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Direct Observation of Electronic Relaxation Dynamics in Adenine via Time-Resolved Photoelectron Spectroscopy

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The UV photostability of biomolecules such as the DNA base adenine is determined by the competition between excited-state relaxation pathways. Photoprotective mechanisms must operate on ultrafast time scales to dominate over competing photochemical processes. A case of fundamental interest, adenine has been the focus of several spectroscopic studies.[1,2] High-resolution spectra of adenine show only a limited number of resolved features which evolve into a broad band at energies above 37 000 cm^{-1}. A transition to the first $\pi\pi^*$ state at 36 105 cm^{-1} dominates the spectrum of the 9H tautomer of adenine. Recent transient absorption measurements of aqueous DNA nucleosides revealed lifetimes of a few hundred femtoseconds at 263 nm excitation.[3] In the gas phase, lifetimes of isolated DNA bases were measured via time-resolved photoionization mass spectrometry to be a few picoseconds at 267 nm excitation.[2,4] Kang et al.[5] used substitution and deuteration to perturb the adenine $n\pi^*$ and $\pi\sigma^*$ states and, having observed no significant effects, suggested that the $\pi\sigma^*$ state is not actively involved. In an ab initio study on 9H adenine, Broo[6] suggested that the avoided crossing of the $n\pi^*$ and $\pi\pi^*$ states occurs with a barrier of 0.6 kJ/mol and that coupling of the excited states through ring puckering leads to out-of-plane distortion and internal conversion to the S_0 ground state. By contrast, Sobolewski and Domcke suggested an internal conversion along the azine NH stretch coordinate.[7] The repulsive $\pi\sigma^*$ state intersects both the first excited $\pi\pi^*$ state and the S_0 state, leading to internal conversion via large amplitude N−H motion. Here, we describe the detailed analysis of the excited-state dynamics of isolated adenine in a molecular beam observed by femtosecond time-resolved photoelectron spectroscopy (TRPES). Photoelectron spectroscopy is sensitive to both electronic configurations, via Koopmans' theorem, and vibrational dynamics, via Franck−Condon (FC) factors. TRPES can allow for direct identification of the electronic states involved in ultrafast processes and has been applied to a range of problems.[8]

The present experimental configuration is described in detail elsewhere.[8a] A heated glass nozzle with a 500 μm orifice was used to introduce adenine, seeded in helium, into a magnetic bottle photoelectron spectrometer. Femtosecond pump wavelengths of 250, 267, and 277 nm were employed, and ionization was promoted by a femtosecond 200 nm probe pulse. The laser cross-correlation was ~160 fs fwhm. Mass spectra confirmed that the adenine monomer was the dominant species in the molecular beam. High-resolution spectroscopic studies previously determined that the 9H tautomer of adenine is most abundant in the gas phase.[9]

In Figure 1, we present TRPES spectra of adenine recorded at pump wavelengths of 250 and 267 nm. (The TRPES spectrum at 277 nm pump is not shown.) These contour maps present photoelectron signals as a function of both time delay and photoelectron kinetic energy. The data are fit at all time delays and all electron

