Nonradiative Deactivation of Excited Hemicyanines Studied with Submolecular Spatial Resolution by Time-Resolved Surface Second Harmonic Generation at Liquid−Liquid Interfaces

Gaelle Martin-Gassin, Diego Villamaina, and Eric Vauthey*

Department of Physical Chemistry, University of Geneva, 30 Quai Ernest-Ansermet, 1211, Genève 4, Switzerland

S *Supporting Information*

ABSTRACT: The excited-state dynamics of aminostilbazolium dyes is known to be dominated by nonradiative deactivation through large-amplitude motion. In order to identify the coordinate(s) responsible for this process, the excited-state lifetimes of two dialkylaminostyryl-methylpyridinium iodides have been measured at liquid−liquid interfaces using time-resolved surface second harmonic generation. We found that the decay time of the excited-states of both compounds was increasing with the viscosity of the apolar phase, consisting of n-alkanes of varying length, but was unaffected by that of the polar phase, made of water/glycerol mixtures. This indicates that the nonradiative deactivation is associated with the twist of the dialkylaniline group, which is located in the apolar part of the molecule.

Chart 1. Chemical Structure of the Hemicyanines

DBASP: R=C$_4$H$_9$
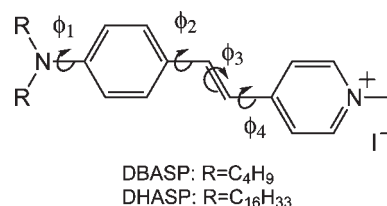DHASP: R=C$_{16}$H$_{33}$

Nonradiative deactivation via structural reorganization is known to be the main relaxation pathway of the first singlet electronic excited state of many flexible molecules, among them those involved in vision or responsible for the emission of fluorescent proteins.[1,2] In many cases, this occurs via rotational motion around single bonds or a weakened double bound that lowers the energy and brings the S$_1$ state toward a conical intersection with the electronic ground state.[3] If there is no intrinsic barrier between the Franck−Condon region of the excited-state potential and this intersection, the nonradiative deactivation is then purely controlled by the friction exerted by the environment. Experiments have shown that, in such cases, the excited-state lifetime τ exhibits the following dependence on viscosity η:[4]

$$\tau \propto \eta^{\alpha} \qquad (1)$$

where α varies between ∼0.1 and 1, an α value lower than 1 indicating that local friction is not properly described by viscosity.

Although measurements at varying viscosity can reveal the occurrence of nonradiative relaxation via large-amplitude motion, they do not allow identification of the coordinate involved in this process. Therefore, the mechanistic information obtained in these experiments is limited when the molecule possesses several bonds where torsion is possible. Until now, the relevant coordinate has been estimated by comparing the excited-state dynamics of analogues with bond torsion blocked upon substitution

with bulky substituents or upon selective bridging.[5] This strategy is not only costly in terms of synthetic effort but also may lead to erroneous conclusions if the electronic structure of the molecule is changed. We present here another approach allowing investigation into the effect of friction on different parts of a molecule independently. This is done by probing molecules located at the interface between two immiscible liquids and by measuring the effect of viscosity of each phase on their excited-state lifetime. To demonstrate this, we have studied two aminostilbazolium iodide dyes, 4-(4-(dibutylamino)styryl)-N-methylpyridinium iodide (DBASP) and 4-(4-(dihexadecylamino)styryl)-N-methylpyridinium iodide (DHASP) (Chart 1), belonging to the hemicyanine family. These compounds have been used for numerous applications,[6] such as fluorescent probes of neuron membranes,[7] laser dyes,[8] and non nonlinear optical material.[9] Their fluorescence quantum yield and lifetime have been shown to increase substantially with the viscosity of the environment because of an efficient nonradiative deactivation channel of the S$_1$ state involving intramolecular coordinate(s) with large-amplitude motion.[10] As shown in Chart 1, torsion around four different bonds could be responsible for the nonradiative deactivation and several studies have been devoted to the identification of the relevant one.[5,11−14] It was concluded that the trans−cis isomerization around the central bond, ϕ_3, is not involved because the photoisomerization yields is negligible.[15] On the other hand, rotation of the dialkylamino group, ϕ_3, has been shown to be associated with a high barrier.[12] Thus, the two remaining coordinates are the rotations of the dialkylaniline, ϕ_2, and of the pyridinium group, ϕ_4. Both DBASP and DHASP are amphiphilic molecules, and when at the interface between two immiscible liquids, they are oriented almost perpendicularly with the charged pyridinium head in the polar phase and the dialkylaniline end in the apolar phase.[16,17] Therefore, the possible occurrence of large-amplitude motion in

