ARTICLE

Laser Flash Photolysis Mechanism of Anthraquinone-2-Sodium Sulfonate in Pyridine Ionic Liquid/Water Mixed System[†]

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The photochemical reaction process of anthraquinone-2-sodium sulfonate (AQS) in the mixture of water (H_2O) and N-butylpyridinium tetrafluoroborate ([BPy][BF$_4$]) was studied using the laser flash photolysis technique. Experimental results show that the excited triplet of AQS (^{3}AQS*) could react rapidly with H_2O and the transient absorption spectra greatly changed by increasing the volume fraction of the ionic liquid (V_{IL}) in [BPy][BF$_4$]/H_2O mixtures. The absorbance at 510 nm increased gradually with increasing V_{IL} when $0 < V_{IL} < 0.1$. By contrast, the absorbance decreased gradually when $V_{IL} > 0.1$. Otherwise, the absorbance of the band near 380 nm steadily increased. The apparent kinetic parameters of transient species B and ^{3}AQS* are obtained approximately. ^{3}AQS* abstracting hydrogen from [BPy]$^+$ was also explored. It was deduced that the $350-420$ nm band was the superposition of the peaks of ^{3}AQS* and AQSH$^.$. The two reactions of ^{3}AQS* with [BPy][BF$_4$] and H_2O are a pair of competitive reactions. We also concluded that the entire reaction processes slow down in the case of high [BPy][BF$_4$] concentrations.

Key words: Laser flash photolysis, Anthraquinone-2-sodium sulfonate, Ionic liquids, Transient absorption, Hydrogen abstraction

I. INTRODUCTION

Room temperature ionic liquids (ILs) are liquids, which are composed of organic cations and inorganic anions at room temperature or near room temperature. Due to the unique structure and the strong Coulomb interaction between cations and anions, ILs show many unique properties compared to traditional solvents, such as high viscosity, less volatile, strong polarity, high thermal stability, and so on [1−3]. These excellent properties make it receive extensive attention of the researchers. As a promising new kind of green solvents, ILs have been used in various fields [4−6], especially in organic reactions and green separation.

Yago *et al.* studied the diffusion and solvation of radical ions in an IL [7]. Compared with the neutral radicals, it was found that the radical ions are rigidly solvated in the IL and the nanometer-scaled charge-ordering structures are created around the radical ions [7]. Sarkar *et al.* reported that the photoinduced electron transfer (PET) rate in ILs was much lower than that in traditional solvents, but the rate could significantly increase in the mixed system between IL and traditional solvents [8, 9]. Li *et al.* and Koch *et al.* reported that the electron transfer process would be controlled by solvent dynamics in both IL and traditional solvents [10, 11].

We have studied electron transfer process between duroquinone and triethylamine in acetonitrile (MeCN) and N-butylpyridinium tetrafluoroborate ([BPy][BF$_4$]) mixed systems, and found that changing the proportion of the ionic liquid could regulate the PET reaction rate of the system [12]. ILs have many excellent advantages as solvents, but sometimes they could also be involved in the reaction. Muldoon *et al.* studied photochemical reaction process of benzophenone (BP) in different ILs and found that the excited triplet of benzophenone could convert to benzophenone carbonyl radicals (BPK) through hydrogen abstraction reaction with cations of the ILs [13]. Nishiyama *et al.* reported that diffusion coefficient of BP is bigger than the BPK in IL, it suggests that BPK has strong Coulomb interaction with polar ions around it in ILs [14].

Anthraquinone-2-sodium sulfonate (AQS) is an important anthraquinone compound, which has got great attention for its applications in the biological field [15−27]. Loeff and Moore *et al.* detailedly studied photochemical reaction process of AQS in water, and deduced the possible reaction mechanism [15, 18]. They concluded that ^{3}AQS* could react rapidly with H_2O to generate the transient species B and C, B has a great

absorption around 480 nm and C has a weak absorption near 580 nm. Ito *et al.* obtained the characteristic absorption peaks of anion radical AQS$^{\cdot-}$ at 385 and 500 nm [19]. Ma and Sheng *et al.* also did many significative researches to the AQS [20−23].

In this work, 355 nm was used as the excitation wavelength to study the transient reaction mechanism of AQS in the mixed system of the pyridine ionic liquid [BPy][BF$_4$] and H$_2$O.

