Photoionization and dynamic solvation of the excited states of 7-azaindole

M. Negrerie  
_Ecole Polytechnique_

F. Gai  
_Iowa State University_

J.-C. Lambry  
_Ecole Polytechnique_

J.-L. Martin  
_Ecole Polytechnique_

Jacob W. Petrich  
_Iowa State University, jwp@iastate.edu_

Follow this and additional works at: http://lib.dr.iastate.edu/chem_pubs  
Part of the Physical Chemistry Commons

The complete bibliographic information for this item can be found at http://lib.dr.iastate.edu/chem_pubs/808. For information on how to cite this item, please visit http://lib.dr.iastate.edu/howtocite.html.
Photoionization and dynamic solvation of the excited states of 7-azaindole

Abstract
The excited-state photophysics of the biological probe, 7-azaindole, are examined in water and methanol. Electrons in a presolvated state absorbing in the infrared appear within the excitation pulse width of 130 fs. 330 i 100 fs is required for the presolvated electron to achieve the spectrum characteristic of the completely solvated electron. An excited-state transient absorbance decays in ~350 fs for 7-azaindole and its methylated analog, N1-methyl-7-azaindole (1M7AI), in the region 400-450 nm in water and methanol. The instantaneous appearance of the electron in the infrared is attributed to the decay of the IIb excited-state that overlaps the 'Lα excited state of 7-azaindole. The rapid decay of the excited-state transient absorbance is attributed to preferential, dynamic solvation of the 'Lα state. 7-Azaindole thus provides an interesting example of a molecule whose excited state is continuously and dynamically solvated but which also produces a species, eν', whose solvation appears to occur in a stepwise process.

Disciplines
Chemistry | Physical Chemistry

Comments

This article is available at Iowa State University Digital Repository: http://lib.dr.iastate.edu/chem_pubs/808
The excited-state photophysics of the biological probe, 7-azaindole, are examined in water and methanol. Electrons in a presolvated state absorbing in the infrared appear within the excitation pulse width of 130 fs. 330 ± 100 fs is required for the presolvated electron to achieve the spectrum characteristic of the completely solvated electron. An excited-state transient absorbance decays in ~350 fs for 7-azaindole and its methylated analog, N1-methyl-7-azaindole (1M7AI), in the region 400–450 nm in water and methanol. The instantaneous appearance of the electron in the infrared is attributed to the decay of the 1La excited-state that overlaps the 1Le excited state of 7-azaindole. The rapid decay of the excited-state transient absorbance is attributed to preferential, dynamic solvation of the 1Le state. 7-Azaindole thus provides an interesting example of a molecule whose excited state is continuously and dynamically solvated but which also produces a species, \( e_{aq} \), whose solvation appears to occur in a stepwise process.

### Introduction

7-Azaindole has been used as a model system for problems of biochemical and physical chemical interest. Kash and co-workers originally proposed dimers of 7-azaindole in nonpolar solvents as a model for DNA base pairs.\(^1\) These investigators and subsequently others\(^4,5\) proposed and characterized an excited-state double proton transfer that occurs in 7-azaindole dimers in nonpolar solvents in 1.4 ps.\(^5\) In 7-azaindole complexes with linear alcohols such as methanol, this nonradiative process occurs in 140 ps.\(^6\) We have recently focused attention on 7-azaindole because it is the chromophore of the biological probe, 7-aza-tryptophan, which is spectroscopically distinguishable from tryptophan and can be incorporated into synthetic peptides and bacterial protein.\(^11\) The importance of water as a solvent for biochemical and physical chemical interest. 7-Azaindole has been used as a model system for problems of biochemical and physical chemical interest. Kash and co-workers originally proposed dimers of 7-azaindole in nonpolar solvents as a model for DNA base pairs.\(^1\) These investigators and subsequently others\(^4,5\) proposed and characterized an excited-state double proton transfer that occurs in 7-azaindole dimers in nonpolar solvents in 1.4 ps.\(^5\) In 7-azaindole complexes with linear alcohols such as methanol, this nonradiative process occurs in 140 ps.\(^6\) We have recently focused attention on 7-azaindole because it is the chromophore of the biological probe, 7-aza-tryptophan, which is spectroscopically distinguishable from tryptophan and can be incorporated into synthetic peptides and bacterial protein.\(^11\) The importance of water as a solvent for biochemical systems requires that the photophysics of 7-azaindole be characterized fully in polar solvents, especially water, if it is to be useful as a biological probe.

We have previously observed by means of fluorescence-excitation anisotropy spectra that 7-azaindole and its derivatives possess closely spaced 1Le and 1La excited states as evidenced by a strongly excitation-wavelength-dependent fluorescence anisotropy in both the steady state and the time domain.\(^12\) Here we discuss the importance of the 1Le and 1La states in the photophysics of 7-azaindole and consider in particular their role in photoionization and dynamic solvation.

