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Two-photonic photochemistry of NaBr in methanol solutions

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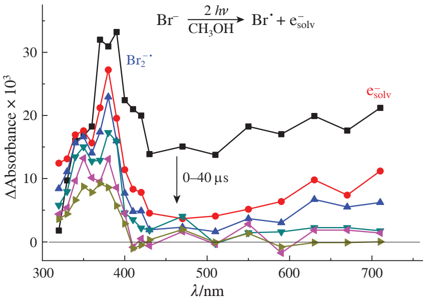
Two-photonic ionization of NaBr in methanol solutions at 266 nm was studied by nanosecond laser flash photolysis. The mechanism of photolysis includes reactions of a solvated electron and a dibromide radical anion. For quantitative description, two-photonic ionization of methanol should be taken into account.



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Second-order processes can play an important role in laser flash photolysis experiments.[1–4] Irradiation by a focused laser beam can initiate two-photon (simultaneous absorption of two photons *via* a virtual state[5]) and two-quantum (absorption of a second light quantum by an excited state of a molecule[6]) processes. The rapidly developed fields of biphotonic process applications are organic synthesis,[3] photon upconversion,[4] two-photon excited photodynamic therapy (2PE-PDT)[7] and two-photon fluorescence microscopy.[8] The laser flash photolysis experiments are often performed in aqueous and methanol solutions, and these solvents can be ionized under irradiation at 266 nm (frequently used 4th harmonics of a YAG laser) with the formation of an aquated (solvated) electron.[9,10] This two-photon process should be taken into account when working with water and methanol, as it can significantly influence the overall kinetic scheme.

In this work, we report on two-photon ionization of a bromide anion in methanol. Photochemistry of aqueous Br^- solutions was studied previously,[11,12] and in both cases the reaction was driven by low-intensity irradiation at $\lambda < 250$ nm in a one-photon regime. Our study was inspired by the efforts in understanding of $Br_2^{\bullet -}$, $Cl_2^{\bullet -}$ and $BrCl^{\bullet -}$ radical anions' formation and laser flash photolysis-induced decay of hexahalide complexes of platinum metals in the presence of free halide anions in aqueous[13–15] and methanol[16] solutions. When these experiments are performed with the excitation at 266 nm, two-photon processes both for solvent molecules and halide anions must be considered. We performed herein the two-photon formation of $Br_2^{\bullet -}$ upon the 266 nm laser flash photolysis of NaBr in methanol. To our knowledge, this is the first communication on the two-photon ionization of the Br^- anion. Experiments were performed using the laser flash photolysis setup described in detail.[17]

The dissociation constant of NaBr in MeOH is 0.04 M,[18] and so at high concentrations dissociation, of the salt is not complete. The dependence of the ionic strengths of the solution *vs*. the initial salt concentration is presented in Online Supplementary Materials, Section S2. Sodium bromide does not absorb at the irradiation wavelength [266 nm, Figure 1(*a*)]. Despite that, irradiation by the focused laser beam resulted in the formation of absorption with the maximum at 270 nm [Figure 1(*b*)], definitely belonging to the Br_3^- anion.[19]

In addition, intermediate absorption was detected in the laser flash photolysis experiments. Intermediate absorption spectra are shown in Figure 2(*a*), and an example of a kinetic curve is presented in Figure 2(*b*). There are two species responsible for the intermediate absorption spectrum. The initially formed wide band covering all the visible spectral range (with the weakly pronounced maxima at 600 and 750 nm) belongs to the solvated electron e^-_{solv}.[20] The band with the maximum in the range of 380 nm, which became pronounced after the decay of a solvated electron [see spectra corresponding to the time delays 0.8 μs and longer in Figure 2(*a*)], belongs to the $Br_2^{\bullet -}$ radical anion (see works[20,21] for aqueous solutions and work[16] for methanol solution). The formation of $Br_2^{\bullet -}$ is the result of the two-photon ionization of a bromide anion [reaction (1)] followed by the capture of a bromine atom by another bromide anion [reaction (2)]. The two-photon character of the radical anion formation is supported by the parabolic dependence of the $Br_2^{\bullet -}$ absorption amplitude on the laser pulse energy (Figure 3). The rate constant k_2 was measured to be 1.2×10^{10} dm³ mol⁻¹ s⁻¹ in