these two different parts of the molecules can be investigated selectively by varying alternatively the viscosity of the polar and apolar phases. The interfacial excited-state dynamics of DB(H)ASP was probed by using time-resolved surface second harmonic generation (TRSSHG). SSHG has been shown to be very powerful for obtaining information on the structure and properties of liquid interfaces.[18,19] TRSSHG offers the additional advantage of giving direct access to the dynamics of interfacial processes.[18] The interfacial selectivity is due to the dependence of the signal intensity on the second-order nonlinear optical susceptibility, which is zero in bulk materials but nonzero at the interface between two bulk media. Moreover, the electronic resonance enhancement of the signal allows selective probing of a solute molecule at the interface without interference from the nonresonant response of the solvent. Hemicyanines are well suited for SSHG measurements because of their orientation at the interface and because of their large hyperpolarisability.[20−22]

The viscosity dependence of excited-state dynamics of DBASP has first been investigated in bulk water/glycerol mixtures between 1 and 6 cP using femtosecond transient absorption, and the results are detailed in the Supporting Information. The transient spectra can be analyzed globally with the sum of three exponential functions with τ_{b1} ranging between 1 and 2.5 ps, τ_{b2} around 15 ps, and τ_{b3} varying between 40 and 225 ps. Both τ_{b1} and τ_{b3} were found to increase with viscosity according to eq 1 with α values of 0.54 and 1.0, respectively (Figure S3, Supporting Information). From the decay associated spectra (Figure S2, Supporting Information), the shortest time constant could be assigned to solvent relaxation and the longest one to the nonradiative relaxation of the S_1 state to the ground state. The α value found with τ_{b3} is fully consistent with the involvement of a mode with large-amplitude motion in the nonradiative deactivation of the excited state. On the other hand, τ_{b2} is assigned to aggregates, which are generally known to undergo very efficient nonradiative deactivation independently of the solvent viscosity.[23]

