ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 99 (1996) 13-21

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

Photoionization mechanism of α,ω-diphenylpolyenes in polar solvents investigated by using coherent Raman spectroscopy

Toshio Kamisuki *, Chiaki Hirose

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226, Japan

Received 20 December 1995; revised 21 March 1996

Abstract

By applying coherent Raman spectroscopy of nanosecond laser pulses the solvent-induced photoionization of some all-*trans*-α, ω-diphenylpolyenes has been investigated in resonance with the transient absorption bands of the radical ions in polar solvents having different electron-donating and electron-accepting properties. The experimental results reported so far are summarized and a whole picture of the mechanism of the photoionization is derived.

Keywords: Photoionization; Raman spectroscopy; Nanosecond laser pulse

1. Introduction

The shorter polyenes serve as a model compounds for the chromophores as their transient species and ion radical species are expected to play key roles in mediating the interaction of light with these molecules. Photoionizations have been studied so far mainly by using electronic spectroscopy. Vibrational spectroscopy, however, has been used in fewer cases for the study of photoionization.

The vibrational spectra of short all-*trans*-α, ω-diphenylpolyenes (Ph-$(CH{=}CH)_n$-Ph; $n = 2$–5, DPP) in the lowest singlet state S_1 and lowest triplet state T_1 have been observed by using the coherent anti-Stokes Raman scattering (CARS) or coherent Stokes Raman scattering (CSRS) technique [1]. Recently the transient resonance CARS or CSRS spectra of the radical cation and anion have been observed for all-*trans*-1,4-diphenyl-1,3-butadiene (DPB) [2–4], all-*trans*-1,6-diphenyl-1,3,5-hexatriene (DPH) [4–6], all-*trans*-1,8-diphenyl-1,3,5,7-octatetraene (DPO) [7]. The spectra illustrated the excellent capability of the CARS method to discriminate different transient species because of intrinsically higher resolution of vibrational spectra in solution compared with that of electronic spectra, selectivity of electronic resonance conditions, and high rejection capability of coexisting fluorescence.

A number of investigations of photoionization in solutions using transient electronic absorption and/or photoconductivity excitation spectroscopies have been reported. Most of them were focused on the formation of cation radicals, and the results were interpreted by a photoionization mechanism in which cation radicals are produced in solution via solute(in an excited state)-solvent charge-transfer (CT) type of interaction or through a direct electron ejection from a state lying above the ionization threshold. It was reported that the photoinduced ionization of aromatic molecules in acetonitrile occurred with monophotonic excitation for a variety of compounds which absorb at a relatively short wavelength (249 nm) [8,9]. The presence of radical ions was established by transient absorption spectroscopy following nanosecond laser excitation, but in some cases the assignment is ambiguous, when the radical cation and radical anion show similar spectra in frequency and band profile, as in the cases of some alternant hydrocarbons such as naphthalene [10]. Guerry-Butty et al. [11] reported that the anion radical of chloranil was observed in acetonitrile by excitation of nitrogen laser pulse [11]. They suggested that the mechanism of the radical anion formation is due to an electron transfer reaction of chloranile in the T_1 state with acetonitrile.

Simultaneous formation of the transient radical cation and anion of perylene was studied by using the electronic spectroscopy with a flash technique in polar solvents for the first time by Leonhardt and Weller [12]. The photoinduced electron-transfer processes of perylene in polar solvents have been the object of several investigations [13–16] which have led to contradictory conclusions. Konuk et al. [15] reported a study of photoionization of perylene in polar solvents such

---

* Corresponding author.

PII S1010-6030(96)04384-5

as acetonitrile and dimethylformamide by using transient absorption method. They proposed a mechanism for the photoionization process namely that an electron is injected from perylene to the electrophilic solvent (acetonitrile) and a hole is injected from perylene to the nucleophilic solvent (dimethylformamide). Different lifetimes of the species in the solutions have not been referred to partly because of low resolution of the reported transient spectra and their temporal behavior. Vauthey et al. [16] concluded that the electron-transfer reactions of photoexcited perylene in acetonitrile illustrated the range of unimolecular and bimolecular processes which were in principle feasible in acetonitrile and were all monophotonic processes. The effect of the solvent properties on the photoionization process has not been studied in detail. Detailed investigations of other relevant systems and/or by other spectroscopic methods, are therefore needed to generalize or to promote a better understanding.

The photoinduced radical ions (either or both cation and anion) of DPB, DPH and DPO have been detected in polar solvents on transient resonance CARS (or CSRS) by selecting appropriate solvents such as acetonitrile, dimethylformamide and dimethyl sulfoxide [2–7]. The solvent effects on the formation ratios and lifetimes of both the ions of DPB, DPH and DPO have been found by measuring the changes in the transient CARS (or CSRS) signals on the solvents and on delaytimes between pump and probe pulses.

Isomerization of diphenylpolyenes is recognized as an important photochemical pathway [17]. Recently photochemical isomerization of the cation radicals of DPB, DPH and DPO has been investigated [18,19]. Wang and McGimpsey [19] concluded that by two-laser (UV + 590 -nm dye laser) nanosecond flash photolysis (all-*trans*) $DPH^{\cdot+}$ isomerizes to a *cis* form which, in turn, thermally isomerizes to the *trans* form. In the case of the resonance CARS (CSRS) measurements a photoisomerization process may compete with photoionization process of DPP in the ground state or the transient state. The frequencies of the dye lasers for CARS (CSRS) were selected rigorously to be resonant with the corresponding absorption peak of $DPP^{\cdot+}$ (or $DPP^{\cdot-}$) assigned to the all-*trans* form [20–23]. The observed data on the radical ions of DPP [2–7] have to be attributed to the all-*trans* forms.

