excitation. For example, as shown in Fig. 1(b) and Fig. 1(c), the transient absorption spectra of excited DPB, obtained in polar solvents, reveal

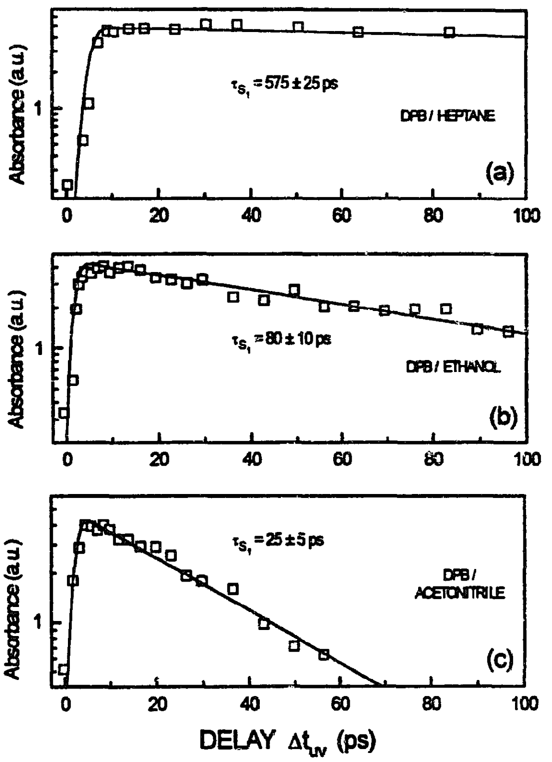

Fig. 2. Kinetics of the intensity of the 650 nm absorption band as a function of the UV pulse delay: (a) in *n*-heptane (10^{-3} M); (b) in ethanol (10^{-3} M); (c) in acetonitrile (10^{-3} M).

an unusually long-lived (much greater than 1 ns) band centred near 540 nm with considerable amplitude. Unfortunately, owing to the strong overlap between this band and the main broad $S_1 \rightarrow S_n$ band, it is very difficult to deduce a reasonably accurate formation rate (risetime) for this new band, which only appears in polar solvents. These results are consistent with the studies of DPB cation formation by Dudev et al. [2] and Hug et al. [15] in polar solutions. These workers measured the $DPB^{\cdot +}$ radical cation absorption spectra and reported wavelength maxima peaking at 545–550 nm, i.e. similar to the new band observed in our transient spectra. Moreover, they estimated the lifetime of the cation to be about 500 ns [2]. According to these results and the similarities with our observations, it is quite natural to attribute this new band to cation formation. However, with regard to the exact mechanism of formation of the radical cation, these partial results cannot lead to precise interpretations.

Nevertheless, the pump–probe results show that the formation of the $DPB^{\cdot +}$ cation radical seems to be on a picosecond timescale, according to the transient spectra obtained after 20 ps (Fig. 1(b) and Fig. 1(c)). For a better understanding of the $DPB^{\cdot +}$ radical cation formation, we performed CARS experiments to obtain vibrational rather than electronic spectra.

3.2. CARS experiments

It is well known that spontaneous and coherent Raman spectroscopy techniques are reliable tools for obtaining detailed information about the structural changes and dynamics of fast molecular processes [16,17]. By using the strong enhancement of the CARS signal when the CARS wavelengths are resonant with the electronic absorption [18,19], we attempted to observe the modifications of the Raman bands after UV excitation, which could be attributed to the cation radicals of DPB.

Typical transient resonance CARS spectra of excited and non-excited DPB dissolved in *n*-heptane (measured in the 1000–1700 cm^{-1} anti-Stokes region) are shown in Fig. 3(a), without any correction other than subtraction of the ambient light background. The electronic resonance conditions can be seen in Fig. 1(a), where arrows on the transient absorption spectra indicate the wavelengths of the ω_1 and ω_2 pulses and the ω_{CARS} signal. All the Raman bands in Fig. 3(a) without UV excitation are due to *n*-heptane according to the following assignments: 1280 cm^{-1} (in-phase $-(CH_2)_n-$ twist); 1430 cm^{-1} (CH_3 asymmetric bending). As mentioned above, we did not observe any Raman band from the DPB ground state S_0.

