Excited states dynamics of DNA and RNA bases: Characterization of a stepwise deactivation pathway in the gas phase

Clélia Canuel, Michel Mons, François Piuzzi, Benjamin Tardivel, Iliana Dimicoli, and Mohamed Elhanine[a)]
Laboratoire Francis Perrin [CNRS URA 2453], DRECAM/SPAM, CEA Saclay, 91191 Gif-sur-Yvette, France

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Radiationless deactivation pathways of excited gas phase nucleobases were investigated using mass-selected femtosecond resolved pump-probe resonant ionization. By comparison between nucleobases and methylated species, in which tautomerism cannot occur, we can access intrinsic mechanisms at a time resolution never reported so far (80 fs). At this time resolution, and using appropriate substitution, real nuclear motion corresponding to active vibrational modes along deactivation coordinates can actually be probed. We provide evidence for the existence of a two-step decay mechanism, following a 267 nm excitation of the nucleobases. The time resolution achieved together with a careful zero time-delay calibration between lasers allow us to show that the first step does correspond to intrinsic dynamics rather than to a laser cross correlation. For adenine and 9-methyladenine a first decay component of about 100 fs has been measured. This first step is radically increased to 200 fs when the amino group hydrogen atoms of adenine are substituted by methyl groups. Our results could be rationalized according to the effect of the highly localized nature of the excitation combined to the presence of efficient deactivation pathway along both pyrimidine ring and amino group out-of-plane vibrational modes. These nuclear motions play a key role in the vibronic coupling between the initially excited $\pi\pi^*$ and the dark $n\pi^*$ states. This seems to be the common mechanism that opens up the earlier phase of the internal conversion pathway which then, in consideration of the rather fast relaxation times observed, would probably proceed via conical intersection between the $n\pi^*$ relay state and high vibrational levels of the ground state. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1850469]

I. INTRODUCTION

Due to its maximum absorbance near 260 nm, DNA is considered as the primary UV chromophore of living matter. The absorption spectrum of DNA corresponds to the electronic excitation of some of its elementary building blocks, namely, the nucleobases adenine (Ade), cytosine (Cyt), guanine (Gua), and thymine (Thy).[1,2]

Apparent UV photodamage yields, seem however to be relatively limited, compared to the strong UV absorption of genetic material.[1–3] The efficient DNA-repair system present in the cell partly explains this limitation. The intrinsic photophysical properties of the DNA chromophores that prevent excited state photochemistry are often evoked[1–6] as an equally relevant protection against harmful UV effects.

To explore the intrinsic protecting deactivation mechanisms, several groups have been investigating spectroscopy and dynamics of DNA chromophores over decades.[4–10] An excellent review of the most recent studies of nucleic acids photophysics both experimentally, in condensed and gas phases, and theoretically has been published by Kohler and co-workers.[11] Room temperature aqueous solution studies show that the singlet excited state dynamics of nucleobases is dominated by an ultrafast (picosecond range) decay, and correspondingly small fluorescence and phosphorescence quantum yields.

The mechanism for the ultrafast electronic deactivation of the nucleobases excited states relies on internal conversion. Theoretically, two different relaxation pathways for the energy disposal are suggested[12–14] and need further elucidation. Theoretical investigations[12,13] have pointed out that for nitrogen-heterocyclic and aromatic-carbonyl compounds, with low-lying excited states of $\pi\pi^*$ and $n\pi^*$ character, nuclear motions with appropriate out-of-plane vibrational modes could increase drastically the probability of radiationless transition between the two electronic manifolds. Experimental support for the close proximity of $n\pi^*$ and $\pi\pi^*$ states in adenine and their involvement in the excited state dynamics has been reported in several spectrally and time-resolved studies.[15,16] According to both the theoretical models and the observation of a rather ultrafast conversion dynamics, presence of conical intersections between excited and ground state have been suggested.[17,18] On the other hand, Sobolewski and Domcke[14] raised the possibility of a $\pi\sigma^*$ state, repulsive along the azine NH stretch coordinate, that intersects with the first $\pi\pi^*$ excited and the S_0 ground states.