In this review article the experimental results of the solvent-induced photoionization of DPP by using the transient resonance CARS (CSRS) method published so far are summarized and the mechanism of the processes is discussed to derive a whole picture of the mechanism. In the next section the experimental outline of the observations of the transient resonance CARS (CSRS) spectra and of their temporal behaviors is presented. In Section 3 the theoretical background of CARS and CSRS is briefly outlined to ensure easy understanding of the experimental results. Then in Section 4 the experimental results reported so far are given and discussed. The proposed photoionization mechanism for DPP is summarized to derive a whole picture of the mechanism.

2. Transient resonance coherent anti-stokes Raman scattering (coherent stokes Raman scattering) experiments

Molecular transient species are populated by UV pulse photoexcitation in the lowest singlet excited state S_1, lower triplet excited state T_1 or other transient states such as photoionized states. In order to detect CARS spectra of the species with small amounts of population, a considerable (electronic resonance) enhancement must be used by selecting a suitable frequency ω_1 close to the transient absorption peak for CARS (CSRS) measurements. The degree of signal enhancement depends on the population of the transient species, the cross-sections of transient absorption and Raman scattering, and the frequency ω_1. Experimental conditions for observing enhanced spectra of transient species depend on several experimental conditions, which determine the above factors, such as the solute concentration of the starting solution, the excitation power, the focusing condition of excitation light pulses, the optical path length of a sample cell, the condition for preventing saturation effects of a detector and CARS generation, and so on.

The experimental setup used to obtain transient resonance CARS spectra has been described in previous papers [24,25]. Briefly, a nitrogen laser (Molectron UV-24; 9 mJ pulse^{-1}; 337 nm, with a 10 ns pulse width) was used to pump two dye lasers which generated ω_1 and ω_2 beams. Part of the UV light emitted by the nitrogen laser was used for photoexcitation of the samples when no delay time was imposed between sample excitation and CARS generation. The pump beam (ω_1), was set in resonance with the absorption bands of the radical ions which lie in the 540–570 nm region for DPB, 580–650 nm for DPH and 650–700 nm for DPO [20–23].

In the time-resolved (pump-probe) CARS (CSRS) measurement, the third harmonic (355 nm) of a neodymium-doped yttrium aluminum garnet laser (Molectron MY-32; 15 ns pulse width) output was used for photoexcitation and the nitrogen laser which pumped the two dye lasers was operated by taking an appropriate delay time (30 ns–2.8 μs) from the 355 nm pulse. Jitter in the delay time was about ± 15 ns. To determine the lifetime of the radical ions, the CARS (CSRS) signals were measured as a function of the delay time.

All measurements were carried out at room temperature. The concentrations of solutes in solutions were of the order of millimolar. Degassed solutions as prepared by repeated freeze-pump-thaw method under vacuum, as well as air-saturated solutions, were used. Typical CARS spectra of the radical ions of DPB as an example are given in Fig. 1.

3. Brief description of (coherent anti-Stokes Raman scattering (coherent Stokes Raman scattering) theory and simulation procedure of profile

In single degenerate (two-color) CARS (or CSRS), the total non-linear polarization $P^{(3)}$ at the anti-Stokes (or

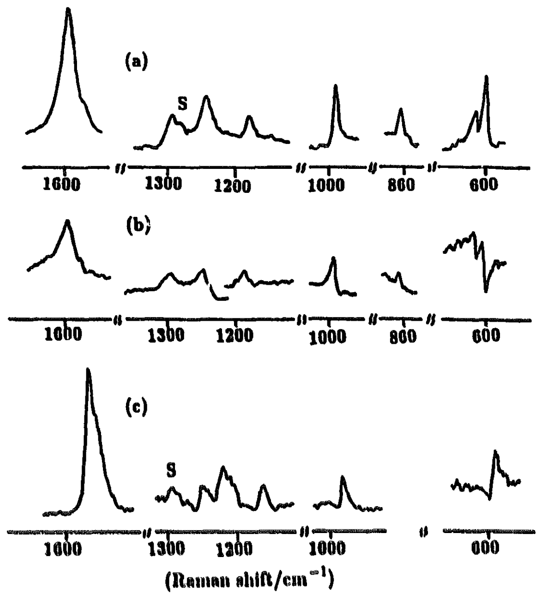

Fig. 1. Transient (radical ion) resonance CARS spectra of DPB in (a) DCNB-*p*-dioxane, (b) acetone and (c) DMA-*p*-dioxane observed under 337 nm UV irradiation. For (a) and (b), $\omega_1 = 18\,300$ cm^{-1} (1700–900 cm^{-1} region) and 18 000 cm^{-1} (900–500 cm^{-1} region) and, for (c), $\omega_1 = 17\,800$ cm^{-1} (1700–900 cm^{-1} region) and 18 000 cm^{-1} (900–500 cm^{-1} region). s denotes the solvent band. (Taken from [2]).