II. EXPERIMENTS

Anthraquinone-2-sulfonate (>98%) was obtained from TCI. Acetonitrile (99%, J&K) and redistilled water were used as the solvent. [BPy][BF$_4$] was provided by the Center for Green Chemistry and Catalysis of Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, and it was kept in vacuum for 12 h at 60−65 °C to remove any volatile organic impurities and moisture.

Laser photolysis experiments were carried out using a Nd:YAG laser that provides 355 nm laser pulse with a duration of 6 ns and a maximum energy of 20 mJ/pulse. The probe light source was a 300 W xenon lamp. The brightness of xenon lamp can instantly enlarge 100 times after trigger pulse of xenon lamp power was triggered. The laser and analyzing light beam passed perpendicularly through a quartz cell. Then the analyzing light that passes through the monochromator can be detected by a photomultiplier tube (R955) whose effective detection range is 280−750 nm. The signals were collected using HP54510B 300 MHz transient recorder and processed with the dynamic data processing software. All samples were bubbled with high purity nitrogen or oxygen (99.99%) for 20 min. The experiments were performed at room temperature.

III. RESULTS AND DISCUSSION

A. Laser flash photolysis of AQS in acetonitrile

Transient absorption spectra of AQS in N$_2$-saturated acetonitrile solution observed at different delay time after the laser excitation are shown in Fig.1. There are two obvious absorption peaks around 370 and 480 nm. Absorbance of time profiles at 370 and 480 nm under O$_2$ could decay to zero less than 1 μs, which are shown in Fig.2. It suggests that the two characteristic peaks are generated by the same transient species, and it can be quenched by oxygen. The transient species was assigned to ^{3}AQS* which cannot react with MeCN [15, 20]. Upon excitation by a 355 nm laser, the ground state of AQS was excited to the single excited state ^{1}AQS*, and then ^{3}AQS* formed through intersystem crossing (ISC) (Eq.(1)). ^{3}AQS* can go back to the ground state through radiationless transition (Eq.(2)). It can also be
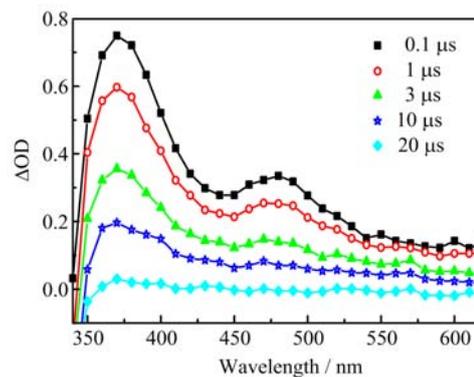

FIG. 1 Transient absorption spectra of 0.2 mmol/L AQS in N$_2$-saturated acetonitrile solution recorded at 0.1, 1, 3, 10, and 20 μs after laser excitation.
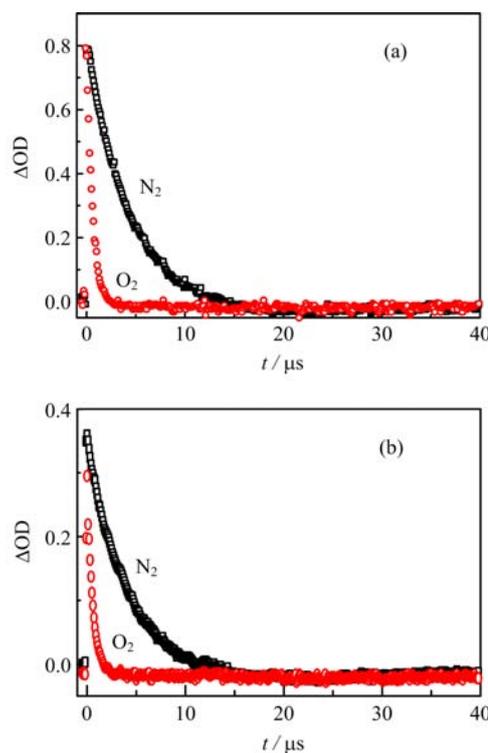

FIG. 2 Decay profiles of ^{3}AQS* at (a) 370 nm and (b) 480 nm under different atmosphere in acetonitrile solution.