Most recently, experiments on isolated nucleobases in supersonic jets opened an exciting research area using high resolution spectroscopy to understand the intrinsic photo-

[a)]Author to whom correspondence should be addressed. Electronic mail: elhanine@cea.fr

physical properties of nucleobases in the absence of a solvent. DNA bases in the gas phase are found in many tautomers formed by permuting hydrogen atoms among the set of heteroatoms. Vibronic spectra of the first singlet excited state of selected tautomers have been measured using fluorescence and resonance enhanced miltiphoton ionization (REMPI) detection as well as IR/UV double-resonance spectroscopies.[19–25]

Excited state dynamics of the gas phase nucleobases has been inferred by measuring fluorescence lifetimes or by time resolved pump-probe REMPI detection with nanosecond, picosecond, and femtosecond laser pulses.[19,20,24,25]

The first femtosecond pump-probe mass spectrometry study of gas phase nucleobases was reported by Kang *et al.*[17,18] In this experiment, excitation was at 267 nm and ionization was performed by three photons from the laser fundamental at 800 nm. Because of the particular excitation scheme (1+3) and the time resolution of 400 fs, the authors described the dynamics of all nucleobases by a simple monoexponential decay in the picosecond range following a Gaussian-like component resulting from coherent pump-probe absorption (cross correlation). They reported very similar lifetimes close to 1 ps for Ade, 9-methyl adenine (9MAde), and 7-methyl adenine (7MAde), therefore ruling out a predominant role of the NH stretch coordinate in the relaxation mechanism.

Further support for the model involving the $n\pi^*$ state comes from the first time-resolved photoelectron spectroscopic study of nucleobases.[26] This method could provide relevant information about the electronic character of the states reached during the decay. The authors assigned the two major bands of different lifetimes ($<$50 and 750 fs) in the photoelectron spectrum of adenine at 267 nm to the $\pi\pi^*$ and $n\pi^*$ states. A minor third channel ($<$50 fs), absent in the photoelectron spectrum at 250 nm, has been tentatively assigned to dynamics involving a $\pi\sigma^*$ state. These values, obtained in an experiment without any tautomer resolution, stem from a two-dimensional (time versus photoelectron energy) fitting procedure, which is delicate to carry out. Because of the difficulty of the global fitting procedure,[26] additional data were indeed needed, for instance, the long lifetime component was taken from literature,[18] given the too small delay range recorded in the experiment. Because of the relative limited resolution (140 fs) and the poor signal-to-noise ratio, the lifetime of the first step could not be extracted easily and was given to be smaller than 50 fs. One should mention that this signal could actually also be interpreted as a simple cross correlation rather than true dynamics, as suggested by the authors in the case of the pyrimidine bases. In addition, the probe wavelength used (200 nm) leads to a non-negligible probe-pump process, which is arbitrarily fitted by a single exponential and can perturb the fit of the short time component.

The present experimental study of DNA and RNA bases in the gas phase addresses several open issues related to the excited state dynamics of the nucleobases. First, we report pump-probe transients for all bases with an excellent time resolution (excitation at 267 nm; 80 fs), accurate zero time-delay measurements, and tautomer selectivity for adenine. This enables us to rationalize the fitting procedure of the signals by exhibiting the absence of coherent absorption process and the presence of a two-component decay. Second, in order to elucidate details of the mechanism of the ultrafast deactivation, we focused our efforts on the properties of Ade and its methylated derivatives, namely, 9MAde, *N*,*N*-dimethyladenine (DMAde), and 2-aminopurine (2AP), a highly fluorescent isomer of 9HAde. Our results show unambiguously that nucleobases excited state dynamics exhibit an ultrafast two-component stepwise decay dominated in the early times by vibronic coupling between the $\pi\pi^*$ and $n\pi^*$ states readily mixed by out-of-plane vibrational modes.

II. EXPERIMENT

The experimental setup was described in details elsewhere.[27] Briefly, it combines a supersonic argon jet, seeded with nucleobases produced in a temperature-controlled pickup source, femtosecond pulsed lasers, and a mass spectrometric detection. The oven containing the nucleobase powder was placed in front of the pulsed nozzle. Typical operating temperature was between 140 and 180 °C. Commercial products from Aldrich were used without further purification. The Laser Ultra-Court Accordable (LUCA) laser facility at Saclay delivers the second (400 nm) and third (267 nm) harmonics of the output of a titane:sapphire regenerative amplifier operating around 800 nm at a 20 Hz repetition rate. The second harmonic output of the laser goes through a delay line, allowing us to vary the time delay relative to the 267 nm laser pulse. Positive times correspond to the probe pulse (2×400 nm) coming after the pump pulse (267 nm). For all measurements, pump and probe laser energies and their focusing conditions were carefully adjusted to avoid any one-color ionization. The IR fundamental light (800 nm) was carefully eliminated by successive reflections on interferometric multilayer mirrors. The two nearly collinear laser beams cross the molecular beam in the extraction region of a linear time-of-flight mass spectrometer. The ions are detected by a microchannel plates detector and data acquisition is achieved through home-made Labview software.