After UV excitation, new Raman bands develop superimposed on the Raman solvent bands, which are due to UV excitation. The main new band at 1580 cm^{-1} has previously been observed and assigned to the vibrational mode (C=C stretch) of the S_1 excited state of DPB [20,21]. The other previously observed bands located in the 1100–1300 cm^{-1} range [20,21] are not well resolved in the spectrum, because they overlap with the solvent Raman bands and are strongly

Table 1
Maximum wavelengths (λ_{max}) of the transient spectra and lifetimes (τ_{S1}) of the S_1 excited singlet state measured at λ_{max} of the S_1–S_n absorption spectra

Solvent (permittivity)	Absorption S_1–S_n λ_{max} (nm)	Lifetime τ_{S1} (ps)	Cation absorption band λ_{max} (nm)	Risetime of 1580 cm^{-1} Raman band (ps)	Lifetime of 1580 cm^{-1} Raman band (ps)	Risetime of 1580 cm^{-1} band shift (ps)
Heptane ($\epsilon \approx 0$)	650	575 ± 25	No cation	< 1[a]	550 ± 50	No shift
Ethanol ($\epsilon = 25.3$)	640	80 ± 10	540	15 ± 3	> 3 ns	20 ± 5
Methanol ($\epsilon = 33.5$)	650	55 ± 10	535	13 ± 3	> 3 ns	19 ± 5
Acetonitrile ($\epsilon = 37.5$)	640	25 ± 5	540	10 ± 3	> 3 ns	20 ± 3
Propylene carbonate ($\epsilon = 66$)	650	50 ± 10	545	14 ± 3	> 3 ns	20 ± 5

[a] Limited by the time resolution of the experimental set-up.

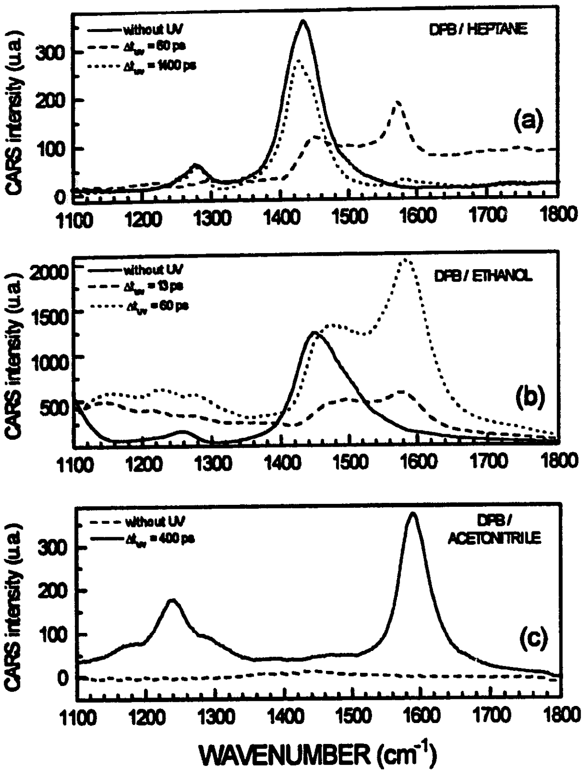

Fig. 3. Transient polarization-sensitive CARS spectra of DPB at different delays (Δt_{uv}) after UV excitation. As explained in the text, the non-resonant CARS signal has been suppressed. The solvent contribution is shown by the spectrum obtained without UV excitation. (a) In *n*-heptane (3.5×10^{-3} M). (b) In ethanol (2.5×10^{-3} M). (c) In acetonitrile (2×10^{-3} M).

