

Abstract

In this work the photophysics and photochemistry of the biochromophore molecules pyrrole, indole and adenine as well as the cluster species indole(NH₃)_n, indole(H₂O)_n, (adenine)₂ and adenine(H₂O)_n are investigated by time-resolved methods. The main objective is to clarify the role of an optical forbidden, repulsive ¹πσ* 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 *ab initio* calculations.

For pyrrole the existence of the πσ* 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 ππ* states ¹L_a and ¹L_b at 239 – 263 nm but no coupling with the πσ* state. The photophysics of adenine is dominated by a low lying nπ* state.

The clusters indole(NH₃)_n show a complex photoinduced dynamics on the fs and ps time scale. For small clusters (n ≤ 3) both the ultrafast internal conversion ππ* → πσ* and an exothermic H atom transfer from indole to NH₃ can be observed occurring in less than 1 ps. A subsequent *decaying* dynamics on the long time scale (several 10 ps) is discussed in terms of reorientation, IVR and/or a nonadiabatic tunneling πσ* → S₀. For larger cluster the ultrafast processes are not observable while an *increasing* dynamics on the ps time scale is clearly caused by a structural rearrangement after the H transfer. This different behavior for n ≥ 4 can be explained by changed Franck-Condon factors in the ionization process respectively a proton transfer geometry in the ion state. For n ≤ 6 a small percentage of the clusters experiences a ps dissociation after the H transfer which yields the radicals NH₄(NH₃)_{n-1}. The role of NH₃ evaporation in the cluster ions is investigated by means of a KETOF analysis.

The clusters indole(H₂O)_n also show an internal conversion ππ* → πσ* 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 nπ* decay competes with the πσ* decay which – as for indole – becomes relevant in a polar environment due to the large πσ* dipole moment. For the same reason in the clusters adenine(H₂O)_n the observed dynamics can be nearly exclusively attributed to the transition ππ* → πσ*.