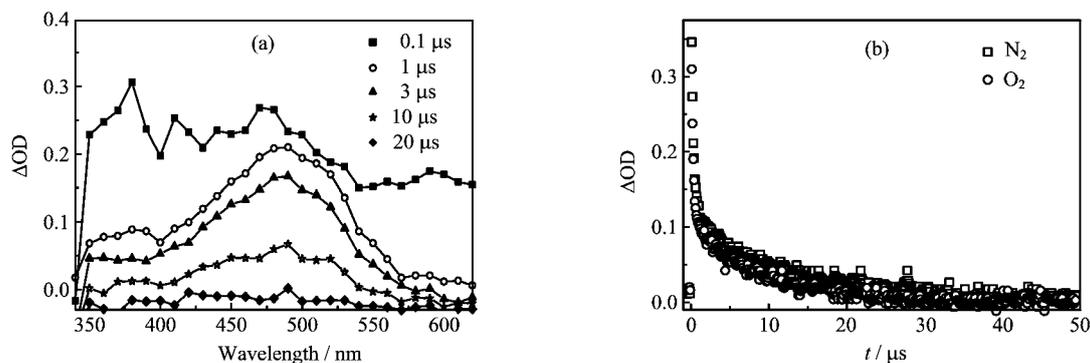quenched by oxygen (Eq.(3)). The reaction processes are as follows [24]:

$$AQS \xrightarrow{h\nu} {}^1AQS^* \xrightarrow{ISC} {}^3AQS^* \qquad (1)$$

$$^3AQS^* \rightarrow AQS \qquad (2)$$

$$^3AQS^* \xrightarrow{O_2} AQS \qquad (3)$$

FIG. 3 (a) Transient absorption spectra of AQS in N_2-saturated aqueous solution recorded at 0.1, 1, 3, 10, and 20 μs after laser excitation. (b) Time profiles observed at 370 nm under N_2 and O_2.

B. Laser flash photolysis of AQS in aqueous solution

Replacing MeCN by H_2O, the transient absorption spectra of AQS change obviously (Fig.3) compared to Fig.1. Within 1 μs, the absorbance around 370, 480, and 590 nm can be observed. After 1 μs, a very strong absorption centered at 490 nm and the absorption around 370 nm decreased sharply. The spectra band near 590 nm also weakened. These great changes are owing to $^3AQS^*$ reacting very rapidly with H_2O [15, 18]. The strong absorption centered at 490 nm after 1 μs could be assigned to transient species B and the weak absorbance at 590 nm comes from transient species C [15, 18]. The photolysis of AQS in water is very complex and researchers still have not clearly determined the structures of B and C so far. Loeff *et al.* guessed that B and C could be carbonyl and benzoid-ring adducts, respectively [15]. The generation and quenching paths of the transient species B and C are shown in the following equation, where ROH is hydroxylated anthraquinones [15].

$$^3AQS^* + H_2O \rightarrow B \tag{4}$$

$$B \rightarrow AQS + H_2O \tag{5}$$

$$^3AQS^* + H_2O \rightarrow C \tag{6}$$

$$C + AQS \rightarrow \cdots \rightarrow ROH \tag{7}$$

$$C \rightarrow AQS + H_2O \tag{8}$$

It can be found that the absorption of transient species C in our experiments is very weak, which is consistent with the conclusion that the concentration of C is very low in neutral aqueous solutions [18]. Only the obvious characteristic absorption band of C could be observed in alkaline aqueous solution. Since the solutions we used are basically neutral, transient species B is our main research object. We also found that the absorption spectra of the B hardly changed in O_2-saturated aqueous solution (Fig.3(b)). It could be concluded that the reaction of $^3AQS^*$ with H_2O was much faster than the quenching of $^3AQS^*$ by oxygen. This conclusion could be supported by fitting the time profile at 370 nm. The observed decay rate of $^3AQS^*$ is
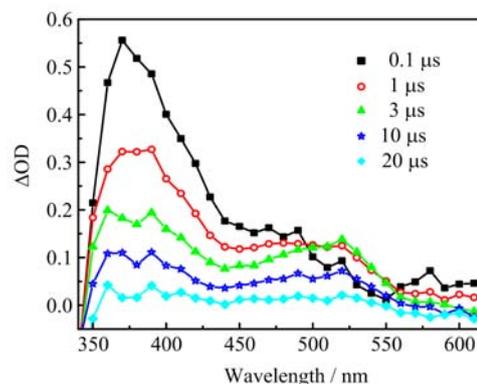

FIG. 4 Transient absorption spectra of AQS in N_2-saturated [BPy][BF$_4$]/H_2O solution when V_{IL}=0.6 recorded at 0.1, 1, 3, 10, and 20 μs.