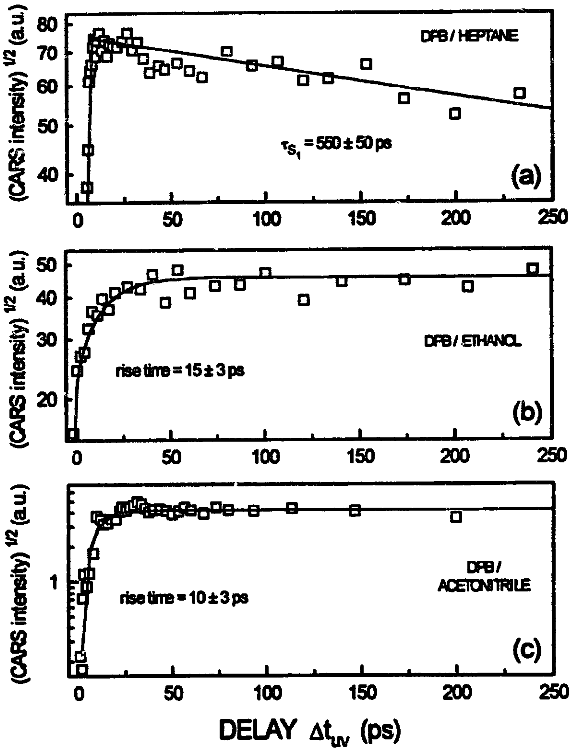

Fig. 4. Kinetics of the square root of the intensity of the DPB CARS signal of the 1580 cm^{-1} band after corrections for the re-absorption process by scaling to the solvent bands (see text): (a) in *n*-heptane (3.5×10^{-3} M); (b) in ethanol (2.5×10^{-3} M); (c) in acetonitrile (2×10^{-3} M).

hidden. The intensity of the solvent Raman bands decreases on excitation because of the resonance conditions. These bands appear at wavelengths corresponding to the strong absorption of the excited state S_1 of DPB (see Fig. 1(a)); their intensities are reduced by re-absorption of the CARS signal by excited DPB molecules. We carefully checked that no differences were observed in the CARS spectra of the pure solvent with and without UV excitation.

The observed kinetics of the 1580 cm^{-1} band are shown in Fig. 4(a). Re-absorption effects were taken into account by scaling the spectra to the 1430 cm^{-1} solvent band which was also disturbed by the re-absorption process as explained above. In good agreement with the pump–probe results, the square root of the intensity of the 1580 cm^{-1} band exhibits a 550 ± 50 ps monoexponential decay correlated with the excited DPB lifetime deduced from the transient absorption experiment (see Table 1). We can therefore be confident that the Raman bands of excited DPB are observed.

The situation is quite different in polar solvents (see Fig. 3(b) and Fig. 3(c)). In Fig. 3(b), without excitation, the well-known Raman bands of ethanol located at 1275 cm^{-1} (in-phase CH_2 twist) and 1450 cm^{-1} (CH_3 asymmetric bending) are clearly visible. On UV excitation, new Raman bands appear which can be unambiguously attributed, on the basis of previous work [20,21], to the excited DPB vibrational modes. The mode observed in heptane solution at 1580 cm^{-1} and the two vibrational modes at 1170 cm^{-1} (C–H bending) and near 1230 cm^{-1} (corresponding to the commonly called "broad structure" [22]) are clearly visible in ethanol, because the overlap with the solvent band is smaller in ethanol than in heptane. However, kinetic studies reveal unexpected behaviour not observed in heptane. In contrast with *n*-heptane solution, the kinetics of the intensity of the strong 1580 cm^{-1} band (Fig. 4(b)) cannot be correlated with the DPB S_1 lifetime (80 ps) deduced from transient absorption measurements. Indeed, a risetime of 15 ± 3 ps is observed, followed by an extremely slow decay (more than 1 ns) which can be correlated with the $DPB^{\bullet+}$ radical cation time evolution, as observed in transient absorption experiments. We also deduced from this behaviour that the contribution of the DPB S_1 Raman band in the 1580 cm^{-1} spectral range is negligible, since there is no short decay component (80 ps) which can be assigned to the S_1 state decay time (80 ps, see Table 1). Moreover, during the first few picoseconds after excitation, the slow risetime observed reinforces the idea that mainly radical cation formation is observed. Indeed, a vibrational band due to excited DPB should give an instantaneous risetime (limited by the pulse duration as observed in *n*-heptane solution). From these different observations, we may conclude that radical cation formation occurs in a time shorter or equal to 15 ± 3 ps. However, the band near 1580 cm^{-1}, just after UV excitation at short times, is probably a mixture of a strong $DPB^{\bullet+}$ and a weak DPB S_1 vibrational band. Therefore it is interesting to seek spectral changes in the vibrational band near 1580 cm^{-1}.