The setup for the TRSSHG experiments has already been described elsewhere[24,25] (see also Supporting Information). Excitation was performed at 500 nm, at the maximum of the $S_1{\leftarrow}S_0$ absorption band of both compounds, and probing was achieved with 800-nm pulses. A first series of measurements was carried out with DHASP at alkane/water interfaces. The dye was first dissolved in chloroform, and 2 nmol was then deposited on the surface of water. The apolar phase was changed from pentane to pentadecane, allowing the viscosity to be varied from 0.3 to 3 cP. Typical TRSSHG profiles recorded with pentane and decane are illustrated in Figure 1A. These profiles have been obtained by taking the square root of the raw data (to scale linearly with population changes) and by intensity normalization for better comparison (see Supporting Information). The decrease of the signal intensity upon 500 nm excitation and its recovery to its original value within a few hundreds of picoseconds suggest a resonance enhancement of the signal at 400 nm associated with the $S_1{\leftarrow}S_0$ transition. Consequently, these profiles should mainly reflect the ground-state recovery dynamics of DHASP. They were analyzed using the convolution of the sum of two exponential functions with the instrument response function. The shortest time constant, τ_{i1}, with a relative amplitude of 0.2−0.3, lies between 10 and 30 ps and does not correlate with solvent viscosity, whereas the longest one increases from 120 to 330 ps by going from pentane to pentadecane and depends on viscosity according to eq 1 with α ≈ 0.5 (Figure 1B). The short time
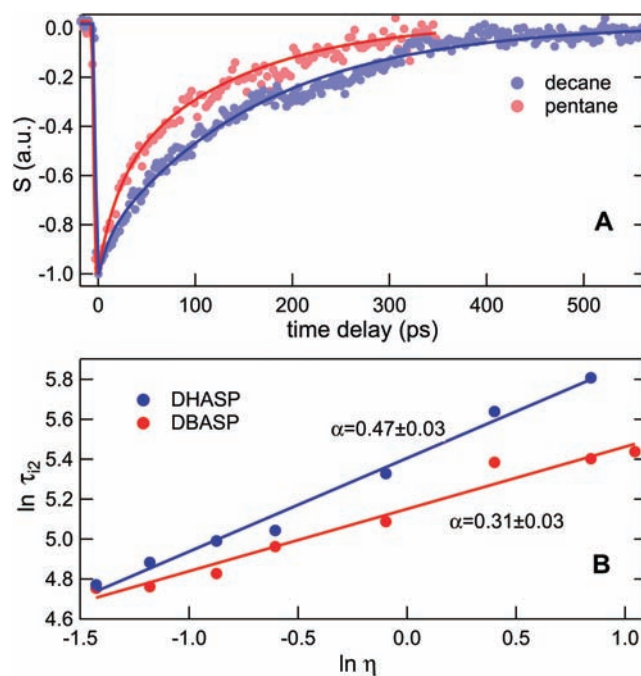

Figure 1. (A) TRSSHG profiles measured with DHASP at alkane/water interfaces and (B) viscosity dependence of the ground-state recovery time of DB(H)ASP at water/alkane interfaces.

constant, τ_{i1}, is close to τ_{b2} measured in the bulk solutions and most probably originates from aggregates as well. On the other hand, the long time constant, τ_{i2}, can be assigned to the ground-state recovery and its α clearly points to large-amplitude motion in the nonpolar part of DHASP. The same measurements were repeated with DBASP, but using a 90/10% water/glycerol mixture for the polar phase. Very similar results were obtained, with the slowest component having a viscosity dependence with α = 0.3.

In a second series of measurements, the upper apolar phase was kept constant, namely hexane with DHASP and dodecane with DBASP, whereas the viscosity of the polar phase was varied from 1 to 4 cP using water/glycerol mixtures of different compositions. Although its interfacial composition might differ from the bulk one, the glycerol/water mixture has already proven to be an efficient system for tuning interfacial friction.[24] For both dyes, the measured TRSSHG profiles were independent, within the experimental error, of the glycerol content of the mixture (Figure 2A). With DHASP, the long lifetime remains around 125 ps, whereas it is of the order of 240 ps with DBASP, and with both dyes its relative amplitude stays around 0.75. Analysis of the viscosity dependence of this time constant in terms of eq 1 gave α values of 0.07 ± 0.12 and 0.11 ± 0.08 for DHASP and DBASP, respectively (Figure 2B). This absence of viscosity effect indicates that, if occurring, large-amplitude motion in the polar part of the dyes has no influence on the excited-state lifetime.