Stokes) frequency $\omega_3 = 2\omega_1 - \omega_2 (\omega_1 > \omega_2$ for CARS or $\omega_1 < \omega_2$ for CSRS) can be written as

$$P^{(3)} = P^{(3)\mathrm{NR}} + P^{(3)\mathrm{R}} = \chi^{(3)} E_1 E_1 E^*_2. \tag{1}$$

where $P^{(3)\mathrm{NR}}$ denotes the Raman non-resonant electronic contribution which arises from both solvent and solute and $P^{(3)\mathrm{R}}$ denotes the Raman resonant term. The susceptibility $\chi^{(3)}(\omega_3)$ derived from the quantum-mechanical study is composed of a large number of terms corresponding to four photon processes usually arranged in the following form [26,27]:

$$\begin{aligned}\chi^{(3)}(\omega_3) = {} & \sum_r \frac{\chi_r}{\omega_{rg} - (\omega_1 - \omega_2) - i\Gamma_{rg}} \\ & + \sum_r \frac{\chi_r'}{\omega_{rg} + (\omega_1 - \omega_2) + i\Gamma_{rg}} \\ & + \sum_t \frac{\chi_t}{\omega_{tg} - 2\omega_1 - i\Gamma_{tg}} \\ & + \sum_t \frac{\chi_t'}{\omega_{tg} + 2\omega_1 + i\Gamma_{tg}}\end{aligned} \tag{2}$$

where ω_{ab} denotes $\omega_a - \omega_b$ and Γ_{ab} is the electronic damping constant. Here the explicit expressions for χ_r, χ_r', χ_t and χ_t' each of which contains transition dipole moments and energy denominators are not given. When dealing with an isolated Raman mode, the susceptibility may be expressed in a compact form:

$$\chi^{(3)}(\omega_3) = \chi^{\mathrm{NR}} + \frac{\chi_{\mathrm{R}}}{(\delta - i\gamma)} \tag{3}$$

where

$$\delta = \omega_{\mathrm{R}} - (\omega_1 - \omega_2) \tag{4}$$

ω_{R} and γ denote the frequency of a Raman transition and a Raman damping constant respectively. Here all the contributions in Eq. (2) except for the resonant term with a particular Raman mode have been packaged into a single notation χ^{NR}. Then the CARS (CSRS) intensity which is proportional to $|\chi^{(3)}|^2$ can be written

$$I(\omega_3 = 2\omega_1 - \omega_2) \propto |\chi^{\mathrm{NR}} + \frac{\chi_{\mathrm{R}}}{(\delta - i\gamma)}|^2. \tag{5}$$

In electronic resonance conditions the Raman resonant term χ_{R}, giving a considerable enhancement and a complicated band shape, has to be taken as a complex value (real and imaginary parts) depending on ω_1 frequencies:

$$\chi_{\mathrm{R}} = R' + iI' = C(R + iI) \tag{6}$$

where C denotes the concentration of the species under study. For real valus of $\chi_{\mathrm{NR}} = B \rangle 0$,

$$I(\omega_3) \propto B^2 + \frac{1}{\delta^2 + \gamma^2}[2BC\,(R\delta - I\gamma) + C^2(R^2 + I^2)] \tag{7}$$

The Raman non-resonance susceptibility $B = \chi^{\mathrm{NR}}$ is nearly frequency independent over the measured Raman frequency range and can be taken as a real constant for the solvents such as n-heptane, acetonitrile, dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and p-dioxane used in this work. So we can use the background contribution from $B = \chi^{\mathrm{NR}}$ of solvent molecules in solution as an internal standard for the intensity of resonance CARS (CSRS) signals which are Raman resonant owing to photoexcited species of the solute molecules. By using Eq. (7), the observed transient resonance CARS (CSRS) spectra in solution can be simulated as a function of relative concentrations of the transient species under consideration using a background signal due to the solvent as an internal standard. Typical example of DPH$^{\cdot+}$ is shown in Fig. 2 [6].

Even in dilute solution (typical concentration is millimole), the χ^{NR} component due to solute molecules may contribute to CARS (CSRS) background signals. This can be estimated by observing (and simulating if necessary) the UV power dependence of one of the intense CARS (CSRS) signals due to solvent molecules with respect to the total background signal. When both the band shape and the relative intensites of a Raman resonant signal due to the solvent and background signals change little, the background signal is essentially attributed to solvent molecules. An example is shown for DPO$^{\cdot+}$ in Fig. 3 [7]. Similar results were obtained for the radical ions of DPB and DPH [2–4].

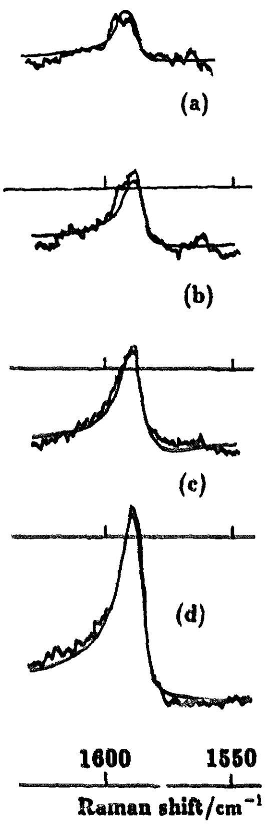

Fig. 2. UV power dependence of the resonance (ω_1 = 16 300 cm^{-1}) CARS signal at 1590 cm^{-1} of $\mathrm{DPH}^{\cdot+}$ in acetone under the relative intensity of UV irradiation of (a) $(0.7)^3$, (b) $(0.7)^2$, (c) 0.7 and (d) 1.0. The corresponding simulations made by assuming a linear dependence of the population of $\mathrm{DPH}^{\cdot+}$ on UV power are shown by smooth curves. (Taken from [6]).