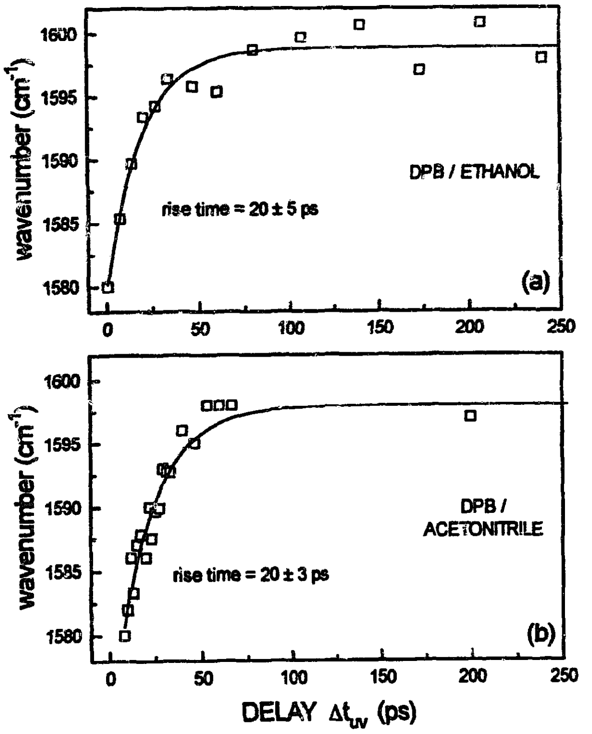

Fig. 5. Spectral change of the maximum of the DPB 1580 cm^{-1} band as a function of the UV pulse delay (Δt_{uv}) after deconvolution with the CARS fitting program (see text). The full line is obtained from a monoexponential fit. (a) In ethanol (2.5×10^{-3} M). (b) In acetonitrile (2×10^{-3} M).

Using the CARS fitting program, we deconvoluted the 1580 cm^{-1} band from the 1450 cm^{-1} solvent band to obtain the spectral development of the former band. In the fitting procedure, non-resonant parameters from the ground state, polarization and vibration resonant phases of the S_1 vibrations were first introduced and assumed to be constant. As shown in Fig. 5(a) and Fig. 5(b), this procedure clearly reveals a time-dependent shift of the band from 1580 to 1600 cm^{-1} with an accuracy after deconvolution of about 5 cm^{-1}. The frequency reaches a maximum in about 60 ps (Fig. 5(a)), with an exponential growth of the 20 ± 5 ps risetime, and no further shift is observed thereafter. This is in good agreement with Dudev et al. [2] who measured the CARS spectrum of the DPB cation radical and observed a shift of 23 cm^{-1} between DPB S_1 and DPB$^{\bullet+}$ bands located at 1575 cm^{-1} and 1598 cm^{-1} respectively.

To confirm experimentally the presence of this shift in polar solutions, the same measurements were performed in other polar solvents. As shown in Table 1, in all polar solvents studied and within experimental uncertainty, the same slow risetime and frequency shift of the 1580 cm^{-1} band are measured without any significant differences between the solvents. In all polar solvents, the decay of this band is longer than 1 ns, showing that it cannot be assigned to the DPB S_1 excited singlet (see Table 1). This behaviour is therefore peculiar to polar solvents. The available spectral resolution, however, does not allow us to separate and to distinguish formally between these two bands. Nevertheless, this shift can be attributed to the evolution of the excited DPB molecule interacting with the polar solvent and leading to the formation of the radical cation DPB$^{\bullet+}$.

In addition, just after excitation from S_0 to S_1, various processes can influence the CARS signal and lead to spectral changes.

