Photoreaction of neutral 9-aminoacridine in glycerol:water glass characterized by satellite holes and antiholes

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Abstract

Satellite holes and antiholes in the hole burned (HB) spectrum are used to determine the photoproduct of 9-aminoacridine (9AA) doped in glycerol:water (Gl:H$_2$O) glass with pH = 13. Although monoprotonated 9AA is the photoproduct of the imino form of neutral 9AA, antihole recovery implies that the excited state 9AA returns to original form of 9AA predominantly. Furthermore, similar satellite holes but different antihole structures are observed in the HB spectrum of 9AA doped in polyvinyl butyral film, implying that different HB mechanisms are involved. © 1997 Elsevier Science B.V.

1. Introduction

Photo-induced reaction of chromophores doped in amorphous glasses can deplete the population at the original site and produce a persistent hole in the absorption spectrum at low temperature [1–5]. When tuning the excitation to the vibronic absorption band, several satellite holes resulting from Franck–Condon (FC) active vibrational modes can be produced in the hole burned (HB) spectrum [6–10]. Recently, the high resolution of satellite holes have been used to characterize the tautomeric structures of 9-aminoacridine (9AA) doped in glycerol:water (Gl:H$_2$O) glasses at various pH values [10]. Specifically, the 514 and 1368 cm^{-1} satellite holes can be used to characterize the monoprotonated 9AA, while the absence of the 514 cm^{-1} satellite hole and the

frequency shift from 1368 cm^{-1} to the 1338 cm^{-1} satellite hole can be used to identify the imino form of neutral 9AA. Furthermore, stronger couplings among the 390, 1162 and 1338 cm^{-1} modes were present in the combination modes in the imino form of neutral 9AA, but more fundamental modes, for instance, the 514, 650 and 690 cm^{-1} modes, were observed for monoprotonated 9AA. In addition, the coincidence between the antiholes in the spectrum of neutral 9AA and the absorption bands of monoprotonated 9AA suggests that monoprotonated 9AA is the dominant photoproduct of the neutral 9AA. The antihole in the HB spectrum has been used to characterize the mechanism of the photochemical HB of chlorin [11].

Very recently, Chiang et al. [12] have confirmed that proton transfer between the chromophores and the matrix upon electronic excitation is the main mechanism for the hole-burning of the protonated acridine derivatives doped in polyvinyl alcohol (PVOH) films. Although we proposed that excited

state proton transfer between the 9AA and the matrix is the mechanism for the HB spectrum of neutral 9AA, it is surprising that monoprotonated 9AA is the dominant photoproduct of neutral 9AA at pH 13 since the pK_a of 9AA is 9.9 [13]. Furthermore, we suspect that the weaker satellite holes at 514, 650 and 690 cm^{-1} in the spectrum of neutral 9AA [10] are due to the satellite holes of photoproduct. More interestingly, distinct holes were also observed in the system of 9AA doped in polyvinyl butyral (PVB) film, even though there is no acidic proton in the matrix [14]. In this work, we present a new approach to distinguish the satellite holes between photoreactant and photoproduct. In addition, antihole recovery provides more dynamic information of the excited state of 9AA. Finally, a comparison of the HB mechanisms between 9AA/Gl:H$_2$O and 9AA/PVB is discussed.

2. Experimental

The experimental setup of the HB method was described elsewhere [15]. The absorption spectrum was obtained by using a home-made double beam spectrometer with a resolution of ≈ 0.03 nm. An intracavity frequency-doubled optical parametric oscillator (OPO) pumped by a Q-switched and mode-locked Nd:YAG laser (Quantronix 416) was constructed in our laboratory to serve as a burning light source [9]. The laser emitted trains of ≈ 10 pulses separated by 13 ns at a repetition rate of 500 Hz. The output wavelength of the OPO system can be tuned from 380 to 480 nm with a bandwidth less than 2 cm^{-1}.

The 9AA molecule was purchased from Acros and used without further purification. The sample of 9AA doped in glycerol–water glass was prepared from a saturated aqueous solution of 9AA by diluting it to 1/50 with glycerol:water solution (5:4 v/v) at pH 13. The ≈ 1 magnitude of the optical density at 435 nm absorption band corresponds to the concentration of $\approx 5 \times 10^{-4}$ M. Solutions were introduced into a quartz tube with an inner diameter of 1.5 mm and placed in a brass holder with several drill holes of ≈ 1 mm diameter. Clear glasses were normally formed by introducing the sample directly into a Janis dewar from room temperature to 6 K.