These interfacial measurements reveal unambiguously that the nonradiative decay of the S_1 state of DB(H)ASP is due to large-amplitude motion of the part of the molecules located in the nonpolar phase. Although SSHG allows the orientation of the hyperpolarisability tensor relative to the interface to be determined, it does not yield information on the position of the molecules at the interface. As DBASP is soluble in polar solvents only, one can exclude a position where the whole molecule is
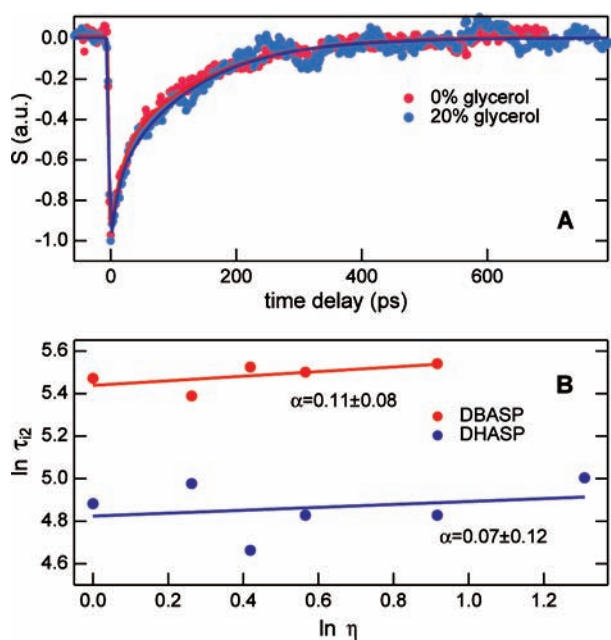
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Figure 2. (A) TRSSHG profiles measured with DHASP at hexane-water/glycerol interfaces and (B) viscosity dependence of the ground-state recovery time of DHASP at hexane-water/glycerol interfaces and of DBASP at dodecane-water/glycerol interfaces.

located in the nonpolar phase. Similarly, the molecules are most certainly not entirely in the polar phase, because of the long alkyl chains and because DHASP is not soluble in water. The most plausible position is that with the charged pyridinium head in the aqueous phase and the N,N-dialkylaniline tail in the nonpolar phase. Consequently, our observation of a viscosity dependence arising exclusively from the nonpolar phase points to the rotation of the N,N-dialkylaniline group (ϕ_2, Chart 1) as the mode associated with the nonradiative deactivation of these molecules.

The location of the molecules at the interface can be modified by changing the nature of the polar phase. Indeed, we found that the excited-state lifetime of DBASP at the interface between dodecane and a 70/30% water/methanol mixture is much shorter (τ_{i2} = 132 ps) than with the water/glycerol mixtures ($\tau_{i2} \approx 240$ ps) (Figure S4, Supporting Information). Furthermore, this lifetime is close to that measured at the octane-water/glycerol interface (τ_{i2} = 140 ps), with octane having the same viscosity as the water/methanol mixture. One can conclude that DBASP penetrates deeper in the polar phase when using methanol instead of glycerol, in agreement with the better solubility of DBASP in the former solvent. As a consequence, large-amplitude motion takes place, at least partially, in the polar phase. Further TRSSHG investigations on the effect of the nature of the polar phase are planned.

Finally, it should be noted that at a given viscosity, the interfacial dynamics are always much slower than that in the bulk, revealing that the friction experienced at the interface is probably substantially larger than that in the bulk medium. Moreover, the smaller α values at the interface indicate that this difference is diminishing with increasing bulk viscosity. This effect most probably stems from the anisotropic nature of the solvent structure in the interfacial region. As consequence, bulk viscosity does not account properly for friction at interfaces. The differences in decay times between bulk solutions and interfaces at a given viscosity could also partially stem from a different

intrinsic barrier for the nonradiative deactivation process due to some changes in the electronic structure of the dyes brought about by the anisotropic interfacial environment.[26] However, if occurring, this effect should be mostly negligible when comparing the dynamics measured at different interfaces.

This investigation shows that measurements of the excited-state dynamics of a probe solute at liquid—liquid interfaces not only delivers precious details on the properties of interfaces but also yields original mechanistic information on the probe itself.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Experimental details, femtosecond transient absorption experiments in bulk solutions, and results at alkane-water/methanol interfaces. This information is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

eric.vauthey@unige.ch

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■ REFERENCES

(1) Kukura, P.; McCamant, D. W.; Yoon, S.; Wandschneider, D. B.; Mathies, R. A. *Science* **2005**, *310*, 1006–1009.

(2) Mandal, D.; Tahara, T.; Meech, S. R. *J. Phys. Chem. B* **2004**, *108*, 1102–1108.