III. RESULTS AND DISCUSSION

Figure 1 displays transients of DNA and RNA nucleobases: Cyt, Gua, Thym, and Uracil (Ura), together with the dimethylether (DME) signal used for an accurate internal calibration. The full width at half maximum (FWHM) of the pump-probe cross correlation and the zero time position were determined carefully using the DME transient which was fitted to the convolution of a Gaussian and an exponential decay functions. Assuming the same width for the pump and probe pulses, a laser pulse FWHM of 80 fs and a DME excited state lifetime of 15 fs were found.

The analysis of nucleobase transients in terms of convolution of multiexponential decays to the Gaussian instrumental response function results in two components. The ultrafast one typically occurs in the 100 fs range and is followed by a slower step in the picosecond time scale (see Table I). The choice of such a fitting function over the different ones chosen by other groups[18,26] deserves further ex-

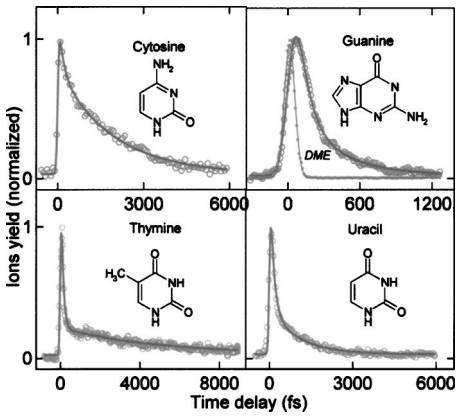

FIG. 1. Femtosecond transient ionization signals for cytosine, guanine, thymine, and uracil in molecular beam. Excited state was prepared at 267 nm and dynamics followed with 2×400 nm ionization. The pump-probe signal of DME used for internal calibration is shown with the guanine plot. All nucleobases transients display a biexponential behavior with a short and a long component. Note that the four time scales are different.

planation. Kang, Jung, and Kim[18] chose to fit with a single exponential added to a Gaussian cross-correlation accounting for a coherent absorption component, and Ullrich *et al.*[26] chose to fit adenine with a triexponential decay, but arbitrarily convoluted a biexponential decay added to a Gaussian cross correlation for the other bases Cyt, Thy, and Ura. In our work, two observations ensure that no measurable multiphoton coherent absorption is present. First, the fast-to-slow component ratio observed in systematic laser intensity studies displays no variations, and more important the nucleobase short component display a significant delay of 45, 57, 84, 76, 65 fs for Ade, Gua, Cyt, Thy, and Ura, respectively, compared to the rise time position of the DME calibration signal. Our excellent time resolution with a good signal-to-noise ratio showed that an accurate fit is obtained with the biexponential decay model only, and that the addition of a third very long-lived channel is unnecessary, even when decay measurements on very long time range (tens of picoseconds) were performed to achieve an accurate fitting of the slow component. Comparison of the nucleobases transients with the DME calibration signal in terms of rise time position and line shape shows that the observed transients correspond to a real electronic state relaxation, free from instrumental artifact. The differences observed for these two parameters in each molecule underline the intrinsic character of the observed transients.

The present biexponential decays can be compared with previously published results on free nucleobases, keeping in mind the differences in the fitting procedures. A qualitative agreement is found in the ordering of the long components observed here with the monoexponential decays of Kim and co-workers,[17,18] namely, 1.0, 3.2, 0.8, 6.4, and 2.4 ps for Ade, Cyt, Gua, Thy, and Ura, respectively, although these values are systematically higher (except for adenine), in agreement with the fact that they fit an average of the short and long components. Furthermore, the observed transients reported by Kim's group[18] are well reproduced with a biexponential model using our lifetimes, provided that the laser FWHM is fixed to about 400 fs.

TABLE I. Decay times obtained in biexponential fits of transients of free nucleobases UV excited states. Estimated relative uncertainty is 10%.