The sample of 9AA/PVB film was prepared by dissolving the 9AA and the PVB powder (Polysciences, Inc.) in organic solvent of CH$_2$Cl$_2$. The syrupy solutions were poured onto a glass plate and then placed into a desiccator to dry into a film of thickness ≈ 70 μm.

3. Results and discussion

The dashed line and dotted line in Fig. 1a show the absorption spectra of 9AA doped in Gl:H$_2$O glasses with pH = 7 and 13, respectively. Our previous study indicated that the monoprotonated 9AA is predominant at pH 7 and the imino form of neutral 9AA is dominant at pH 13 [10]. The lowest absorption band of the monoprotonated 9AA is located at ≈ 425 nm, whereas that of the neutral 9AA is located at ≈ 435 nm. The solid line in Fig. 1a shows the absorption spectrum of neutral 9AA doped in Gl:H$_2$O glass after three consecutive burnings at 437
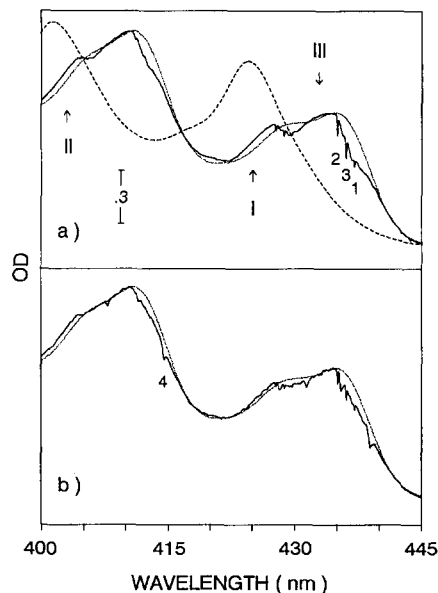

Fig. 1. (a) Absorption spectra of the 9AA doped Gly–H$_2$O glass with pH = 7 (dashed line) and pH = 13 (dotted line). Solid line shows the postburned absorption spectrum of the pH = 13 glass with consecutive burning at 435, 437 and 436 nm. (b) Solid line is the postburn absorption spectrum after additional 1 h burning at 415 nm. The numerical number presents the burning order and the arrow indicates the location of antihole.

(hole 1), 435 (hole 2) and 436 nm (hole 3) with the pulse energies of ≈ 2.5, 3 and 4 μJ and the burning time of 60 min for each excitation, respectively. The most important features presented in Fig. 1a are the antiholes in the region of 420–430 nm (antihole I) and the blue-side of the 405 nm (antihole II). These are consistent with the absorption bands of the monoprotonated 9AA. It is noted that antiholes I and II in Fig. 1a continue growing during the consecutive excitations. We further examine whether the satellite holes of photoproduct can be produced.

The solid line in Fig. 1b shows the further absorption spectrum of the solid line in Fig. 1a after burning at 415 nm with the pulse energy of 1.5 μJ and the burning time of 60 min. The difference between the two solid lines in Fig. 1a and 1b gives the HB spectrum as shown in Fig. 2a. For reference, Fig. 2b and the inset in Fig. 2b show the HB spectra of neutral 9AA and monoprotonated 9AA at ≈ 415 nm, respectively. A comparison between the satellite holes in Fig. 2a and Fig. 2b shows that the 514 cm^{-1} is a new satellite hole. In addition, the satellite holes at 650 and 690 cm^{-1} become stronger relative to the 555 cm^{-1} satellite hole. It is found that the 514, 650

and 690 cm^{-1} satellite holes are prominent in the HB spectrum of monoprotonated 9AA as shown in the inset of Fig. 2b. In our previous work [10], the 514 cm^{-1} satellite hole was assigned to the NH$_2$ vibration of monoprotonated 9AA and the 555 cm^{-1} satellite hole was attributed to a difference of the overtone of the 390 cm^{-1} mode and the 1338 cm^{-1} mode of neutral 9AA. Apparently, Fig. 2a contains not only the satellite holes of neutral 9AA but also the satellite holes of photoproducts. Although the 1368 cm^{-1} SH is difficult to justify because of the interference from the tail of the strong SH at 1338 cm^{-1}, we believe that the 514, 650 and 690 cm^{-1} holes in Fig. 2a are the satellite holes of photoproduct. In summary, these distinct satellite holes confirm that monoprotonated 9AA is the photoproduct of neutral 9AA in Gl:H$_2$O at pH 13.