3.2×10^6 s^{-1} (quenched mainly by reacting with H_2O, without O_2) in N_2-saturated aqueous solution, while that is 1.4×10^6 s^{-1} (quenched mainly by O_2, without H_2O) in O_2-saturated acetonitrile solution. The results are consistent with the conclusion of Loeff *et al.* [15].

C. Laser flash photolysis of AQS in [BPy][BF$_4$]/H_2O solution

1. Effects of [BPy][BF$_4$] on the reactions between AQS and H_2O

To study the effects of [BPy][BF$_4$] on the photochemical processes of AQS in aqueous solution, the transient absorption spectra and time profiles of AQS (0.2 mmol/L) in a series of [BPy][BF$_4$]/H_2O solutions have been recorded. The typical transient absorption spectra of AQS in [BPy][BF$_4$]/H_2O were shown in Fig.4 when the volume fraction of ionic liquid V_{IL}=0.6. It is obvious that the spectra band around both 380 and 510 nm are different from that in aqueous solution without IL.
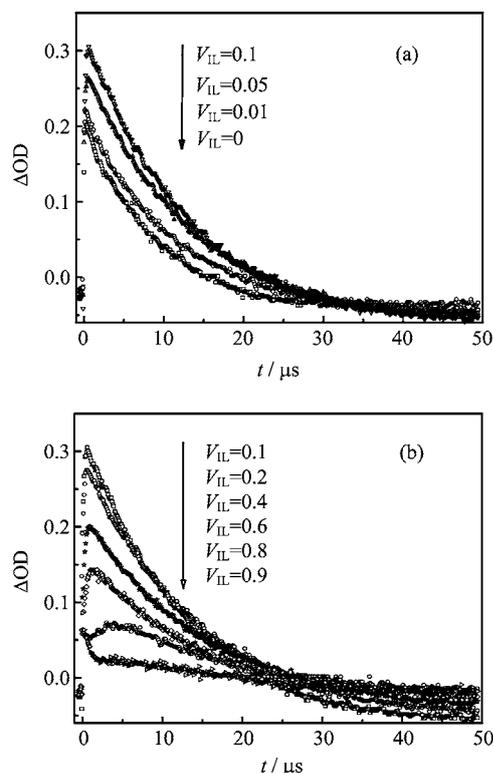
To further understand effects of IL on the photochem-

FIG. 5 Time profiles observed at 510 nm of different volume fraction V_{IL} in [BPy][BF$_4$]/H$_2$O mixed solution containing 0.2 mmol/L AQS under N$_2$ purging. (a) $0 \leq V_{IL} \leq 0.1$ and (b) $0.1 \leq V_{IL} \leq 0.9$.

FIG. 6 Decay profiles monitored at 380 nm with different volume fraction V_{IL} in [BPy][BF$_4$]/H$_2$O mixed solution containing 0.2 mmol/L AQS under N$_2$ purging.

TABLE I Estimated apparent kinetic parameters of transient species B and ^{3}AQS^{*a}

V_{IL}	B		^{3}AQS*	
	$k_{gr}/10^6$ s^{-1}	τ_{gr}/μs	$k_{obs}/10^6$ s^{-1}	τ_{obs}/μs
0	11.1	0.06	3.2	0.21
0.2	6.0	0.12	2.1	0.33
0.4	4.7	0.15	1.2	0.60
0.6	3.1	0.22	1.9	0.70
0.8	1.1	0.64	0.6	1.11

^{a} V_{IL} is the volume fraction of [BPy][BF$_4$] in the mixture. k_{obs} is the apparent decay rate constant. k_{gr} is the apparent growth rate constant. τ_{obs} is the decay halftime of ^{3}AQS*, and τ_{gr} is the growth halftime of transient species B.