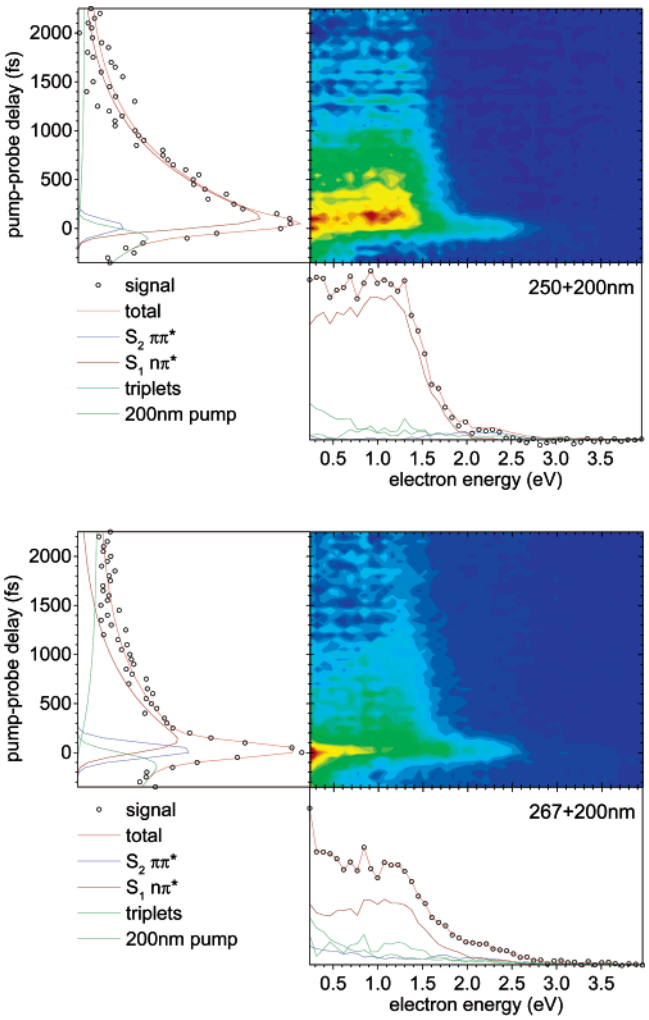

Figure 1. TRPES of adenine excited at 250 and 267 nm and ionized at 200 nm. Center: Color coded map of photoelectron intensity as a function of time delay and kinetic energy. Left: Evolution of each photoelectron channel as a function of time delay. Bottom: Time-integrated photoelectron spectra. The identification and assignment of different ionization channels are discussed in the text.

kinetic energies, allowing us to extract both lifetimes and photoelectron spectra of the excited states, as shown in Figure 1. Projection of the fit onto the energy axis (i.e., integration over delay times) yields the energy-resolved photoelectron spectrum of each resolved channel. Projection onto the time axis (i.e., energy integration over each photoelectron channel) yields the lifetime of each state. We observed three channels due to the desired pump−probe process (250/267 nm pump, 200 nm probe ionization), and they are shown in blue, brown, and green. A short-lived state (blue, $t < 50$ fs) and one with intermediate lifetime (brown, $t = 750$ fs)

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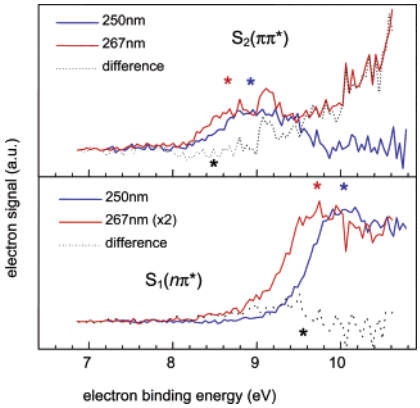

Figure 2. Time-integrated photoelectron spectra of $S_2(\pi\pi^*)$ (top) and $S_1(n\pi^*)$ (bottom). The stars denote the He(I) vertical ionization potential[10] for D_0 (π^{-1}) and D_1 (n^{-1}) (in black) and the vertical IPs expected for the vibrationally excited states at 267 nm (red) and 250 nm (blue). At 267 nm, an additional ionization channel contributes to the nominal $S_2(\pi\pi^*)$ band but not the $S_1(n\pi^*)$ band, as is apparent from the energy-corrected difference spectra.

are respectively assigned to $S_2(\pi\pi^*)$ and the $S_1(n\pi^*)$. We assign the long-lived channel at 267 nm excitation (green, nanosecond lifetime) to triplet states observed previously.[2] A fourth channel is due to a competing probe−pump process (pump at 200 nm, probe ionization at 250/267 nm) evolving toward negative time delays and is displayed in dark green.

The assignment of the $S_2(\pi\pi^*)$ and the $S_1(n\pi^*)$ ionization channels is based on the comparison of observed ionization thresholds with those expected from Koopmans' ionization correlations. We calculated Koopmans' ionization correlations for adenine (TD-B3LYP/6-31++G**): S_1, the lowest $n\pi^*$ state, preferentially ionizes into the D_1 (n^{-1}) cation excited state, whereas S_2, the lowest $\pi\pi^*$ state, and S_3, a $\pi\sigma^*$ state, both preferentially ionize into the D_0 (π^{-1}) cation ground state. The corresponding vertical ionization potentials $IP_0 = 8.48$ eV and $IP_1 = 9.58$ eV are known from He(I) photoelectron spectroscopy.[10]