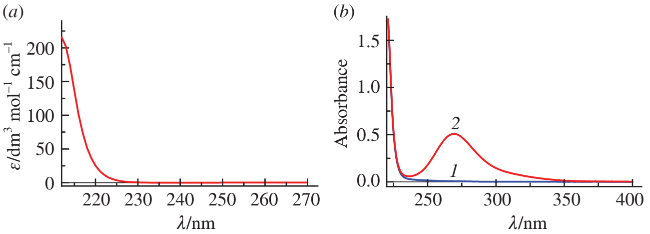

Figure 1 (*a*) Electronic absorption spectrum of NaBr (0.05 M) in MeOH. (*b*) Results of focused laser beam irradiation (266 nm, 200 mJ cm⁻²) of 0.5 M air-saturated NaBr in MeOH. Curves *1* and *2* are the spectra corresponding to 0 and 1000 laser pulses.

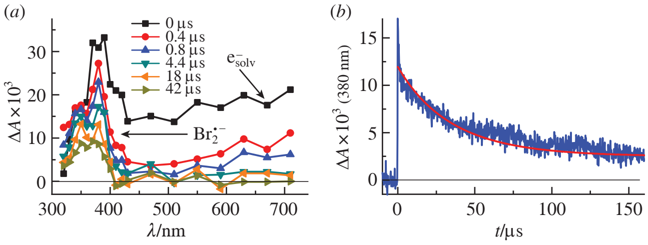

Figure 2 Results of laser flash photolysis (266 nm) experiment with 0.5 M NaBr in MeOH (1 cm cell, air-saturated solution). (*a*) Time evolution of intermediate absorption spectrum. (*b*) Example of an experimental kinetic curve with modeling using reactions (3), (4), (8) and (12a) with the rate constants $k_3 = 5.5\times 10^8$, $k_4 = 5.8\times 10^2$, $k_8 = 4.0\times 10^8$ and $k_{12a} = 6.0\times 10^9$ dm^3 mol^{-1} s^{-1}, as well as $\varepsilon = 9000$ dm^3 mol^{-1} cm^{-1} and residual absorption corresponding to the product Br_3^-.

water[22] and 1.5×10^{10} dm^3 mol^{-1} s^{-1} in acetonitrile;[23] in methanol it should be similar. At 0.5 M of Br^-, the characteristic lifetime of $Br_2^{\bullet-}$ formation is *ca.* 0.2 ns; *i.e.*, at the end of the laser pulse all the bromine atoms have formed radical anions.

$$Br^- \xrightarrow[CH_3OH]{2h\nu} Br^{\bullet} + e^-_{solv} \tag{1}$$

$$Br^{\bullet} + Br^- \xrightarrow{k_2} Br_2^{\bullet-} \tag{2}$$

$$Br_2^{\bullet-} + Br_2^{\bullet-} \xrightarrow{2k_3} Br_3^- + Br^- \tag{3}$$

$$Br_2^{\bullet-} + CH_3OH \xrightarrow{k_4} {}^{\bullet}CH_2OH + 2Br^- + H^+ \tag{4}$$

Now, let us discuss the kinetics of intermediate absorption decay [see Figure 2(*b*), as an example]. In the time interval $t > 5$ μs, all the reactions with the participation of e^-_{solv} are finished, and $Br_2^{\bullet-}$ is the only absorbing species. Assuming that disproportionation [reaction (3)] and reaction with methanol [reaction (4)] are responsible for $Br_2^{\bullet-}$ decay, the kinetics curves [see Figure 2(*b*)] can be fitted by the combined (1 + 2) order reaction kinetic law equation:

$$A(t) = \frac{A_0 e^{-k'_4 t}}{1 + \dfrac{2k_3 A_0}{\varepsilon / k'_4}(1 - e^{-k'_4 t})} + A_{fin} \ .$$