1. Intramolecular vibrational relaxation (IVR) may play a role in the first few picoseconds after excitation if the photon energy of excitation is well above the 0–0 electronic transition S_0–S_1 [23], as is the case in our experiments. In the case of a large energy excess, the molecule after excitation has a high vibrational temperature which does not correspond to the solvent temperature. Therefore a cooling process may occur by vibrational coupling with the low-frequency modes of the solvent until thermal equilibrium with the surrounding solvent molecules is reached. Such thermalization occurs on a 5–20 ps timescale for short diphenylpolyenes, depending on the solvent [24], and may lead to a spectral shift of the vibrational band.
2. After excitation, the molecular conformation must change to accommodate the excited state reorganization. Bond lengths and bond angles may change during this reorganization, and so the peak positions and bandwidths of the different vibrational bands must change. Such processes may also exist in non-polar heptane solution. We did not observe such a shift in heptane solution, thus showing that these processes cannot explain the shift observed in polar solvents.

It is also interesting to note that the contribution of the Raman bands of the excited singlet state S_1 of DPB is very weak in the CARS signal. Within experimental error, there is no short decay component corresponding to the lifetime of S_1 of DPB in the decay of the Raman line. Such a short component would be observed if the contribution of the S_1 state to the CARS signal was important. Therefore the main contribution to the CARS signal is due to the radical cation which obscures the possible S_1 contribution. Consequently, the hyperpolarizability of the DPB$^{\bullet+}$ radical cation (involved in CARS signal generation) is larger than that of DPB S_1, this difference originating from the resonance conditions. It is interesting to note that the ω_{cars} frequency exactly matches the maximum of the radical cation absorption spectrum. Although the ω_1 and ω_2 frequencies of the generating CARS pulses are out of resonance for long periods after excitation (when the S_1 state population is relaxed as shown in Fig. 1), the CARS signal from the cation remains strongly enhanced by resonance on the ω_{cars} frequency, which corresponds to the absorption maximum of DPB$^+$ (545 nm).

3.3. Formation process of the DPB cation radical

To identify the formation process, we studied the dependence of both the transient absorption and the CARS signal of the DPB$^{\bullet+}$ radical cation on the UV excitation power. Fig. 6(a) shows the dependence of the DPB$^{\bullet+}$ absorption band (545 nm) in acetonitrile on the excitation energy I_{uv}.

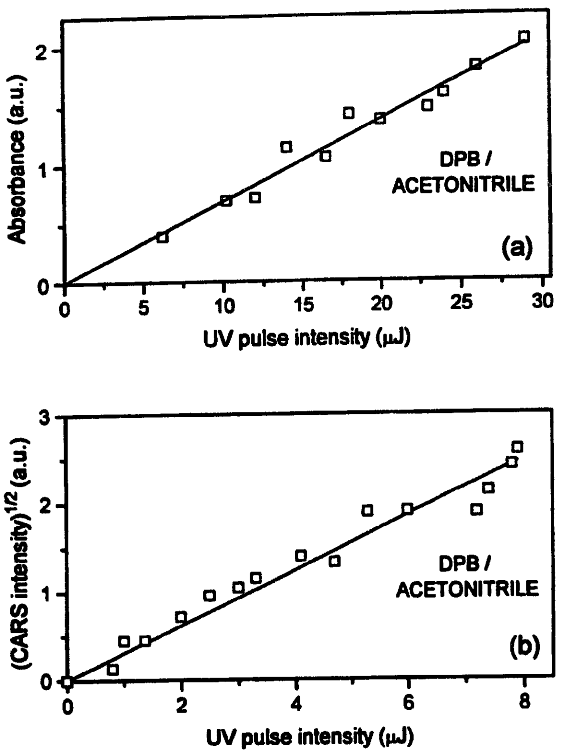

Fig. 6. (a) Absorbance of the cation absorption band (540 nm) of DPB in acetonitrile (10^{-3} M) as a function of the UV pulse energy. The UV pulse delay is fixed to 150 ps. (b) Square root of the intensity of the 1580 cm^{-1} CARS band as a function of the UV pulse energy. The UV pulse delay is fixed to 150 ps and the result is obtained from DPB in acetonitrile (2×10^{-3} M).