	Adenine	Cytosine	Guanine	Thymine	Uracil
τ_1 (fs)	100	160	148	105	130
τ_2 (ps)	1.10	1.86	0.36	5.12	1.05

It is more difficult to compare with the work of Stolow and co-workers.[26] For Cyt, Thy, and Ura, the authors attribute the early dynamics of the signal to a coherent absorption and an unwanted intense probe-pump signal, that may perturb the observation of an ultrafast first component, while the long-lived component is fixed to the monoexponential values of Kang, Jung, and Kim.[18] This leads to superfluous short lifetimes of 820, 490, and 530 fs, respectively, accounting for a weak component in the decay. Alternatively, the authors also mention that the same fitting procedure as the one used for Ade leads to a fit of similar quality. The short lifetimes observed this way for Ade, Cyt, Thy, and Ura are all <50 fs and the long components 750, 1140, 1020, and 750 fs are directly comparable to our results though sensibly shorter, probably because of the arbitrary introduction of a third long time-scale channel fixed to 1 ns.

Finally, our results provided evidence that two component only transients are suitable for the fit of the decays observed. Our time resolution enables us to show that the first component is not a cross-correlation signal but a real exponential decay of the order of 100–160 fs, depending on the base considered.

Comparison with decay times in aqueous solution is not straightforward and has to take into account many parameters such as tautomers populations, excited states order, solvation effects, and temperature, which are not yet well known. Lifetimes of single DNA bases as well as ribonucleosides obtained by transient absorption or fluorescence measurements in aqueous solution are subpicosecond as expected. Biexponential fit of fluorescence data results in the following lifetimes: 0.1/0.42, 0.18/0.92, 0.16/0.78, and 0.15/0.72 ps for Adenosine, Cytidine, Guanosine, and Thymidine, respectively.[9] These data exhibit similar biexponential decays as the present gas phase results, although the ordering of the lifetimes is somewhat different. Interestingly, in the case of Ade, a two-components decay with 180 fs and 8.8 ps lifetimes was measured and assigned to 9HAde and 7HAde tautomers, respectively.[11] It is noteworthy, that for this base (and for Cyt) the methyl (or sugar) substitution on the 9*N* (1*N*) position enables tautomer-selective dynamics to be measured.

In the following we will focus our attention on the derivatives of Adenine, which is one of the most experimentally and theoretically studied bases.[11,23–26] To test the different electronic relaxation mechanisms described above, comparative studies of excited state dynamics of Ade and 9MAde with some relevant derivatives as DMAde and 2AP, were performed. Our strategy was to probe the localization of the excitation as well as the role of the pyrimidine ring deformations and the amino group inversion mode in the relaxation process and finally, the role of this group in the

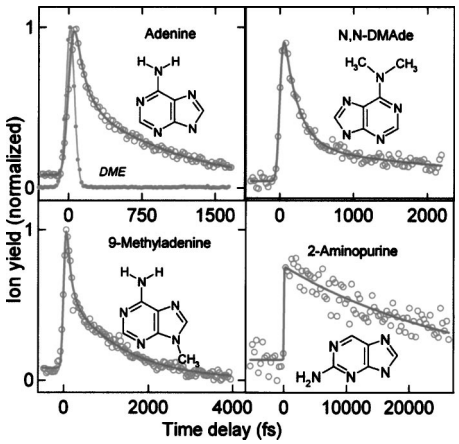

FIG. 2. Femtosecond transient ionization signals for adenine, 9-methyladenine, *N*,*N*-dimethyladenine, and 2-aminopurine. The pump-probe signal of DME used for internal calibration is shown with the adenine plot. Excited state was prepared at 267 nm and dynamics followed with 2 $\times$400 nm ionization. Note that the four time scales are different.

ring's buckling. The transient decay times observed are shown in Fig. 2 and derived lifetimes are given in Table II.

Ade and 9MAde exhibit very similar biexponential transient decays of 100/1100 and 110/1300 fs, respectively. Assumption that the 9HAde tautomer predominates in the molecular beam may give a preliminary explanation of this remarkable similarity. 7HAde was indeed found to be a minor species in the gas phase[16] although a significant population of $\sim$20% was found in water.[11]