INDO calculations [16] indicated that the electron density of neutral 9AA migrates from the endocyclic nitrogen atom to the carbon atom in the short axis and the exocyclic nitrogen atom during excitation. As a result, the exocyclic nitrogen becomes more basic, while the endocyclic nitrogen becomes more acidic. Consequently, a photoinduced proton transfer occurs from solvent to the exocyclic nitrogen of 9AA, and another photoinduced proton transfer takes place from the endocyclic nitrogen of 9AA to solvent. Therefore, Chiang et al. [10] proposed that the intermolecular proton transfer between the chromophore and matrix, triggered by electron migration along the short axis of 9AA via electronic excitation, is the main mechanism for the hole formation.

The hydrogen bonding between the 9AA and the neighboring matrix would alter the environmental configurations after electronic excitation. As a result, spectral holes can be also produced. A weak blue-shifted antihole III near the ZPH is observed in Fig. 1a. The possible mechanism for the blue-shifted antihole of the ZPH was discussed by Shu and Small [17]. They suggested that nonphotochemical hole burning (NPHB) occurs as a result of an outside-in hierarchy of tunneling events, triggered by electronic excitation. Consequently, the free volume for the chromophore increases for the postburn configuration. The increase in free volume can explain the blue-shifted antihole since $\pi\pi^*$ transitions typically undergo a red-shift from gas to condensed phases. We believe that the HB mechanism of 9AA/Gl:H$_2$O
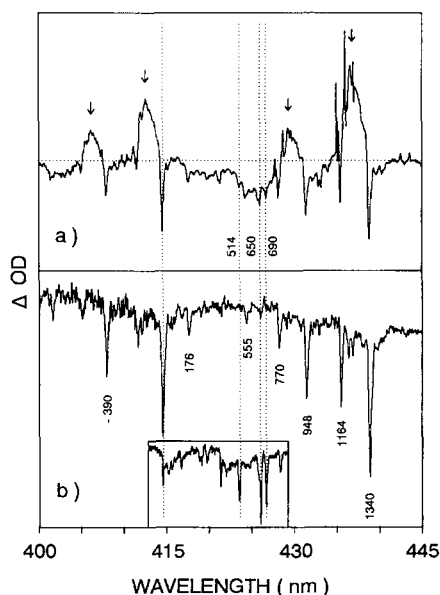

Fig. 2. (a) The HB spectrum obtained from the difference between the two solid lines in Figs. 1a and 1b. (b) The HB spectra of neutral 9AA and monoprotonated 9AA (insert) after burning 1 h at 415 nm.

consists of both photochemical hole burning and NPHB processes. However, the relative intensities between two antiholes resulted from these two mechanisms suggest that photochemical hole burning is much more dominant.

The HB spectrum of 9AA/PVB film has been studied by Bogner et al. [14] for the application of optical data storage. In the system of 9AA/PVB, no proton is available for proton transfer between the chromophore and the PVB film matrix. The distinct holes observed in their HB spectra implies that proton transfer between the 9AA and the matrix is not necessary for the hole formation in the spectrum of 9AA/PVB. In order to examine the HB mechanism of 9AA, we have further studied the satellite holes and antiholes of 9AA doped in PVB film.