In rigid aromatic systems, similar geometries obtain for the ground and low-lying excited states, allowing the observed vertical IPs to be directly compared to the He(I) values, simply shifted (i.e., FC diagonality) by the excited-state vibrational energy.[8] In Figure 2, we show the measured photoelectron spectra for $S_2(\pi\pi^*)$ (top) and $S_1(n\pi^*)$ (bottom) and the expected vertical ionization potentials, confirming this assignment. The amplitude of $S_1(n\pi^*)$ relative to $S_2(\pi\pi^*)$ is $\sim 2\times$ smaller at 267 nm than at 250 nm. This is an indication that another decay pathway from $S_2(\pi\pi^*)$ may exist. For the $S_1(n\pi^*)$ state, the form of the Franck−Condon envelope is very similar at 267 and 250 nm (Figure 2, bottom). For $S_2(\pi\pi^*)$ (Figure 2, top), this is not the case, and the vibrational energy corrected (i.e., shifted by 0.316 eV, the energy difference between 267 and 250 nm) difference spectrum reveals an additional channel at 267 nm. We speculate as to the origin of this additional channel. Sobolewski and Domcke[7] proposed an additional decay pathway for $S_2(\pi\pi^*)$ via the dissociative $S_3(\pi\sigma^*)$ state along the NH-stretch coordinate. According to Koopmans' correlations, the $S_3(\pi\sigma^*)$ state should ionize into D_0 (π^{-1}). This places this new band in the energy range observed, and, additionally, the dissociative nature of $S_3(\pi\sigma^*)$ should result in a broad and diffuse photoelectron band, as observed. The state lifetime would be within the time resolution of our experiments ($\tau < 50$ fs). Our calculations suggest that 200 nm excitation of higher states would show Koopmans' ionization to D_0, D_1, and D_2. Hence, probe−pump processes also conceivably contribute to this photoelectron band. However, we estimate these to be $\sim 8\times$ smaller than the observed signals. Further TRPES experiments with different ionization schemes are planned to fully resolve this issue. The 277 nm TRPES spectrum looks qualitatively similar to that at 267 nm but, due to the low absorption cross section at the S_2 origin, suffers from poor signal-to-noise ratios. Nevertheless, in agreement with Lührs et al.,[2] the integrated photoelectron signal is fit with a double exponential decay. An excited-state lifetime of >2 ps was extracted, and an additional very long-lived (ns) channel attributed to a triplet state is observed.

We propose the following model for internal conversion pathways in adenine. Excitation at 250, 267, and 277 nm prepares the optically bright $S_2(\pi\pi^*)$ state. Close to the band origin (277 nm), the lifetime is several picoseconds. Higher vibronic levels (267 and 250 nm excitation) show much shorter lifetimes of $t < 50$ fs, and we observe strong coupling between $S_2(\pi\pi^*)$ and $S_1(n\pi^*)$, as suggested previously by Kang et al.[4] Rapid internal conversion ($t < 50$ fs) populates the lower lying $S_1(n\pi^*)$ state which has a lifetime of 750 fs. We observed only minor signals from long-lived (ns) triplet states with decreasing yields at higher excitation energies, consistent with the low triplet yields reported in the literature. This suggests that $S_1(n\pi^*)$ relaxes predominantly to the ground state. At 267 nm, we found evidence for an additional channel which, although not yet proven, is consistent with the dissociative $S_3(\pi\sigma^*)$ state suggested as an ultrafast relaxation pathway from $S_2(\pi\pi^*)$.[7] We observed an energy dependence of the $S_2(\pi\pi^*) \rightarrow S_1(n\pi^*)/S_2(\pi\pi^*) \rightarrow S_3(\pi\sigma^*)$ branching ratio which suggests the apparent reduction of this proposed new channel at 250 nm. Within this picture, we assume that the rate of $S_2(\pi\pi^*)$ to $S_1(n\pi^*)$ internal conversion is greatly enhanced for vibrationally excited states (250 nm excitation) whereas the rate of $S_2(\pi\pi^*)$ to $S_3(\pi\sigma^*)$ internal conversion is not greatly affected. Further experimental and theoretical work is clearly required to refine our understanding of the photophysics of the DNA bases.

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