ical reaction, we choose some systems to analyze the kinetics of transient species (Fig.5). Since the characteristic absorption peak of B is near 510 nm, therefore the absorbance at 510 nm could predominantly reflect the concentration change of transient species B. As shown in Fig.5, the absorbance firstly increased with increasing [BPy][BF$_4$] concentration when $0 < V_{IL} < 0.1$, then it decreased gradually when $V_{IL} > 0.1$. It can be found that with the increase of [BPy][BF$_4$], the growth of B can be distinguished fairly. When $V_{IL} = 0.9$ (Fig.5(b)), the time profile has become complicated superposition spectra. It consists of the fast decay part and the long lifetime part, which could be attributed to the superposition of ^{3}AQS* and B. The apparent kinetic parameters are listed in Table I, which are approximately computed by fitting time profiles.

As shown in Fig.6, the decay profiles at 380 nm were also recorded. They all have a fast decay process when $t < 1$ μs. The whole time profile can not be fitted with first order law. But the fast decay part follows pseudo-first order kinetic, which could be mainly attributed to the decay of ^{3}AQS*. Therefore, the apparent kinetic parameters of ^{3}AQS* can be approximately fitted with the fast decay part (Table I).

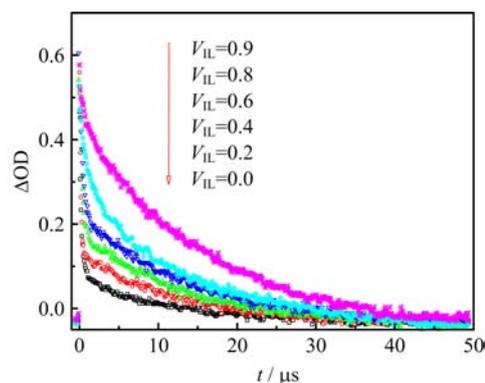From Table I, we can infer that the growth rate of B and the decay of ^{3}AQS* generally slow down gradually

with increasing V_{IL}. At the same time, the growth halftime of B decrease while the decay halftime of ^{3}AQS* increase. The above results indicate that high V_{IL} makes all reactions become slower, which may be related to the viscosity of system. On the whole, the viscosity of IL mixed with molecular solvent system could increase with increasing of V_{IL} [28, 29]. The viscosity changes very slowly when IL is dilute, but it would be raised sharply in high V_{IL}. The increase of viscosity is not advantageous to molecules diffusion. Therefore, contact probability among molecules could decrease, which could make both the growth rate and the decay rate of the transient species slow. As a result, the growth of B slows down and thus the decay of ^{3}AQS* also slows down in high V_{IL}. Some processes could be distinguished in this condition.

The decay of B can also be obtained by analyzing the kinetics of 510 nm with different V_{IL}. It was found that all the decays nearly follow pseudo-first order. Figure 7 shows the observed decay rate constants (K_{obs}) as the function of V_{IL} values. We can find that the changes of K_{obs} synchronize with the absorbance. When V_{IL} is close to 0.1, K_{obs} reaches the maximum, which can be
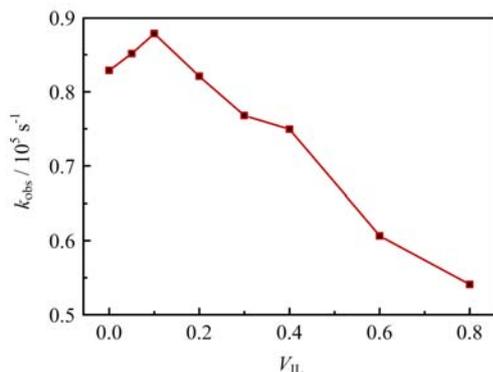

FIG. 7 Dependence of observed decay rate constant (k_{obs}) of B on the volume fraction V_{IL} of [BPy][BF$_4$].

FIG. 8 Time profiles observed at 380 and 480 nm in different saturated gas of N$_2$ and O$_2$, V_{IL}=0.9.