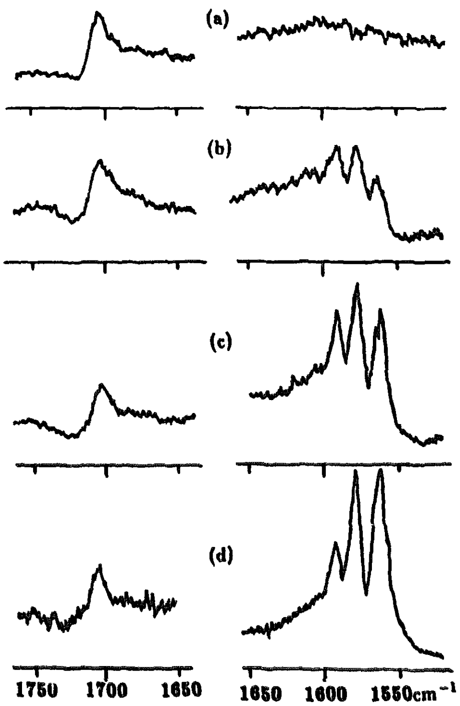

Fig. 3. Change in CSRS signals of $\mathrm{DPO}^{\cdot+}$ (right) and acetone (left) on the intensity of 337 nm UV irradiation. The spectral features observed after 337 nm UV irradiation are for pulse energies of (a) 0 mJ, (b) 0.17 mJ, (c) 0.35 and (d) 0.5 mJ. (Taken from [7]).

4. Summary of results obtained by coherent Raman spectroscopy and discussion

4.1. Overall features of transient resonance coherent anti-Stokes Raman scattering (coherent Stokes Raman scattering) spectra for the radical ions

The transient absorption spectra of the radical ions of DPB, DPH and DPO have been reported in the literature [20–23]. By using the frequencies ω_1 near the respective peaks of the transient (radical ion) absorption bands in the visible region, the transient resonance CARS (CSRS) spectra were observed. For DPB [2] and DPH [3] the peak frequencies and intensity patterns of the transient resonance CARS (CSRS) spectra observed in polar solvents such as acetone and acetonitrile and in dicyanobenzene (DCNB)-p-dioxane were essentially same, by using the frequencies ω_1 near the absorption peaks of the radical cations. In polar solvents such as DMSO and in dimethylaniline (DMA)-p-dioxane, essentially the same transient CARS (CSRS) spectra were observed by using resonance conditions of ω_1 inside the absorption bands of the radical anions. For DPH the transient CARS spectrum in DMA-p-dioxane was quite similar to that of $\mathrm{DPH}^{\cdot-}$ which was produced by chemical reduction with Na metal in a tetrahydrofuran (THF) solution. For DPO the transient resonance CARS (CSRS) spectra have hardly been observed in the systems of DCNB (DMA)-p-dioxane in accord with no observation of exciplex fluorescence, by using the frequency ω_1 in which the CSRS spectra of the radical anion are observed easily in polar solvents such as acetone and acetonitrile [7]. The resonance features and the frequencies of the CSRS spectrum of DPO in DMF are consistent substantially with that of $\mathrm{DPO}^{\cdot-}$ chemically produced by Na reduction in THF [7]. No evidence has been observed so far for conformational isomers except all-*trans* radical ions of DPP by CARS (CSRS).

The spectra assigned to the radical ions of the DPP are clearly different from the transient CARS (CSRS) spectra for the S_1 and T_1 states observed previously in *n*-heptane by the present authors' group [1]. Sometimes in the cases where transient absorption features in frequency and/or time behavior are similar or resemble each other for different electronic species, transient vibrational spectra may differ, requiring a higher resolution capability for identification or discrimination.

4.2. Solvent effects on the radical ion formation

In an attempt to determine the mechanism of photoionization of the DPP in solution, a series of polar solvents with different electron-donating (electron-accepting) properties was chosen [2,4,7].

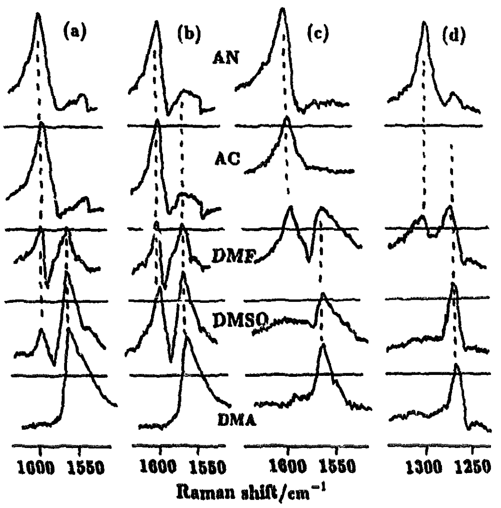

Fig. 4. Change in transient resonance CARS (CSRS) spectra of DPH (a), (b) CARS, $\omega_1 = 15\,300$ cm^{-1}), DPB (c) CARS, $\omega_1 = 18\,000$ cm^{-1}), and DPO (d) CSRS, $\omega_1 = 15\,200$ cm^{-1}) on the polar solvents acetonitrile (AN) and acetone (AC). Delay times between pump UV and probe visible pulses are 0 ns for (a), (c) and (d) and 50 ns for (b). The higher wavenumber signal is the radical cation and the lower wavenumber signal the radical anion in each spectrum.

By choosing an appropriate frequency ω_1 between the transient absorption peak of the radical cation and that of the radical anion for electronic resonance, one can detect simultaneously the CARS (CSRS) signals of both the ions, because the peaks of the transient absorption bands of the ions for DPB, DPH and DPO are not very different from each other Fig. 4 shows the transient resonance CARS spectra of DPH [3], DPB [2] and DPO [7] in different solvents obtained with no delay time ($\tau = 0$) and $\tau = 50$ ns for DPH) between the pump (for sample excitation) and probe (for CARS generation) beams. For DPH and DPB the effects of the solvent on the formation of the radical ions are shown to be substantially the same; in DMF both the radical ions are generated simultaneously (at least within the pulse width of 10 ns), in acetone or acetonitrile the radical cations were mainly observed, and in DMA only the radical anions were detected. For DPO the situation is similar; the main product is the radical cation in acetonitrile and the radical anion in DMSO and DMA, and both the radical ions are generated in DMF. The results imply that the interaction between the solute in an excited electronic state and the solvent molecules surrounding it plays a crucial role in producing either or both of the ion radicals of the DPP in solution and that the electron-donating or electron-accepting power of the solvent determines the production ratio of the radical cation and anion.