The linear relationship between the cation concentration (directly related to the absorbance) and I_{uv} indicates that, within experimental error, the formation process is mainly monophotonic. The same conclusion is deduced from a plot of the square root of the CARS signal intensity at 1580 cm^{-1} (attributed to the $DPB^{\cdot +}$ Raman band) vs. I_{uv} (see Fig. 6(b)). Within the experimentally available energy range, we did not observe any deviation from linearity, indicating that, in this range, the influence of a biphotonic process, as observed in 1,6-diphenylhexatriene (DPH) polar solutions, superimposed on the monophotonic process is very weak and cannot be revealed in the present experiments [3].

The above findings suggest that we are dealing with a solvent-assisted, monophotonic process. In non-polar solvents, the monophotonic formation process of the radical cation is not observed, but it occurs in polar solvents. All our data support previous results concerning, for example, the ionization process of excited *p*-phenylenediamine [5], DPB, DPH and 1,8-diphenyloctatetraene (DPO) [2–4,25], which have been explained as follows. The formation of the ion pair is promoted by a decrease in the ionization energy in polar solvents. In our experiments, ionization occurs at 300 nm (4.13 eV), but it has been shown that it also occurs at lower excitation energy (for example, by Kamisuki et al. [3,4] at 337 nm in acetonitrile). After UV excitation of the DPB molecule, ejection of an electron (formation of a solvated electron e_s^-) can occur in the unrelaxed S_1 state. The ejected electron is then trapped (and the ion pair is then stabilized) by the polar solvent surrounding the excited molecule. This process occurs on a finite timescale which should be correlated with the dielectric solvent relaxation time [26]. In non-polar solvents, the ionization threshold is probably too high to allow photoionization at 300 nm, or the ejected electron is not stabilized by the solvent and therefore recombines immediately on a femtosecond timescale as shown in Ref. [27], i.e. the ion pair is not stabilized. Assuming that the intensity, risetime and shift of the Raman band at 1580 cm^{-1} are correlated with the ion pair formation and stabilization, we deduce from our results that the $DPB^{\cdot +}$ radical cation is formed and stabilized in alcohols and acetonitrile in a time shorter or equal to 15–20 ps. This result deserves some comments.

The dielectric relaxation times of the solvents studied vary from less than 1 ps in acetonitrile to several tens of picoseconds in alcohols [23,24]. If the dielectric solvent relaxation alone controls the formation and stabilization rate of the radical cation, we should observe changes when different solvents are used. However, we did not see such a variation in our experiments in various polar solvents (alcohols, acetonitrile, propylene carbonate; see Table 1). This shows that the formation and stabilization rate are not controlled by the dielectric solvent relaxation alone. To explain this behaviour, we must take into account other processes on a timescale of 10–20 ps. The most reasonable is to consider the thermal equilibrium of the solvent shells after excitation, as suggested by Hirata et al. [28]. The radical cation is formed with an excess of energy which can be equilibrated by energy exchange with the solvent and cooling by thermal diffusion in the bath. Such processes typically occur on this timescale [23]. It is therefore reasonable to consider that full stabilization of the radical cation, corresponding to the intensity and shift plateau (see Fig. 4(b), Fig. 4(c) and Fig. 5(a), Fig. 5(b)), occurs when thermal equilibrium is reached, after the formation and intramolecular vibrational relaxation of the radical cation. This does not mean that the formation process may not be faster and controlled by dielectric solvent relaxation, but that the observed formation rate is determined by the slow steps, i.e. vibrational relaxation and solvent cooling, which should be investigated further for confirmation.

4. Conclusions

In this work, we have observed directly, on a picosecond timescale, monophotonic ionization of DPB in polar solvents using a 500 fs UV pump pulse at 300 nm. The transient absorption spectrum of the cation radical of DPB has been measured and, for the first time with a picosecond time resolution, the CARS spectra under resonant conditions have been obtained. From these experiments, we deduce a formation and stabilization rate of 10–20 ps, which does not correlate with the solvent dielectric relaxation time. We suggest that mechanisms other than solvent dielectric relaxation must be taken into account, in particular the vibrational relaxation and solvent thermal cooling processes. We have also demonstrated that, under resonant conditions, polarization-sensitive CARS spectroscopy is a powerful tool for observing directly the photophysical behaviour of a molecule after excitation.

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