Here ε is the molar absorption coefficient of $Br_2^{\bullet-}$, l is the optical path length, $k'_4 = k_4\times[CH_3OH]$, k_4 is the bimolecular rate constant of reaction (4), $[CH_3OH]$ is methanol concentration in neat methanol (24.7 M), k_3 is the rate constant of reaction (3), and A_{fin} is the residual absorption caused by Br_3^- formation.[19] In the course of the fitting procedure, the value of k_4 was taken equal to 5.8×10^2 dm^3 mol^{-1} s^{-1} (see ref. 16) and was not varied (it is reasonable, because this rate constant does not depend on the ionic strength of the solution); A_0, A_{fin} and k_3/ε were varied parameters. The value of k_3/ε was found to be $= (6.2\pm 0.6)\times 10^5$ s^{-1}. Taking the maximal value of $Br_2^{\bullet-}$ molar absorption coefficient equal to 9000 dm^3 mol^{-1} cm^{-1},[21] we obtained the value of the second order rate constant $k_3 = (5.6\pm 0.6)\times 10^9$ dm^3 mol^{-1} s^{-1}. However, the value of k_3 in methanol measured previously is an order of magnitude less: $k_3 \approx 5.5\times 10^8$ dm^3 mol^{-1} s^{-1} (see published data[16,24]), which is 5–6 times lower than in aqueous solutions.[25] The values of ionic strengths in this work and previous work[24] were comparable (for discussion of the ionic strength effect on the rate constant of ionic reactions see Online Supplementary Materials, Section S3). Therefore, fast decay of $Br_2^{\bullet-}$ can be explained by other second order reactions than disproportionation [reaction (3)].

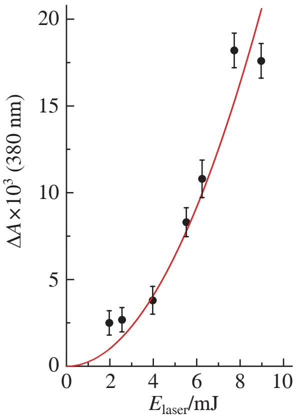

Figure 3 Results of laser flash photolysis (266 nm) experiment with 0.5 M NaBr in MeOH (1 cm cell, air-saturated solution). Dependence of $Br_2^{\bullet-}$ absorption amplitude on the laser pulse energy. Experimental points and parabolic fit.

Other possible reactions (5)–(15) followed the primary process [reaction (1)] are initiated by the solvated electron. Their rate constants apart from reaction (13), as well as estimated characteristic lifetimes of these reactions, under our experimental conditions, are presented in Table S1 (see Online Supplementary Materials, Section S4). The absence of information about the self-reactions of superoxide and $HO_2^{\bullet}$ radicals and their reactions with methanol most likely indicates that these reactions are insufficient. The reaction between $Br_2^{\bullet-}$ and the peroxy radical ${}^{\bullet}OOCH_2OH$ also seems improbable.

$$Br_2^{\bullet-} + e^-_{solv} \xrightarrow{k_5} 2Br^- \tag{5}$$

$$e^-_{solv} + CH_3OH \xrightarrow{k_6} CH_3O^- + H^{\bullet} \tag{6}$$

$$e^-_{solv} + O_2 \xrightarrow{k_7} O_2^{\bullet-} \tag{7}$$

$$Br_2^{\bullet-} + O_2^{\bullet-} \xrightarrow{k_8} 2Br^- + O_2 \tag{8}$$

$$Br_2^{\bullet-} + H^{\bullet} \xrightarrow{k_9} 2Br^- + H^+ \tag{9}$$

$$H^{\bullet} + CH_3OH \xrightarrow{k_{10}} {}^{\bullet}CH_2OH + H_2 \tag{10}$$

$$H^{\bullet} + O_2 \xrightarrow{k_{11}} HO_2^{\bullet} \tag{11}$$

$$HO_2^{\bullet} + Br_2^{\bullet-} \xrightarrow{k_{12a}} 2Br^- + H^+ + O_2 \tag{12a}$$

$$HO_2^{\bullet} + Br_2^{\bullet-} \xrightarrow{k_{12b}} Br_2 + HO_2^- \tag{12b}$$

$$Br_2^{\bullet-} + {}^{\bullet}CH_2OH \xrightarrow{k_{13}} 2Br^- + CH_2O + H^+ \tag{13}$$