The donor number DN and acceptor number AcN which were given by Gutmann [28] have been used successfully to describe the nature of solvents as one of available measures. Gutmann defined the DN by using heat of reaction when $SbCl_5$ was dissolved into various solvents as

$$DN = -\Delta H_{SbCl_5} \tag{8}$$

where a large value of DN means that the affinity between $SbCl_5$ (as a Lewis acid) and a solvent is large, and hence the value of DN is regarded as a measure of the basicity of the solvent. The AcN which is used as a measure of the acidity of a solvent was defined as a percentage of a chemical shift δ of ^{31}P nuclear magnetic resonance of Et_3PO in the solvent with respect to δ of $SbCl_5Et_3PO$ in dichloroethane as follows:

$$\mathrm{AcN} = \frac{(\delta \text{ of } Et_3PO)_{\text{solvent}}}{(\delta \text{ of } SbCl_5Et_3PO)_{\text{dichloroethane}}} \times 100 \tag{9}$$

Kagiya et al. [29] defined the electron-donating power of a solvent as the relative difference $\Delta\nu_D$ (cm^{-1}) of the O–D or the C–O stretching absorption band observed in the compound from that in benzene. The orders of magnitude of the DN and $\Delta\nu_D$ values for the studied solvents are the same, as shown in Table 1. The tendency of the radical cation formations for DPH and DPB as given in Fig. 4 correlates well with DN and $\Delta\nu_D$. No correlation, on the contrary, is found between the AcN values and the behavior of the radical anion formation; in acetonitrile and DMSO with the same AcN value (19.3) the formation behaviors of the radical anions of DPH and DPP are quite different. In the present case the AcN described above is not suitable for describing the nature of the solvents for the radical anion formation.

4.3. UV power dependence of the formation of $DPP^{\cdot +}$

One important advantage of the transient CARS method in solution is that the Raman non-resonant background due to the solvent can be used as an internal standard of the relative intensity for a Raman resonant signal of the transient species. The UV power dependence on the $DPP^{\cdot +}$ photogeneration for sample excitation has been examined in the acetone solutions of DPB [2], DPH [3] and DPO [7]. For UV power of up to 0.01–0.03 mJ at the front of the sample cell, the linear plots of the population density of $DPP^{\cdot +}$ were obtained by simulating the observed spectra with Eq. (7). A cross-check was made for DPH in DCNB (as a strong electron acceptor)-containing *p*-dioxane [3]. The straight lines of the population densities of the both systems vs. UV power indicate that the radical cation of DPH is generated monophotonically via a CT-type interaction between the S_1 solute and a DCNB or acetone molecule(s) located nearby. The situations were similar for DPB [2] and DPO [7].

Subsequent measurement at a higher UV power (from 0.07 to 0.3 mJ) proved, however, that a biphotonic process cannot be excluded for the production of $DPH^{\cdot +}$ [5]. By choosing the frequency ω_1 near the $S_n \leftarrow S_1$ absorption, the transient CARS spectrum of DPH in acetone shows two signals at 998 cm^{-1} and 974 cm^{-1} which originate from $DPH^{\cdot +}$ and DPH in the S_1 state respectively. Under high UV power excitations, the intensity of the $DPH^{\cdot +}$ signal increased significantly much more than that of the S_1 signal, suggesting the second UV photon is used for the additional $DPH^{\cdot +}$ generation.

Table 1
Lifetimes of diphenylhexatriene cation and anion radicals in deaerated and air-saturated [a] solutions and characteristic values of the solvents

Solvent [b]	Lifetime [a] (μs)		DN		AcN From [28]	Dielectric constant	Viscosity
	DPH $^+$	DPH $^-$	From [28]	From [29] (cm^{-1})			
AN	3.2	?	14.1	49	19.3	37.5	0.325
AC	1.[illegible](2.5)	2(<1)	17.0	64	12.5	20.7	0.304
MTHF	0.072	0.1	20.0 [c]	90 [c]	8.0 [c]	7.6 [c]	0.460 [c]
DMF	0.6(2.3)	3.3(1.2)	26.6	107	16.0	36.1	0.802
DMSO	0.38(2.5)	0.73(0.5)	29.8	141	19.3	45.0	1.996
DMA	–	0.1	–	148 [d]		6.9 [d]	3.770 [d]
DCNB [e]	0.11						
DMA [e]		0.061					
1,4-dioxane			14.8	77	10.8	1.88	

[a] The values for air-saturated solutions are given in parentheses.

[b] AN, acetonitrile; AC, acetone; MTHF, methyltetrahydrofuran; DMF, dimethylformamide; DMSO, dimethylsulfoxide; DMA, dimethylaniline; DCNB, 1,4-dicyanobenzene.

[c] Values for THF.

[d] Values for aniline.

[e] 0.1M DCNB or DMA in 1,4-dioxane.