(3) Migami, A.; Olivucci, M. In *Conical Intersections. Electronic Structure, Dynamics and Spectroscopy*; Domcke, W., Yarkony, D. R., Köppel, H., Eds.; World Scientific: Singapore, 2004; pp 271–320.

(4) Velsko, S. P.; Fleming, G. R. *Chem. Phys.* **1982**, *65*, 59.

(5) Sczepan, M.; Rettig, W.; Tolmachev, A. I.; Kurdyukov, V. V. *Phys. Chem. Chem. Phys.* **2001**, *3*, 3555–3561.

(6) Mishra, A.; Behera, R. K.; Behera, P. K.; Mishra, B. K.; Behera, G. B. *Chem. Rev.* **2000**, *100*, 1973–2011.

(7) Fromherz, P.; Dambacher, K. H.; Ephardt, H.; Lambacher, A.; Mueller, C. O.; Neigl, R.; Schaden, H.; Schenk, O.; Vetter, T. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, *95*, 1333–1345.

(8) Zhao, C. F.; Gvishi, R.; Narang, U.; Ruland, G.; Prasad, P. N. *J. Phys. Chem.* **1996**, *100*, 4526–4532.

(9) He, G. S.; Bhawalkar, J. D.; Zhao, C. F.; Prasad, P. N. *Appl. Phys. Lett.* **1995**, *67*, 2433–2435.

(10) Ephardt, H.; Fromhertz, P. *J. Phys. Chem.* **1989**, *93*, 7717–7725.

(11) Strehmel, B.; Seifert, H.; Rettig, W. *J. Phys. Chem. B* **1997**, *101*, 2232–2243.

(12) Cao, X.; Tolbert, R. W.; McHale, J. L.; Edwards, W. D. *J. Phys. Chem. A* **1998**, *102*, 2739–2748.

(13) Kim, J.; Lee, M. *J. Phys. Chem. A* **1999**, *103*, 3378–3382.

(14) Huang, Y.; Cheng, T.; Li, F.; Luo, C.; Huang, C.-H.; Cai, Z.; Zeng, X.; Zhou, J. *J. Phys. Chem. B* **2002**, *106*, 10031–1040.

(15) Görner, H.; Gruen, H. *J. Photochem.* **1985**, *28*, 329–350.

(16) Evans, C. E.; Song, Q.; Bohn, P. W. *J. Phys. Chem.* **1993**, *97*, 12302–12308.

(17) Simpson, G. J.; Westerbuhr, S. G.; Rowlen, K. L. *Anal. Chem.* **2000**, *72*, 887–898.

(18) Eisenthal, K. B. *Chem. Rev.* **1996**, *96*, 1343–1360.

(19) Steel, W. H.; Walker, R. A. *Nature* **2003**, *424*, 296–299.

(20) Dian, X.-M.; Konami, H.; Okada, S.; Oikawa, H.; Matsuda, H.; Nakanishi, H. *J. Phys. Chem.* **1996**, *100*, 17780–17785.

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dx.doi.org/10.1021/ja109813j |*J. Am. Chem. Soc.* 2011, 133, 2358–2361

(21) Niidome, Y.; Ayukawa, H.; Yamada, S. *J. Photochem. Photobiol.* **2000**, *132*, 75–80.

(22) Martin-Gassin, G.; Benichou, E.; Bachelier, G.; Russier-Antoine, I.; Jonin, C.; Brevet, P. F. *J. Phys. Chem. C* **2008**, *112*, 12958.

(23) Sundstroem, V.; Gillbro, T. *J. Chem. Phys.* **1985**, *83*, 2733–43.

(24) Fita, P.; Punzi, A.; Vauthey, E. *J. Phys. Chem. C* **2009**, *113*, 20705–20712.

(25) Fedoseeva, M.; Fita, P.; Punzi, A.; Vauthey, E. *J. Phys. Chem. C* **2010**, *114*, 13774–13781.

(26) Sen, P.; Yamaguchi, S.; Tahara, T. *Faraday Discuss.* **2010**, *145*, 411–428.