FIG. 9 Transient absorption spectra of AQS (about 0.1 mmol/L) in N$_2$-saturated [BPy][BF$_4$]/MeCN solution recorded at 0.1, 1, 3, 10, and 20 μs. V_{IL}=0.8.

explained for that ^{3}AQS* and H$_2$O (Eq.(4)) could react more easily when [BPy][BF$_4$] concentration is low. But the reaction intensity will decrease in high IL concentration. This also may be associated with the viscosity of the system.

2. Abstract hydrogen from [BPy][BF$_4$] to AQS

Comparing all the decay profiles at 380 nm under different ratios (Fig.6), it can be found they all have a long lifetime part besides the fast decay part as depicted above. The absorption intensity increased with increasing [BPy][BF$_4$] concentration, which contrasts to the changes around 510 nm. So we presume that there is a new species which leads to such a big difference. With the increase of the IL, the concentration of the new species becomes larger gradually. Reaction 4 and the reaction generating the new species are a pair of competitive reactions. Moreover, the direction of the reactions was preferred to the reaction generating the new species.

In order to verify the presumption, we observed the time profiles at both 380 and 480 nm bubbling with oxygen when V_{IL}=0.9 (Fig.8). It can be observed that the absorption intensity of B is very low in this condition. Hence the influence of B can be ignored. It is obvious that the decays of both 380 and 480 nm were accelerated in the condition of oxygen, the change of 380 nm was more obvious than that of 480 nm. It also implies that there is a new species with long lifetime could generate from ^{3}AQS* in this process. Thus, the spectral band near 380 nm is the superposition of ^{3}AQS* and the new species. In the condition of elevated IL concentrations, the reactions that ^{3}AQS* participates in could slow down overall which leads to the decay of ^{3}AQS* decrease.

Since the new species could be generated in this process, we decided to analyze what it was. It has been found that ^{3}AQS* can easily abstract a hydrogen to produce a neutral radical in previous references [30−32].
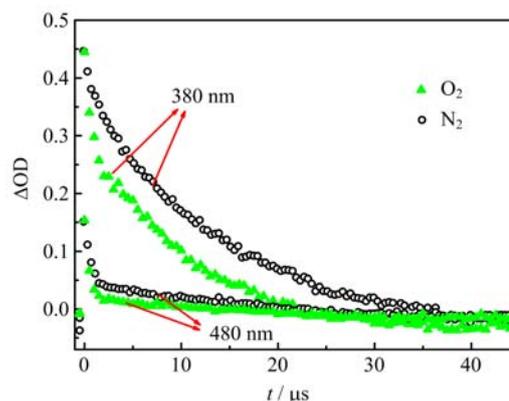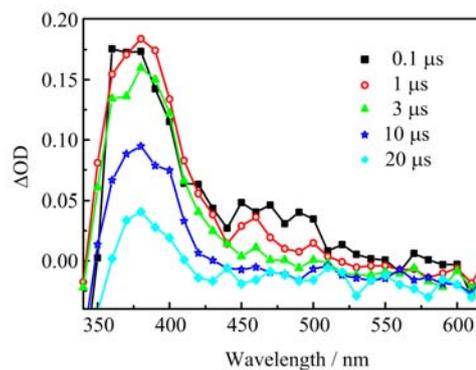
Moribe *et al.* reported that ^{3}AQS* can abstract hydrogen from phosphatidylcholine to generate AQSH$^.$ [30]. Wakisaka *et al.* found that ^{3}AQS* can react with 2-propanol to produce AQSH$^.$ through hydrogen atom transfer in H$_2$O/MeCN mixed solvent. Furthermore, AQSH$^.$ exhibits an absorption band in nearly the same region as ^{3}AQS* (λ_{max}=370 nm) [31]. So we could deduce that 350−420 nm is mainly contributed from the superposition of the absorption band of AQSH$^.$ and ^{3}AQS*.

To confirm the above speculation, we studied the transient absorption spectra of AQS in [BPy][BF$_4$]/MeCN mixed solvent. From Fig.9, we can see that the absorption peak centered at 380 nm after 1 μs, which could be assigned to AQSH*. Otherwise, one of characteristic absorption peak of ^{3}AQS* is near 360 nm (Fig.9), so we can judge the spectra bands of ^{3}AQS* superimposed together with that of AQSH$^.$.