4.4. Time-resolved (pump-probe) measurements

By inspecting the CARS spectra of $DPH^{\cdot +}$ in the polar solvents when delay-times of 0 and 50 ns were imposed between the UV pulse (pump) and dye laser (probe) beams, a slow (relative to the pulse width of 10 ns, 10–50 ns) rise time of the minor (oppositely charged) species was observed for DPH as shown in Figs. 4(a) and 4(b) [4]. For the solutions in electron-accepting solvents such as acetonitrile, acetone and methyl-THF there is no appreciable signal of $DPH^{\cdot +}$ at $\tau = 0$, but the signal became detectable at $\tau = 50$ ns. In the DMSO solution the initially minor signal of $DPH^{\cdot +}$ increased to a comparable intensity after 50 ns. In the DMF solution, both positive and negative ions are produced within the duration time of the UV pulse, and no significant change in relative intensity was observed between 0 and 50 ns. Only $DPH^{\cdot -}$ was detected in the DMA solution as was the case for the DPH–DMA in *p*-dioxane up to a delay time of 150 ns. In the DPH–DCNB system in *p*-dioxane, only $DPH^{\cdot +}$ was observed. The slow formation time of the minor radical ion of DPH appears to disagree with the result for perylene studied by Konuk et al. [15] who reported the instantaneous formation of both radical ions of perylene in acetonitrile and DMF within the time resolution of their experiments (1 ns). Billard et al. [30] reported the extremely slow formation (on a micosecond time scale) of the pyrene radical anion in methanol under the condition that the radical cation are generated instantaneously within the pulse width of the excitation light. Guerry-Butty et al. [11] reported that the absorption due to the radical anion of chloranil in acetonitrile rose instantly during the pulse width of 12 ns flash and then more gradually over a time of micoseconds [11]. That observation was explained as electron capture from neat acetonitrile by photoexcited chloranil taking place from both the S_1 and the T_1 states. In the case of DPH no such long of the order of micoseconds rise time of the radical ion formation (compared with the T_1 lifetime of 70 μs in deoxygenated acetonitrile) was observed, suggesting that there is no participation of the T_1 state for the photoionization under study.

By simulating each time-resolved spectrum by means of Eq. (7), the change in *C* which denotes the change in the concentration of the radical ion was determined as the lifetime of the species [3,4]. In the simulation, *B* was approximated as constant ($B = 1$) as described in Section 3. The obtained lifetimes of the radical ions of DPP in the various solvents are listed in Table 1 together with the values reported in the literature of the dielectric constant ϵ, viscosity η, donor number DN and acceptor number AcN of the solvents. From Table 1 it appears that the lifetimes of the radical cation in the solvents with low ϵ value decrease. The values of DN, which correlate to the formation ratio (forming ability) of both radical ions, do not correlate simply to the lifetimes.

4.5. Role of dissolved molecular oxygen in the stability of the radical ions

The transient CARS spectra of DPH in air-saturated solutions observed with no delay time between the pump and probe pulses ($\tau = 0$) were substantially identical with those observed in the deaerated solutions for the various solvents under study, indicating no influence of dissolved oxygen on the primary process of the photoionization. A drastic change in the lifetimes of both radical ions was obtained in the presence of oxygen in solutions [4]. $DPH^{\cdot +}$ was dominant as a long-lived species in all the air-saturated solutions, and $DPH^{\cdot -}$ was a long-lived species in the deaerated DMF and DMSO solutions; that is, dissolved oxygen shortens the lifetime of the radical anion and prolongs that of the radical cation for the DPH. It was reported that molecular oxygen acts as an efficient quencher of DPH and DPO in both the S_1 and the T_1 states, which contributes to the formation of $^1O^*_2$ [31]. Recently the radical anions of some aromatic molecules such as dicyanoanthracene were found to be scavenged by molecular oxygen [32]. The case of DPH$^{\bullet-}$ is similar to this. DPH$^{\bullet+}$, on the contrary, is stabilized by molecular oxygen as a result of the quenching of DPH$^{\bullet-}$ and/or solvated electron, assuming that main decay channel of DPH$^{\bullet+}$ is recombination with the opposite ion or oppositely charged solvent molecule(s). Stabilization seems to be greater in DMF and DMSO than in acetonitrile and acetone, and the behavior seems to relate to the presence of solvated $O^{\bullet-}{}_2$.

4.6. Exciplex fluorescence and its relation to the radical ion formation

The exciplex fluorescence spectra of the DPP (n = 2–4)-DCNB (or DMA) systems in p-dioxane have been found to depend apparently on the chain length n [2,4,7]. Structureless, broad, and red-shifted bands were observed for DPB. Very large Stokes shifts (more than 5000 cm^{-1}) and no appreciable evidence of specific interaction between DPB in the ground state and DCNB or DMA molecules and of self-association suggest the formation of 1:1 stable exciplexes of DPB with DCNB or DMA. For DPH the exciplex seems to be less stable than the case of DPB, as shown by the small Stokes shift [7].

No evidence for the exciplex formation has been detected in the fluorescence spectrum of DPO in the system containing 0.3 M DCNB or DMA in p-dioxane [7]. This indicates that the intermolecular interaction of DPP molecules in the S_1 state with nearby donor (DMA) or acceptor (DCNB) molecules is much weaker for DPO than for DPH and DPB. It should be mentioned that the reported values of fluorescence lifetimes at room temperature are in the order DPO (about 5 ns) $\approx$ DPH $\rangle$ DPB in polar solvents [33–35]. The duration times of the exciplex fluorescences for DPB and DPH are not more than the pulse width of 10 ns.

The feature of the exciplex fluorescences of the exciplex-forming systems for DPB, DPH and DPO can be correlated to the efficiency of the radical ion formations in the same systems. In the DPO–DCNB (or DMA)-p-dioxane system no appreciable CARS signal of the radical ions was observed in the resonance condition, where the intense signals were observed easily in the polar solvents. This confirms that the long-lived (more than 50 ns) radical ions detected by CARS (CSRS) for DPB and DPH are non-fluorescent solvent-separated ion pairs or solvated free ions generated via CT exciplexes.