### Experimental Section

7-Azaindole was obtained from Sigma and purified.\(^13\) We have previously discussed the synthesis and purification of N1-methyl-7-azaindole (1M7AI).\(^13\) The experiments with ~100-fs pulses were performed in Palaiseau.\(^14\) The duration of the probe pulse is 50–70 fs and that of the pump pulse is 130–180 fs. The ~1-ps experiments were performed in Ames.\(^15\) Sample concentrations were adjusted to provide optical densities of 0.5–0.7 in 1 mm at the exciting wavelengths.

### Results and Discussion

#### A. Photoionization

Using excitation pulses at 294 nm, we have observed that solvated electrons \( (\lambda_{prek} = 580–650 \text{ nm}) \) appear monophotonically with a rise time that is within our 1-ps pulsewidth.\(^15\)–\(^17\) To harmonize this result with the decay of the lowest excited state of 7-azaindole in water as measured by the fluorescence lifetime of 910 ps, we suggested that two excited states lie close to another and that the higher of these two states decays in less than 1 ps by photoionization. The lower of the two states decays by other channels\(^17\) and gives rise to the 910-ps lifetime. The presence of the 1Le and 1La states is clearly indicated in the steady-state fluorescence anisotropy data.\(^12\)

In this work we investigate the photoionization process with improved time resolution. Figure 1 indicates that at 660 nm a transient species appears with a rise time of 330 ± 100 fs, for 7-azaindole in water. The origin of this transient is assigned to the species appearing within the laser pulse duration of 130 fs at wavelengths greater than 880 nm. The infrared transient at 940 nm is fit to a decay time of 570 ± 150 fs. But the noise in the 940-nm data and the presence of the long-lived absorbance render this determination less precise. Within the error of the experiment, we conclude that the decay time of the infrared transient agrees well with the rise of the transient absorbing at higher energy. At 2-ps subsequent to photon absorption of 7-azaindole in water the absorption spectrum is identical to that of the fully solvated electron at 2 ps\(^18\) (Figure 2). The kinetics we observe are consistent with a discrete transition of presolvated electrons to solvated electrons.\(^18,20\) The transient absorbing in the infrared has been attributed to an excited state of the electron.\(^21\) Recently Barbara and co-workers have directly measured the lifetime of this excited state to be 550 ± 170 fs.\(^22\) Pomméret al.\(^22\) have discussed the early time decay channels of the excited state of the electron.

These data suggest a stepwise model for the transition from the presolvated or trapped electron, which gives rise to the infrared absorption, to the solvated electron, the absorption maximum of which is located at 720 nm (Figure 2). Furthermore, for 7-azaindole in methanol we find that the solvated electron appears within the time resolution (≤1 ps) of the apparatus (Figure 3b). We observe similar results for indole in methanol and butanol, unlike Mataga and co-workers\(^20\) who suggest that the rise time of the solvated electron is as long as 32 ps in butanol and who conclude that there is a time-dependent, continuous spectral shift, controlled by the dielectric properties of the solvent.

When pure water is photoionized in a two-photon process in femtosecond pulsed experiments, up to 60% of the solvated electrons recombines geminately on a time scale of about 100 ps.\(^25,26\) Figure 3 indicates that this geminate recombination is absent when the source of the solvated electron is 7-azaindole.
Excited States of 7-Azaindole

Figure 1. Transient absorbance of 7-azaindole in water at room temperature. The 310-nm pump pulse has a full width at half-maximum of 130 fs. The probe has a full-width at half-maximum of 50 fs. (a) \( \lambda_{\text{probe}} = 940 \text{ nm} \). The fit through the data indicates that the transient absorbance appears with an "instantaneous" rise time (\( \leq 130 \text{ fs} \)) and decays with a time constant of 570 \( \pm 20 \text{ fs} \). (b) \( \lambda_{\text{probe}} = 660 \text{ nm} \). The transient absorbance is fit to a rise time of 330 \( \pm 100 \text{ fs} \). The residuals resulting from the fits are displayed above the data.

Figure 2. Absorption spectrum of 7-azaindole in water at a 2-ps delay after photoexcitation. The solid line is only meant to guide the eye. At each wavelength, a measurement at 720 nm is recorded to take into account the drift of the laser. \( \lambda_{\text{pump}} = 310 \text{ nm} \).