In order to eliminate the effect of ^{3}AQS* to AQSH$^.$, we can obtain the subtraction spectrum by subtracting the absorbance at 470 nm multiplied by A_{380}/A_{470} from that at 380 nm [23, 33]. It is obvious that the growth trace of AQSH$^.$ was synchronous with decay of ^{3}AQS* (Fig.10). It can be found that Fig.9 is very dif-
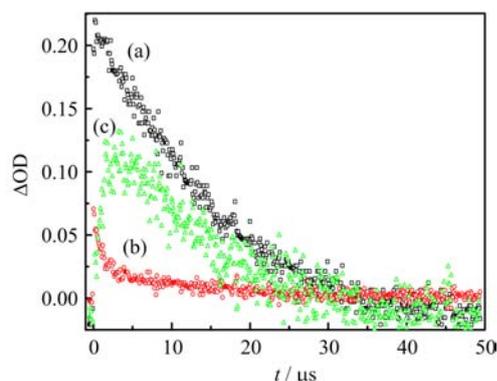
FIG. 10 Time profiles observed at (a) 380 nm, (b) 470 nm, and (c) 380 nm$-P\times$470 nm in [BPy][BF$_4$]/MeCN mixed solution containing 0.1 mmol/L AQS under N$_2$ purging, V_{IL}=0.8. P is a coefficient which means the ΔOD ratio between 380 and 470 nm at nearly 0 μs after 355 nm laser pulse.

ferent from Fig.1, which shows the transient absorption spectra of AQS in pure MeCN. Because ^{3}AQS* can not react with MeCN, we deduce that ^{3}AQS* could react with cations of [BPy][BF$_4$]. Possible reaction equation is as follows:

$$^3\text{AQS}^* + [\text{BPy-H}]^+ \rightarrow \text{AQSH}^. + \text{BPy}^{.+} \tag{9}$$

In a word, we get the possible photochemical reaction mechanism of AQS in [BPy][BF$_4$]/H$_2$O mixed system. The reaction paths are summarized in Scheme 1.

IV. CONCLUSION

The photochemical reaction process of AQS in [BPy][BF$_4$]/H$_2$O mixed system has been studied by laser flash photolysis. We have obtained the characteristic absorption peak of AQSH$^.$ and put forward possible reaction mechanism in the system. Through the analysis of experimental data, we found that ionic liquids with the low concentration could promote the reaction between ^{3}AQS* and H$_2$O. With the increase of IL concentration, the concentration of transient species B decreased for both contact probability and molecular diffusion decreasing. On the contrary, the concentration of AQSH$^.$ produced by hydrogen abstraction reactions between ^{3}AQS* and [BPy]$^+$ increased gradually. Therefore the direction of the competitive reactions could be adjusted by tuning the concentration of IL. In the case of high concentration of IL, the decay of ^{3}AQS* could slow down, so that we can observe a more specific reaction process. As a new kind of green solvents, ILs have shown many different characteristics compared to traditional solvents, which provides a new pathway to study the photochemical reaction process of AQS.
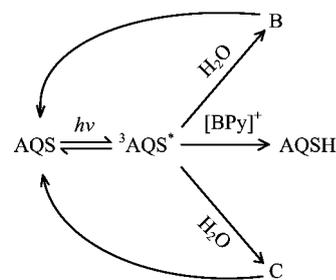
Scheme 1 Proposed reaction scheme of AQS in [BPy][BF$_4$]/H$_2$O mixed solution.