4.7. Behavior of the photoionization in binary solvents

The very large Stokes shift of the exciplex (DPB in DCNB-p-dioxane or DMA-p-dioxane) fluorescence spectrum and high efficiency of the exciplex yields even in the relatively low concentration of 0.1 M DCNB or DMA suggest the formation of 1:1 stable exciplexes. No evidence of specific interaction between DPB in the S_0 state and DCNB or DMA molecules has been observed.

In the polar solvent systems studied (in the absence of DCNB and DMA), multiple solvent molecules surrounding each excited solute molecule play a role as donors or acceptors to produce the radical ions of DPO, DPH and DPB, via the CT interaction of DPB* – (Solv)$_n$ encounter complexes. This was derived from the experiments of DPP in the binary polar solvent system with p-dioxane and compared with the cases of the DCNB (DMA)-p-dioxane system [7]. The formation yield of the radical cations of DPB in neat acetonitrile is comparable with that in the 0.1 M DCNB-p-dioxane solution, indicating the low efficiency in polar solvents. The ratio of the DPB$^{\bullet+}$ populations was estimated from the CARS measurements at the concentrations of 0.1 and 0.2 M DCNB to be $N_{0.2}/N_{0.1} \approx 1.2$, being apparently less than 2.0 and suggesting near-saturation at 0.1 M. From the polar solvents, on the contrary, even in the highest concentration region of 100–25 vol.% (acetonitrile or acetone in p-dioxane) the relative populations of DPB$^{\bullet+}$ and DPH$^{\bullet+}$ estimated from the CARS signals were approximately linear to the concentration of the polar solvent, suggesting the important role of multiple solvent molecules in the photoionization process. The lifetime of DPH$^{\bullet+}$ or DPB$^{\bullet+}$ in p-dioxane as a dilution limit of the binary solution was assumed to be 100 ns (the observed lifetime values for DPH$^{\bullet+}$ and DPB$^{\bullet+}$ in the DCNB-p-dioxane systems). We can assume that the polar solvent and p-dioxane molecules in the binary mixtures should surround a solute (DPP) molecule in the ground state with statistically equal probabilities, because there is no evidence of specific interaction (such as formation of hydrogen bond or other well-defined association) between the solute and solvent molecules or between solutes.

4.8. Photoionization mechanism

The summary of our experimental results for the solvent-induced photoionization of the diphenylpolyenes leads us to derive the following aspects for the photoionization mechanism.

(i) The radical ions are generated, by single-photon absorption at 337 nm, via CT interaction between an excited (S_1) solute molecule and surrounding solvent molecule(s) under a moderate power of excitation pulses. For the DPB and DPH in the polar solvent systems and the DCNB (DMA)-p-dioxane systems the formation mechanism of the radical ions are commonly described by a CT as a primary photoionization process.

(ii) The CT interaction between an excited solute and nearby solvent molecules depends on the electron-donating (or electron-accepting) property of the solvent as electron donor (or acceptor), which affects the formation ratio of the radical ions. Proposed (in the literature) values of (the donor number) DN as a measure of the electron-donating property estimated by different measurements are qualitatively reasonable for the behavior of our results on the photoionization of DPB, DPH and DPO.

(iii) The diphenylpolyenes in the S_1 state act as an amphoteric agent (donor or acceptor) depending on the electron-donating (or electron-accepting) nature of environments. In the DMF (with a middle DN value among the solvents studied) solutions of DPB, DPH and DPO, both radical ions are generated simultaneously. For the solvent having a larger or smaller value of DN, minor radical ion components show a slow rise time, indicating a secondary mechanism of the formation process for the minor species. A possible mechanism is that the solvated electron or solvated hole produced as a result of the primary process of CT can donate an electron to or accept an electron from a neutral DPH molecule located near the charged solvents. Since this secondary process belongs to a diffusion-controlled process, the fast formation of both radical ions in the DMF solution of DPH, DPB and also DPO can be excluded from the secondary mechanism and can be regarded as the primary process for producing simultaneously both ions.

(iv) Especially for electron-donating solvents such as DMF and DMSO the difference between the lifetimes of the radical ions of DPH are very large and cannot be reasonably interpreted by the decay process of a recombination between a pair of the radical cation and radical anion. The relative instability of the radical cation of DPH in DMF or DMSO may be understood by a back CT process between the cation and solvent molecules with a high donor number.

(v) As reported, the molecular oxygen acts as a scavenger of the aromatic radical anion such as dicyanoanthracene; the radical anion of DPH was also scavenged efficiently by dissolved oxygen (probably with the generation of solvated $O^{\bullet -}{}_2$). The increase in the lifetime of the cation may be correlated to the stabilization of the cation by means of the formation of geminate ion pair of $DPH^{+}{}_{s}..O^{-}{}_{2s}$ (the subscript s denotes solvation) and decreasing the back CT process between the radical cation and anion or solvent molecule(s).

(vi) For DPB–DCNB (DMA) and DPH–DCNB (DMA) in *p*-dioxane the radical ions as solvated free ions or solvent-separated (geminate) ion pair which give resonance CARS signals are generated by solvent-assisted relaxation from 1:1 exciplexes. The formation efficiency of such 1:1 exciplexes decreases from DPB to DPO, being consistent with the results of the fluorescence and transient CARS measurements. A relatively low concentration of 0.1 M for DCNB (DMA) is sufficient for generation of the DPH and DPB exciplexes (radical ions), confirming the formation of 1:1 exciplexes via a diffusion-controlled process within the time scale of the fluorescence lifetime.