The similar picosecond decays for Ade and 9MAde are difficult to reconcile with the mechanism involving the $\pi\sigma^*$ state proposed by Sobolewski and Domcke[14] which gives to the *N*9-*H* repulsive coordinate the predominant role in the decay. In this model, *N*9 methylation should dramatically modify the coupling efficiency and therefore the observed lifetimes. In the other model, a negligible effect on the dynamics observed upon *N*9 methylation on the imidazole ring of Ade, can be rationalized according to the assumption that the excitation is highly localized on the pyrimidine ring of the base, as pointed out by theoretical investigations of Ade excited states.[28–31] Link between excitation, structure, and dynamics properties can be rationalized by considering the differences between ground and excited states geometries. Indeed, after excitation, classical effects of π^* antibonding orbitals such as bond lengthening and/or ring buckling mainly affect the pyrimidine part of Ade because of the π^* orbital localization near *C*6. Thus, multimode decay coordinates will mainly involve vibrational modes localized on this pyrimidine ring as well as the amino group out-of-plane motion that gives rise to stabilizing interactions between the nitrogen lone pair and the π-electrons system. Buckling of the ring implies out-of-plane vibrations during the relaxation of the $\pi\pi^*$ state, that will ensure vibronic coupling between this state and the $n\pi^*$ state. Vibronic coupling is expected to be influenced by two factors, namely, the energy gap between the states, and the excitation of an appropriately oriented vibrational mode needed to increase the transition probability between the two states. In this deactivation mechanism, the inversion mode of the extracyclic amino group seems to be critical in the coupling between the two manifolds. The deactivation process efficiency depends then drastically on the frequencies of out-of-plane vibrational modes such as the amino group inversion.

TABLE II. Fitted transients decay times for adenine and derivative compounds. Estimated relative uncertainty is 10%.

	Adenine	9MAde	DMAde	2AP
τ_1 (fs)	100	110	200	···
τ_2 (ps)	1.1	1.3	3.1	30.0

The ultrafast decay of $\sim$100 fs in Ade and 9MAde does match the characteristic oscillation period of low frequencies out-of-plane vibrations, such as ring deformations and NH_2 inversion of the amino group. Comparison of the ultrafast components of Ade and 9MAde ($\sim$100 fs) with DMAde (200 fs) strongly supports the predominant role of the amino group inversion mode in the early dynamics (Table II). Indeed, the longer lifetime observed for DMAde can be related to the corresponding lower inversion mode frequency observed upon hydrogen atoms to methyl groups substitution in the amino group.

The key role of the amino group, in position *C*2 and *C*6 for 2AP and Ade, respectively, could explain the drastic change observed in the dynamics of these bases. A significant lifetime increase in 2AP (Table II) is still in agreement with the assumption that the π^* excitation is highly localized on the *C*6 of the pyrimidine ring. The NH_2 inversion motion brings the lone-pair electrons out-of-plane, to the overlapping region with the ring π electrons, thus enhancing the electronic coupling. In Ade, the amino group inversion leads to a stabilization effect through a delocalization of the nitrogen lone-pair electrons over the ring. In 2AP, the lone-pair electrons of the amino group nitrogen are strongly coupled to the delocalized π system of the rigid planar guanidine-like group. This hinders the amino group inversion mode as well as the local ring distortions, inhibiting the deactivation pathways operative in the other adenine derivatives. Moreover, the strong guanidine conjugation changes drastically the nature of the excited electronic states, so that the $\pi\pi^*$ state is the lowest minimum for this molecule instead of the $n\pi^*$ state for adenine.[13,15,16,25] This could explain the difference observed in the dynamics and the presence of a strong fluorescence for 2AP.

These issues enable a qualitative picture for the deactivation pathways to be drawn (Fig. 3). The earlier step in the range 100–200 fs reflect the initial displacement of the wavepacket along the deactivation channel from the vertical Franck–Condon excitation region toward the geometry-relaxed $\pi\pi^*$ local minimum.[13,28–31] This wave packet motion is mainly driven by appropriate out-of-plane vibration modes as pyrimidine ring distortion and amino group inversion leading to the $\pi\pi^*$ and $n\pi^*$ state vibronic mixing. The second step involves probably an energy barrier crossing to reach the full state switching $\pi\pi^*/n\pi^*$. The long component also include decay further along the same coordinate, in region with a high distortion, toward the ground state to achieve the energy conversion process. Theoretical studies