Identical results are obtained for indole. There is a major difference between the pure water and the 7-azaindole experiments. When 7-azaindole is prepared in its excited electronic state by absorption of a 310-nm (or 4-eV) photon, the nonradiative photoionization process can be considered to deposit most of this excited-state energy into the kinetic energy of the electron. On the other hand, the ionization threshold for pure water is estimated to be 6.5 eV. Absorption of two 310-nm photons will in this case produce an electron with a kinetic energy \( \leq 1.5 \text{ eV} \). A smaller kinetic energy prohibits the electron from thermalizing far from its radical cation and thus enhances the possibility of geminate recombination. Goulet and Jay-Gerin have estimated that the geminate recombination observed in femtosecond ionization measurements of pure water corresponds to an average distance of about 1 nm between the parent radical cation and the fully thermalized or hydrated electron. The absence of observed geminate recombination in our 7-azaindole photoionization measurements suggests an average distance between the pair of \( >2 \text{ nm} \). Similar results are obtained in pulse radiolysis experiments of water, which employ higher ionization energies; here geminate recombination occurs on a longer time scale and to a very small extent.

For our femtosecond experiments, to verify that the photoelectron generated is due to 7-azaindole itself and not to the
water, we noted that the transient absorbance at 940 nm in pure water yielded an absorbance at 940 nm that was four times weaker than that of a solution containing 7-azaindole. If the pump beam is attenuated with a filter of optical density 0.5, approximately the same attenuation of the pump afforded by the 7-azaindole, there is no longer any contribution of photoelectron from water. We thus conclude that in our experiments the signal observed in Figures 1 and 2 is entirely due to 7-azaindole. The peak power of our picosecond pulses was insufficient to ionize pure water.

B. Excited-State Solvation. In methanol (Figure 4a), when the probe wavelength is tuned to 400 nm, a transient absorbance appears within the duration of the laser pulse and decays with a time constant of 360 ± 100 fs. It is tempting to attribute this decay to the rapid excited-state tautomerization of a complex of 7-azaindole and solvent that does not require any large-scale reorganization. This explanation can, however, be excluded since a similar transient is observed for the methylated derivative (1 M7AI), which cannot accomplish proton transfer (Figure 4b).

A more plausible explanation is that the decay reflects the stabilization of the 1Ls state by dynamic solvation of the polar solvent. At time zero when the 1Ls state is prepared, it can absorb radiation at 400 nm, further exciting it into a higher singlet state, S2. As the 1Ls state is solvated, the energy gap between 1Ls and S2 will increase and the absorbance at 400 nm will decay. Preferential solvation of 1Ls in indole and its derivatives in polar solvents is well documented. The time scale for this process, ~350 fs, is in agreement with the results obtained from measurements of transient Stokes shifts of fluorescent probes in water and methanol. The transient Stokes shift can be considered to arise from a "continuous" process of dynamic solvation that appears to be fundamentally different from that which produces the solvated electron. We note that the data in Figure 4 are collected at only one wavelength and hence insufficient to map out a complete time course of the solvation process.

The relatively small extinction coefficient for the S1−S2 transition at 400 nm and the presence of the long-lived absorption prevent the observation of the full complexity of the dynamic solvation process that is manifested, for example, in the inertial contribution of the solvent response. It is conceivable that the fast transient is a result of vibrational relaxation in the excited state, but we believe this is unlikely because we excite at relatively long wavelengths (310 nm). Several groups have commented on the presence of an impurity in commercial 7-azaindole preparations. The rapid absorption transient cannot arise even from residual amounts of impurity in our purified sample since we have observed that the isolated impurity displays no analogous absorption transient.

Conclusions

Ultrafast transient absorption spectroscopy reveals that electrons are produced monophotonically from excited-state 7-azaindole in water. The presolvated electrons appear in 2130 fs and are localized and solvated in 330 ± 100 fs. This latter time agrees with the results obtained in pure water. No geminate recombination of the solvated electron is observed, suggesting that it is solvated more than 2 nm away from its parent cation. The instantaneous appearance of the presolvated electron indicates that its origin is not the fluorescent state, which has a lifetime of 910 fs, but a nearby or overlapping state that we have identified in steady-state fluorescence-excitation anisotropy spectra. Rapid absorption transients are observed for 7-azaindole and its methylated analog (1 M7AI) that are consistent with a preferential dynamic solvation of one state relative to the other (and to other higher-lying singlet states). The presence of the two low-lying singlet states of 7-azaindole may render it less than ideal as a fluorescent probe of solvation dynamics since the two excited states may interact during the solvation process. The processes of photoionization and dynamic solvation afforded to 7-azaindole by the interplay of its 1Ls and 1Ld states constitute a rich behavior that is belied by the well-behaved fluorescence decay of 7-azaindole and 7-azacyryptophan. A discussion of the fluorescence decay of 7-azacyryptophan will be provided in a future publication.

Acknowledgment.

The travel required to perform this research was funded by a NATO grant to J.W.P. and J.-L.M. J.W.P. is an Office of Naval Research Young Investigator. F.G. is the recipient of a fellowship from Phillips Petroleum. This work was partially supported by the ISU Biotechnology Council, University Research Grants, and IPRT. We thank Paul Barbara for sharing a preprint of his recent work.

References and Notes

Excited States of 7-Azaindole