$${}^{\bullet}CH_2OH + O_2 \xrightarrow{k_{14}} {}^{\bullet}OOCH_2OH \tag{14}$$

$$2\,{}^{\bullet}CH_2OH \xrightarrow{k_{15}} \text{products} \tag{15}$$

Despite the large quantity of reactions followed the primary process [reaction (1)], there is no possibility to explain the observed fast decay of $Br_2^{\bullet-}$ in air-saturated solutions. According to the rate constants of reactions (2)–(15) (see Table S1), the presumable way of e^-_{solv} decay is the formation of superoxide [reaction (7)]. However, its reaction (8) with $Br_2^{\bullet-}$ is an order of magnitude slower than it is necessary for successful fitting of the experimental data. That is why, in addition to reaction (1), we consider the two-photonic ionization of methanol under the 266 nm laser irradiation. An example of a kinetic curve of the solvated electron decay is shown in Figure S3.

$$CH_3OH \xrightarrow{2h\nu} {}^{\bullet}CH_2OH + e^-_{solv} + H^+ \tag{16a}$$

$$CH_3OH \xrightarrow{2h\nu} {}^{\bullet}CH_2OH + H^{\bullet} \tag{16b}$$

Reaction (16a) does not provide channels for $Br_2^{\bullet-}$ decay in air-saturated solutions additionally to reactions (1)–(15), because the hydroxymethyl radical would rapidly react with the dissolved oxygen [reaction (14)], giving the inactive peroxy radical. However, one can assume that an electron and a proton can recombine in the solvent cage, resulting in the primary process represented by reaction (16b). In this case, the formation of a hydrogen atom became sufficient. Two main channels of its decay [reactions (10) and (11)] have almost equal probability, and reaction (12a) between $Br_2^{\bullet-}$ and $HO_2^{\bullet}$ can give the necessary additional channel of the dibromide radical anion decay. The kinetic curves of $Br_2^{\bullet-}$ decay were fitted by the solutions of differential equations corresponding to reactions (3), (4), (8) and (12a) with the rate constants (see Table S1) with the possible corrections to the ionic strength. An example of a fit is shown in Figure 2(*b*). Fit results are not unambiguous, because the two parameters, namely, the rate constant k_{12a} and the initial concentration of the $HO_2^{\bullet}$ radicals can be varied simultaneously in opposite directions. Only outdated results for k_{12a} with large scattering are available in the literature (see Table S1); this rate constant should be re-examined using modern experimental techniques. At the moment, we can say that the value of k_{12a} falls into the interval $(2–7)\times 10^9$ dm^3 mol^{-1} cm^{-1}.

Summarizing, we have reported on the two-photonic process for Br^- in methanol [reaction (1)], leading to the formation of a $Br_2^{\bullet-}$ radical anion. This process is accompanied by two-photonic photoionization of methanol. The results are presumably qualitative. Further study is necessary to determine cross-sections of two-photonic processes as well as to re-examine several rate constants important for the quantitative description of the process.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7607.

References

1 U. Lachish, A. Shafferman and G. Stein, *J. Chem. Phys.*, 1976, **64**, 4205; https://doi.org/10.1063/1.431991.

2 I. Carmichael and G. L. Hug, *J. Chem. Phys.*, 1985, **89**, 4036; https://doi.org/10.1021/j100265a021.

3 J. Castellanos-Soriano, J. C. Herrera-Luna, D. D. Diaz, M. Consuelo Jiménez and R. Pérez-Ruis, *Org. Chem. Front.*, 2020, 1709; https://doi.org/10.1039/D0QO00466A.

4 C. Ye, L. Zhou, X. Wang and Z. Liang, *Phys. Chem. Chem. Phys.*, 2016, **18**, 10818; https://doi.org/10.1039/C5CP07296D.

5 K. D. Nanda and A. I. Krylov, *J. Phys. Chem. Lett.*, 2017, **8**, 3256; https://doi.org/10.1021/acs.jpclett.7b01422.

6 O. R. Alzueta, J. Cadet, M. Consuelo Cuquerella and M. A. Miranda, *Org. Biomol. Chem.*, 2020, **18**, 2227; https://doi.org/10.1039/D0OB00132E.