Fig. 3a shows the preburn and postburn absorption spectra of 9AA doped in PVB film taken at $\lambda_B = 439$ nm. The pulse energy is ≈ 2.5 μJ and the burning time is 200 min. The antiholes, barely observed in Fig. 3a, are different from the antiholes observed in Fig. 1a. In addition, the $\approx 7\%$ hole depth of the saturated ZPH at 439 nm in the spectrum of 9AA/PVB is much shallower than the $\approx 35\%$ hole depth of the saturated ZPH at 437 nm in
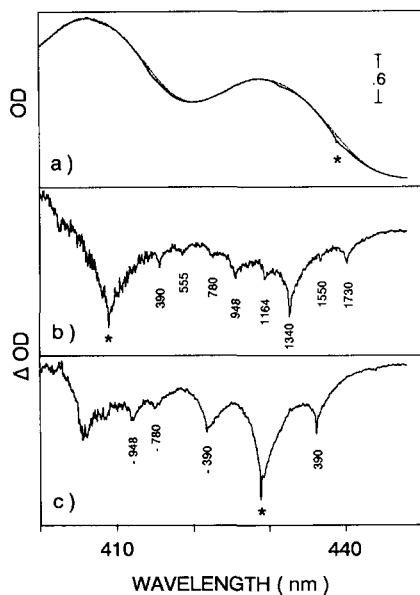

Fig. 3. Preburn and postburn absorption spectra of the 9AA doped in PVB film taken at $\lambda_B = 439$ nm (a), HB spectra at 409 nm (b) and at 429 nm (c).

the spectrum of 9AA/Gl:H$_2$O [10]. Fig. 3b and 3c show the HB spectra of 9AA/PVB taken at $\lambda_B = 409$ and 429 nm, respectively. The pulse energies are ≈ 1.5 μJ and 2.2 μJ and the burning time are 80 and 140 min, respectively. It is found that the satellite holes observed in Fig. 3b are quite similar to that in Fig. 2b. The high resolution of satellite holes is useful for characterizing the tautomer structures of 9AA. According to our previous study of the satellite holes of 9AA [10], the appearance of the 1340 cm^{-1} satellite hole and the absence of 514 cm^{-1} satellite hole in Fig. 3 suggest that the imino form of neutral 9AA is the predominant structure in PVB film.

Considering that electron migrates from the endocyclic nitrogen to the exocyclic nitrogen upon photoexcitation [16], photoinduced intramolecular proton transfer from the endocyclic nitrogen atom to the exocyclic nitrogen atom may be responsible for the 9AA/PVB system. However, the distance between endocyclic and exocyclic nitrogen atoms is estimated to be ≈ 4 Å [18], the imino–amino transformation mechanism is not very favorable. Since the low quantum yield of HB signal can be accumulated, one cannot completely eliminate the possibility of the photoinduced intramolecular proton transfer. Another possible mechanism for the HB mechanism of 9AA/PVB is the NPHB. The absence of the blue-shifted antihole near the ZPH in Fig. 3 may be attributed to the low efficiency of hole formation and the extreme width characteristic of antiholes [19]. In addition, larger electron–phonon coupling can make the justification of the blue-shifted antihole near the ZPH difficult. The Debye–Waller factor measured in the spectrum of 9AA/PVB is 0.2 [20], while the Debye–Waller factor determined by the short time limit HB method for the 9AA/Gl:H$_2$O at pH 13 is ≈ 0.63. Note that the electronic interactions of the 9AA with the PVB can alter the environmental configurations. Consequently, spectral holes are produced. The lower hole burning efficiency and higher electron–phonon coupling observed in the spectrum of the imino form of neutral 9AA doped in PVB relative to that in Gl:H$_2$O suggest that the change of environmental configurations may be one of the mechanism for producing the holes in the spectrum of 9AA/PVB film. More experiments are necessary to determine the HB mechanism of 9AA/PVB. Nevertheless, the main mechanism for the imino form of

neutral 9AA doped in Gl:H_2O glass and in PVB film is quite different according to their HB spectra.

Another noteworthy feature in Fig. 2a is the presence of antiholes. These antiholes are apparently due to laser induced hole filling (LIHF) of the primary holes. The solid-line spectrum in Fig. 1b indicates that there are still holes relative to the original absorption spectrum in the regions labeled as antiholes in Fig. 2a. The phenomena of LIHF have been studied by several group [21–27]. Possible mechanisms of LIHF involve local heating [22], spectral diffusion [23] and reversion resulting from antihole excitation [22,24,25]. In our work, the lack of appreciable line broadening in LIHF allows us to eliminate spectral diffusion. This linewidth behavior has been observed in several other LIHF studies [26]. In the study of a binary mixture of ACMA and BODIPY doped in Gl:H_2O glass [27], Kuo and Chang found that the primary holes of ACMA burned at 428 nm were not filled by the secondary excitation of the absorption band of BODIPY at 555 nm. Similar results were also observed in the study of a mixture of 9AA and BODIPY doped in Gl:H_2O glass. Therefore, local heating is an unlikely mechanism for the hole filling. Shu and Small [25] studied the LIHF of cresyl violet doped in PVOH films and found that hole filling is due to light-induced antihole reversion. They concluded that the dominant mechanism involves electronic excitation of the antihole sites by means of their broad phonon sideband. Olson et al. [22] found that reversion resulting from excitation of primary antihole is the mechanism of LIHF in the system of pentacene doped in benzoic acid. They further suggested that hydrogen bond tautomerization of the host is involved in the hole burning mechanism. Furthermore, antihole recovery of the holes is consistent with the tautomerization mechanism. The photoinduced tautomer is not the most stable form, excitation of the antihole allows the photoinduced tautomer to go back to the stable form.

