In this work the photophysics and photochemistry of the biochromophore molecules pyrrole, indole and adenine as well as the cluster species indole(NH$_3$)$_n$, indole(H$_2$O)$_n$, (adenine)$_2$ and adenine(H$_2$O)$_n$ are investigated by time-resolved methods. The main objective is to clarify the role of an optical forbidden, repulsive $^1\pi\sigma^*$ state and its dynamics. The applied experimental methods comprise femtosecond pump-probe spectroscopy in the near UV, molecular beam techniques, time-of-flight mass spectrometry and photoion-photoelectron coincidence detection. Many results are interpreted with the help of \textit{ab initio} calculations.

For pyrrole the existence of the $\pi\sigma^*$ state could be proven unambiguously by means of femtosecond detection of the dissociated H atom in a novel pump-probe setup. For indole the experimental results indicate a simultaneous excitation of the long-lived $\pi\pi^*$ states $^1L_a$ and $^1L_b$ at 239 – 263 nm but no coupling with the $\pi\sigma^*$ state. The photophysics of adenine is dominated by a low lying $n\pi^*$ state.

The clusters indole(NH$_3$)$_n$ show a complex photoinduced dynamics on the fs and ps time scale. For small clusters ($n \leq 3$) both the ultrafast internal conversion $\pi\pi^* \rightarrow \pi\sigma^*$ and an exothermic H atom transfer from indole to NH$_3$ can be observed occurring in less than 1 ps. A subsequent \textit{decaying} dynamics on the long time scale (several 10 ps) is discussed in terms of reorientation, IVR and/or a nonadiabatic tunneling $\pi\sigma^* \rightarrow S_0$. For larger clusters the ultrafast processes are not observable while an \textit{increasing} dynamics on the ps time scale is clearly caused by a structural rearrangement after the H transfer. This different behavior for $n \geq 4$ can be explained by changed Franck-Condon factors in the ionization process respectively a proton transfer geometry in the ion state. For $n \leq 6$ a small percentage of the clusters experiences a ps dissociation after the H transfer which yields the radicals NH$_3$(NH$_3$)$_{n-1}$. The role of NH$_3$ evaporation in the cluster ions is investigated by means of a KETO$F$ analysis.

The clusters indole(H$_2$O)$_n$ also show an internal conversion $\pi\pi^* \rightarrow \pi\sigma^*$ upon photoexcitation but no complete H atom transfer reaction which in this case exhibits endothermic character. Corresponding to the nonexistence of the transfer there is no hint for a structural rearrangement in larger clusters respectively a fragmentation reaction. In (adenine)$_2$ the $n\pi^*$ decay competes with the $\pi\sigma^*$ decay which – as for indole – becomes relevant in a polar environment due to the large $\pi\sigma^*$ dipole moment. For the same reason in the clusters adenine(H$_2$O)$_n$ the observed dynamics can be nearly exclusively attributed to the transition $\pi\pi^* \rightarrow \pi\sigma^*$. 

### Abstract

In this work the photophysics and photochemistry of the biochromophore molecules pyrrole, indole and adenine as well as the cluster species indole(NH$_3$)$_n$, indole(H$_2$O)$_n$, (adenine)$_2$ and adenine(H$_2$O)$_n$ are investigated by time-resolved methods. The main objective is to clarify the role of an optical forbidden, repulsive $^1\pi\sigma^*$ state and its dynamics. The applied experimental methods comprise femtosecond pump-probe spectroscopy in the near UV, molecular beam techniques, time-of-flight mass spectrometry and photoion-photoelectron coincidence detection. Many results are interpreted with the help of \textit{ab initio} calculations.

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