7 E. M. Boreham, L. Jones, A. N. Swinburne, M. Blanchard-Desce, V. Hugues, C. Terrun, F. Miomandre, G. Lemercier and L. S. Natrajan, *Dalton Trans.*, 2015, **44**, 16127; https://doi.org/10.1039/C5DT01855B.

8 W. Wu, C. Brandt, X. Zhou and S. Tang, *Biomed. Opt. Express*, 2024, **15**, 114; https://doi.org/10.1364/BOE.504550.

9 D. N. Nikogosyan, A. A. Oraevsky and V. I. Rupasov, *Chem. Phys.*, 1983, **77**, 131; https://doi.org/10.1016/0301-0104(83)85070-8.

10 D. Bhattacharyya, Y. Zhang, C. G. Elles and S. E. Bradforth, *J. Phys. Chem. A*, 2019, **123**, 5789; https://doi.org/10.1021/acs.jpca.9b04040.

11 J. Jortner, M. Ottolenghi and G. Stein, *J. Phys. Chem.*, 1964, **68**, 247; https://doi.org/10.1021/j100784a005.

12 J. Kalmár, É. Dóka, G. Lente and I. Fábián, *Dalton Trans.*, 2014, **43**, 4862; https://doi.org/10.1039/C3DT53255K.

13 E. M. Glebov, V. F. Plyusnin, N. V. Tkachenko and H. Lemmetyinen, *Chem. Phys.*, 2000, **257**, 79; https://doi.org/10.1016/S0301-0104(00)00140-3.

14 E. M. Glebov, V. F. Plyusnin, N. V. Tkachenko and H. Lemmetyinen, *Russ. Chem. Bull.*, 2008, **57**, 2487; https://doi.org/10.1007/s11172-007-0375-7.

15 E. M. Glebov, V. P. Grivin, V. F. Plyusnin, A. B. Venediktov and S. V. Korenev, *J. Photochem. Photobiol., A*, 2010, **214**, 181; https://doi.org/10.1016/j.jphotochem.2010.06.024.

16 E. M. Glebov, V. F. Plyusnin, V. P. Grivin, Yu. V. Ivanov, N. V. Tkachenko and H. Lemmetyinen, *J. Photochem. Photobiol., A*, 1998, **113**, 103; https://doi.org/10.1016/S1010-6030(97)00337-7.

17 E. M. Glebov, V. P. Grivin, V. F. Plyusnin, R. G. Fedunov, I. P. Pozdnyakov, V. V. Yanshole and D. B. Vasilchenko, *J. Photochem. Photobiol., A*, 2021, **418**, 113440; https://doi.org/10.1016/j.jphotochem.2021.113440.

18 S. Han and H. Pan, *Fluid Phase Equilib.*, 1993, **83**, 261; https://doi.org/10.1016/0378-3812(93)87029-Z.

19 D. Saffré, E. Atinault, S. Pin, J. P. Renault, J. L. Hazemann and G. Baldacchino, *J. Phys.: Conf. Ser.*, 2011, **261**, 012013; https://doi.org/10.1088/1742-6596/261/1/012013.

20 X. Shi, F. H. Long, H. Lu and K. B. Eisenthal, *J. Phys. Chem.*, 1995, **99**, 6917; https://doi.org/10.1021/j100018a024.

21 G. L. Hug, *Optical Spectra of Nonmetallic Inorganic Transient Species in Aqueous Solution*, National Bureau of Standards, Washington, DC, 1981; https://srd.nist.gov/NSRDS/NSRDS-NBS-69.pdf.

22 G. Merenyi and J. Lind, *J. Am. Chem. Soc.*, 1994, **116**, 7872; https://doi.org/10.1021/ja00096a050.

23 D. Weldon, M. Barra, R. Sinta and J. C. Scaiano, *J. Org. Chem.*, 1995, **60**, 3921; https://doi.org/10.1021/jo00117a055.

24 I. V. Khmelinskii, V. F. Plyusnin and V. P. Grivin, *Russ. Chem. Bull.*, 1988, **37**, 1095; https://doi.org/10.1007/BF00961907.

25 P. Neta, R. E. Huie and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1988, **17**, 1027; https://doi.org/10.1063/1.555808.

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