In this work, 9AA exhibits lower basicity in the first excited state than in the ground state [16]. The excited state pK_a^* of 9AA was estimated to be lower than pK_a by at most 0.6 pH units by Smith et al. [28]. Since the excited state pK_a^* of 9AA is ≈ 9.3, the excited state 9AA is not very favored to be protonated at pH 13. Only minor yield is expected,

the small quantum yield of the photoproduct is a result of strong competition of electronic relaxation from S_1 versus the unfavorable proton transfer processes. In the HB spectra, antihole recovery in Fig. 1b and new antiholes in Fig. 2a resulting from reversion of the photoproduct suggest that the excited state 9AA returns to the ground state imino form of neutral 9AA predominantly. It is reasonable because the imino form of neutral 9AA is more stable than the monoprotonated 9AA at pH 13. Reversion of photoproduct back to the original state has been observed in the photochemistry of chlorin in crystalline n-alkanes [11]. However, the photoinduced antiholes I and II in Fig. 1a remain growing during the consecutive excitations at 437, 435 and 436 nm (not shown), indicating that part of the excited state 9AA can go to the monoprotonated 9AA. The mechanism of photoinduced reaction of neutral 9AA doped in Gl:H_2O glass is summarized in Fig. 4. The advantage of HB method is that the HB signal of low quantum yield photoproduct can be accumulated to produce high resolution spectral holes.

In summary, we have demonstrated that the satellite holes of the photoproduct can be used to characterize the molecular structure of the photoproduct
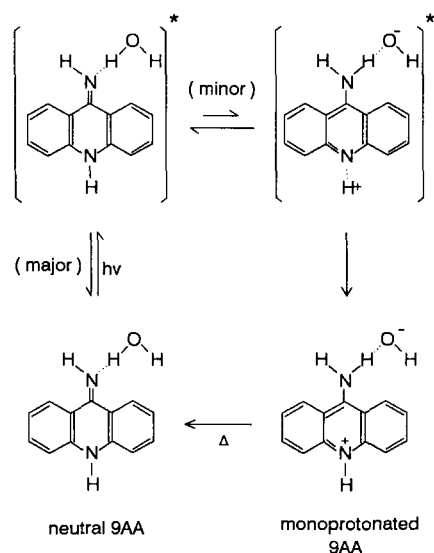

Fig. 4. Schematic diagram of proposed photoreaction for the imino form of neutral 9AA doped in Gl:H_2O at pH 13. The solid line presents a chemical bond and the dash line denotes a hydrogen bond. The triangle delineates the increase of temperature.

and determine the HB mechanism. In addition, the antihole recovery provides additional information about the photoinduced reaction. Although the excited state of 9AA returns directly to the imino form of neutral 9AA at pH 13 predominantly, the low quantum yield photoproduct of the monoprotonated 9AA can be accumulated and clearly identified by the satellite holes in the HB spectrum. It is clear that satellite holes and antiholes can be used to determine the molecular structures of photoproducts and to probe the photoinduced reaction. Furthermore, the HB mechanism of the imino form of neutral 9AA doped in Gl:H_2O glass is mainly due to intermolecular proton transfer between 9AA and matrix. However, the spectral holes in the spectrum of 9AA/PVB film is tentatively ascribed to the change of environmental configurations. The investigation of the distinct satellite holes and antiholes is important for the study of the interactions of 9AA with DNA [29], which is under progress in our laboratory.

Acknowledgements

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