(vii) Contrary to the cases in the presence of DCNB or DMA as a strong electron acceptor or donor, for the cases of DPB, DPH and DPO in polar solvents the participation of multiple solvent molecules should work effectively, allowing the production of the radical ions of the DPP via 1:*n* collisional encounter complexes.

5. Concluding remarks

The work described in this review article clearly demonstrates the advantages for the study of photoionization by using coherent Raman spectroscopy with nanosecond laser pulses. The experimental technique of the transient resonance CARS (CSRS) has successfully provided vibrational data on relative ratios and the temporal behaviors of the radical ions generated in polar solvents by UV irradiation in the cases of fluorescent samples. The results have given considerable insight into the mechanism of the solvent-induced photoionization of the diphenylpolyenes, which it may be difficult to derive using other methods such as electronic spectroscopies.

References

[1] A. Kasama, M. Taya, T. Kamisuki, Y. Adachi and S. Maeda, in J. Atkinson (ed.), *Time Resolved Vibrational Spectroscopy*, Gordon and Breach, New York, 1987, p. 304.

[2] T. Dudev, T. Kamisuki, N. Akamatsu and C. Hirose, *J. Phys. Chem.*, *95* (1991) 4999.

[3] T. Kamisuki and C. Hirose, *J. Raman Spectrosc.*, *25* (1994) 307.

[4] T. Kamisuki, T. Dudev and C. Hirose, *J. Phys. Chem.*, *95* (1991) 5845.

[5] T. Kamisuki and C. Hirose, *J. Phys. Chem.*, *95* (1991) 5003.

[6] M. Watanabe, T. Kamisuki, N. Akamatsu and C. Hirose, *Chem. Phys. Lett.*, *170* (1990) 451.

[7] T. Kamisuki and C. Hirose, *J. Raman Spectrosc.*, *26* (1995) 93.

[8] M.O. Delcourt and M.J. Rossi, *J Phys. Chem.*, *86* (1982) 3233.

[9] E. Vauthey, E. Haselbach and P. Suppan, *Helv. Chim. Acta*, *70* (1987) 347.

[10] T. Shida and S. Iwata, *J. Am. Chem. Soc.*, *95* (1973) 3473.

[11] E. Guerry-Butty, E. Haselbach, C. Pasquier, P. Suppan and D. Phillips, *Helv. Chim. Acta*, *68* (1985) 912.

[12] H. Leonhardt and A. Weller, *Ber. Bunsenges. Phys. Chem.*, *67* (1963) 791.

[13] K.H. Grellmann and A.R. Watkins, *Chem. Phys. Lett.*, *9* (1971) 439.

[14] M. Ottolenghi, *Chem. Phys. Lett.*, *12* (1971) 339.

[15] R. Konuk, J. Cornelisse and S.P. McGlynn, *J. Chem. Phys.*, *82* (1985) 3929.

[16] E. Vauthey, P. Suppan, E. Haselbach and R.S. Davidson, *Helv. Chim. Acta*, *69* (1986) 430.

[17] M.T. Allen and D.G. Whitten, *Chem. Rev.*, *89* (1988) 1691.

[18] S.E. Wallace-Williams, S. Moller, R.A. Goldberg, K.M. Hanson, J.W. Lewis, W.A. Yee and D.S. Kliger, *J. Phys. Chem.*, *97* (1993) 9587.

[19] Z. Wang and W.G. McGimpsey, *J. Phys. Chem.*, *97* (1993) 3324.

[20] Y. Yamamoto, T. Aoyama and K. Hayashi, *J. Chem. Soc., Faraday Trans. I*, *84* (1988) 2209.

[21] T. Shida and W. Hamill, *J. Chem. Phys.*, *44* (1966) 4372.

[22] G. Hoijtink and H. van der Meij, *Z. Phys. Chem. NF*, *20* (1959) 1.

[23] M. Almgren and J.K. Thomas, *Photochem. Photobiol.*, *31* (1980) 329.

[24] S. Maeda, T. Kamisuki, H. Kataoka and Y. Adachi, *Appl. Spectrosc. Rev.*, *21* (1985) 211.

[25] T. Kamisuki, N. Akamatsu, Y. Adachi, C. Hirose, N. Yamamoto, K. Takuma and M. Iwamura, *Bull. Chem. Soc. Jpn.*, *62* (1989) 1415.

[26] J.W. Nibler and G.V. Knighten, in A. Weber (ed.), *Raman Spectroscopy of Gases and Liquids*, Springer, Berlin, 1979, p. 253.
[27] N Bloembergen, H. Lotem and R.T. Lynch, Jr., *Indian J. Pure Appl. Phys., 16* (1979) 151.
[28] V. Gutmann, *Chem. Bri., 7* (1972) 102.
[29] T. Kagiya, Y. Sumida and T. Inoue, *Bull. Chem. Soc. Jpn., 41* (1968) 767.
[30] L.A.H. Billard, F.C. James and G.A. Kenney-Wallace, *J. Phys. Chem., 87* (1983) 2981.
[31] S.K. Chattopadhyay, C.V. Kumar and P.K. Das, *J. Phys. Chem., 89* (1985) 670.
[32] I.R. Gould, D. Ege, J.E. Moster and S. Farid, *J. Am. Chem. Soc., 112* (1990) 4290.
[33] E.D. Cehelnik, R.B. Cundall, J.R. Lockwood and T.F. Palmer, *J. Chem. Phys., 79* (1975) 1369.
[34] S.P. Velsco and G.R. Fleming, *J. Chem. Phys., 76* (1982) 3553.
[35] S.K. Chattopadhyay, P.K. Das and G.L. Hug, *J. Am. Chem. Soc., 104* (1982) 4507.