[1] T. Welton, Chem. Rev. **99**, 2071 (1999).
[2] F. Endres and S. Z. El Abedin, Phys. Chem. Chem. Phys. **8**, 2101 (2006).
[3] R. D. Rogers and K. R. Seddon, Science **302**, 792 (2003).
[4] M. J. Earle and K. R. Seddon, Pure Appl. Chem. **72**, 1391 (2000).
[5] Z. Yang and W. Pan, Enzyme Microb. Technol. **37**, 19 (2005).
[6] H. Zhao, S. Xia, and P. Ma, J. Chem. Technol. Biotechnol. **80**, 1089 (2005).
[7] T. Yago, Y. Ishii, and M. Wakasa, J. Phys. Chem. C **118**, 22356 (2014).
[8] S. Sarkar, R. Pramanik, D. Seth, P. Setua, and N. Sarkar, Chem. Phys. Lett. **477**, 102 (2009).
[9] S. Sarkar, S. Mandal, C. Ghatak, V. G. Rao, S. Ghosh, and N. Sarkar, J. Phys. Chem. B **116**, 1335 (2012).
[10] X. Li, M. Liang, A. Chakraborty, M. Kondo, and M. Maroncelli, J. Phys. Chem. B **115**, 6592 (2011).
[11] M. Koch, A. Rosspeintner, G. Angulo, and E. Vauthey, J. Amer. Chem. Soc. **134**, 3729 (2012).
[12] G. Zhu, Y. Wang, L. Zhang, Y. Liu, and G. Wu, Acta Phys. Chim. Sin. **31**, 419 (2015).
[13] M. J. Muldoon, A. J. McLean, C. M. Gordon, and I. R. Dunkin, Chem. Commun. 2364 (2001).
[14] Y. Nishiyama, M. Fukuda, M. Terazima, and Y. Kimura, J. Chem. Phys. **128**, 164514 (2008).
[15] I. Loeff, A. Treinin, and H. Linschitz, J. Phys. Chem. **87**, 2536 (1983).
[16] I. Loeff, A. Treinin, and H. Linschitz, J. Phys. Chem. **88**, 4931 (1984).
[17] I. Loeff, S. Goldstein, A. Treinin, and H. Linschitz, J. Phys. Chem. **95**, 4423 (1991).
[18] J. N. Moore, D. Phillips, N. Nakashima, and K. Yoshihara, J. Chem. Soc. Faraday Trans. **82**, 745 (1986).
[19] T. Ito, H. Shinohara, H. Hatta, S. Nishimoto, and S. Fujita, J. Phys. Chem. A **103**, 8413 (1999).

[20] J. Ma, W. Lin, W. Wang, Z. Han, S. Yao, and N. Lin, Radiat. Phys. Chem. **54**, 491 (1999).

[21] J. Ma, Nat. Sci. **6**, 1 (2014).

[22] J. Ma, W. Lin, W. Wang, Z. Han, S. Yao, and N. Lin, Sci. China, Ser. B **45**, 384 (2002).

[23] Z. Sheng, Y. Pan, L. Yan, X. Hei, Z. Guo, J. Dai, Q. Song, and S. Yu, J. Photochem. Photobiol. A **161**, 99 (2004).

[24] K. P. Clark and H. I. Stonehill, J. Chem. Soc. Faraday Trans. **68**, 577 (1972).

[25] P. R. Maddigapu, A. Bedini, C. Minero, V. Maurino, D. Vione, M. Brigante, G. Mailhot, and M. Sarakha, Photochem. Photobiol. Sci. **9**, 323 (2010).

[26] A. Bedini, E. De Laurentiis, B. Sur, V. Maurino, C. Minero, M. Brigante, G. Mailhot, and D. Vione, Photochem. Photobiol. Sci. **11**, 1445 (2012).

[27] C. Batchelor-McAuley, Q. Li, S. M. Dapin, and R. G. Compton, J. Phys. Chem. B **114**, 4094 (2010).

[28] B. Mokhtarani, A. Sharifi, H. R. Mortaheb, M. Mirzaei, M. Mafi, and F. Sadeghian, J. Chem. Thermodynam. **41**, 323 (2009).

[29] G. Zhu, Y. Wang, L. Zhang, Y. Luo, M. Sha, and X. Xu, J. Mol. Liq. **203**, 153 (2015).

[30] S. Moribe, T. Ikoma, K. Akiyama, and S. Tero-Kubota, Chem. Phys. Lett. **457**, 66 (2008).

[31] A. Wakisaka, T. W. Ebbesen, H. Sakuragi, and K. Tokumaru, J. Phys. Chem. **91**, 6547 (1987).

[32] G. Zhu, J. Xu, G. Wu, H. Zhu, D. Long, S. Chen, and S. Yao, Int. J. Mol. Sci. **7**, 590 (2006).

[33] H. Zhu, M. Wang, L. Cheng, R. Zhu, X. Sun, S. Yao, Q. Wu, and S. Wang, Acta Phys. Chim. Sin. **26**, 87 (2010).