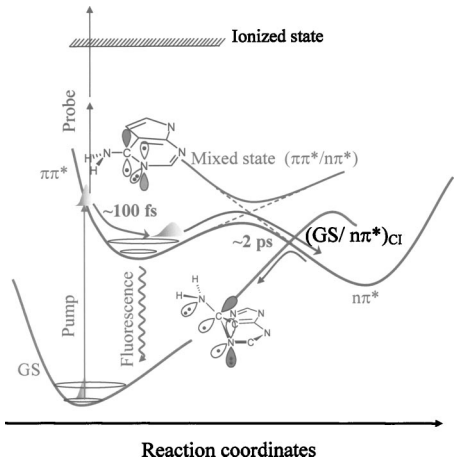

FIG. 3. Schematic representation of the proposed deactivation pathways for the excited states of adenine and derivatives compounds. Reaction coordinate involves out-of-plane vibration modes. The NH_2 inversion and the pyrimidine ring distortion, minimize π^* antibonding interaction and increase the stabilizing effect of the lone-pair orbital of the amino group. The ultrafast component could be related to the wave packet motion toward geometry relaxed $\pi\pi^*$ state. Following this nuclear motion the $\pi\pi^*$ and $n\pi^*$ states mixing is also initiated. The second component is assigned to the relaxation further along the same relaxation coordinates and involves barrier crossing to achieve the $\pi\pi^*$ to $n\pi^*$ switching as well as the $n\pi^*$ state conversion into high vibrational levels of the ground state (GS). This last step is however too fast and probably proceed through peaked conical intersections.

and exploration of potential energy surfaces for Ade excited states lead to a fully avoided crossing with a transition structure located between the $\pi\pi^*$ and $n\pi^*$ local minima.[13,28] The $\pi\pi^*/n\pi^*$ states switching requires a barrier crossing through the transition state, estimated to around 800 cm^{-1} in Ade according to fluorescence and REMP1 spectroscopy investigations.[15,25] The calculated relaxed geometry of the $n\pi^*$ state has been found with a rather large out-of-plane distortion[28,30] that could open-up nonradiative deactivation pathways toward the ground state. This radiationless relaxation is however anomalously fast (typically 1 ps) and probably proceeds via peaked crossing between the $n\pi^*$ and the ground state surfaces with a conical shape, i.e., conical intersection, leading to a rather ultrafast ground state recovery.

The strong dependence observed for the long component decay times following the excitation wavelength for Ade: 1.1 ps at 267 nm−9 ps at 277 nm (Ref. 25) could be rationalized in this dynamics picture assuming that the barrier crossing is actually a kinetic limiting step in the nonradiative decay pathways.

IV. CONCLUSION

In summary, the present dynamics investigation on the DNA and RNA nucleobases gave us more insight in the processes involved in the relaxation of the excited states of nucleobases with significant available internal energy, eliminating the possibility of coherent absorption, and exhibiting an ultrafast two-step internal conversion dynamics. Moreover, these results support the theoretical models of a radiationless decay based on an ultrafast $\pi\pi^*/n\pi^*$ states switch. This deactivation pathway seems to be a common mechanism in these heterocyclic biomolecules that open-up ultrafast energy conversion. In some cases, other doorway states have actually to be taken under consideration, the $\pi\sigma^*$ state could be involved especially at high energies excited states. However, in the case of the nucleobases, the $\pi\pi^*/n\pi^*$ internal conversion probably remain the most operative mechanism because of the occurrence of many concomitants factors. First, the presence of many states of $n\pi^*$ character in the vicinity of the $\pi\pi^*$ manifold, second the $\pi\pi^*/n\pi^*$ internal conversion proceed via a vibronic coupling involving out-of-plane vibrations directly excited upon vertical transition from the ground state. Depending on the nucleobase, n orbitals of both oxygen and/or nitrogen could be involved in the fluorescent-to-dark state switching.[32,33] The initial part of the $\pi\pi^*/n\pi^*$ electronic state mixing is driven by out-of-plane vibration and then occurs in the nuclear motion time scale. The following steps include the full internal conversion to the relay state $n\pi^*$ state and subsequent deactivation process including other electronic states as the ground state. According to the ultrashort lifetimes observed, presence of highly directional conical intersections between the $n\pi^*$ relay state and the high vibrational levels of ground state, is suspected. Nevertheless, localization of such regions with the corresponding molecular configurations needs further investigations, more particularly quantum calculations. In return, this kind of calculations will take advantages from the present work since it supplies enlightenment on the nature of the relevant vibration modes in the deactivation pathways.

The proposed deactivation mechanism could also help to account for the enhancement of the ultrafast dynamics observed in solution according to the possible differential solvation between the ground and open shell excited states.[11,32,33]

Because deactivation rate depend drastically on the available energy, studies of lifetime's variations upon energy excitation are under consideration. For adenines and derivatives compounds the suspected variations would be related to the height of the barrier between $\pi\pi^*$ and $n\pi^*$ states.

Investigations of the other nucleobases as well as their relevant derivatives with appropriate substitution groups, used as probes to test the models for the deactivation mechanism and to point out relevant vibrational modes in reaction pathways are currently under study in our laboratory.

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