

Scientific report of short term scientific mission under the programme of COST Action P9

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In cooperation with Prof Domcke in Munich, we have initiated the investigation of the photochemistry of aromatic amino acids, taking pyrrole and phenol as model molecules. The purpose of this three-week visit was to investigate the photochemistry of the S_1 state of aniline. Recent experimental investigations indicate very fast internal conversion from the excited S_1 state to dark excited states [i]. Furthermore, the main photoreactive channel corresponds to the fast dissociation of H atom [ii]. This component must result from the dissociation in a repulsive excited state of aniline. The theoretical study of several aromatic molecules has revealed the role of dark electronic states of $^1\pi\sigma^*$ character on their photochemistry. Located in the vicinity of the excited S_1 state, it can predissociate it and open the way to H dissociation or internal conversion to the ground state [iii, iv].

We have performed *ab initio* calculations of the vertical and adiabatic excitation energies of the two lowest singlet states which have a $\pi\pi^*$ and $\pi\sigma^*$ character respectively. We have compared several correlated *ab initio* methods, the multi-reference second-order perturbative CASPT2 approach, the variational multi-reference CI (MRCI) method, as well as the response coupled-cluster (CC2) method.

		T_v ($\pi\pi^*$)	T_v ($\pi\sigma^*$)	T_e ($\pi\pi^*$) C_{2v} min.	T_e ($\pi\pi^*$) C_s min.	T_e ($\pi\sigma^*$) C_{2v} min.
Experiment	Ref. v	4.50	-	4.22 (Ref. vi)		-
Theory	Ref. vii	4.20	4.53	4.20		4.53
	CASPT2	4.22	4.90	4.05	3.99	4.56
	RI-CC2	4.77	4.65	4.58	4.48	4.71
	MRCI	4.71	4.76	4.55	4.52	4.58

Table 1. Vertical T_v and adiabatic transition energies T_e in eV, with respect to the C_s ground-state geometry from CASPT2, RI-CC2 and MR-SDCI calculation.

Results from Table 1 indicate that the relative position of the bright $\pi\pi^*$ and the dark $\pi\sigma^*$ singlet states is very sensitive to the correlation treatment. As confirmed by earlier studies^{viii} CASPT2

method tends to underestimate by up to 0.5 eV the energy of the excited states of $\pi\pi^*$ character. However, all methods indicate that the dark singlet $\pi\sigma^*$ lies in the vicinity of the bright ${}^1\pi\pi^*$ state. Its potential energy surface is essentially repulsive along the N-H coordinate as indicated by Figure 1.

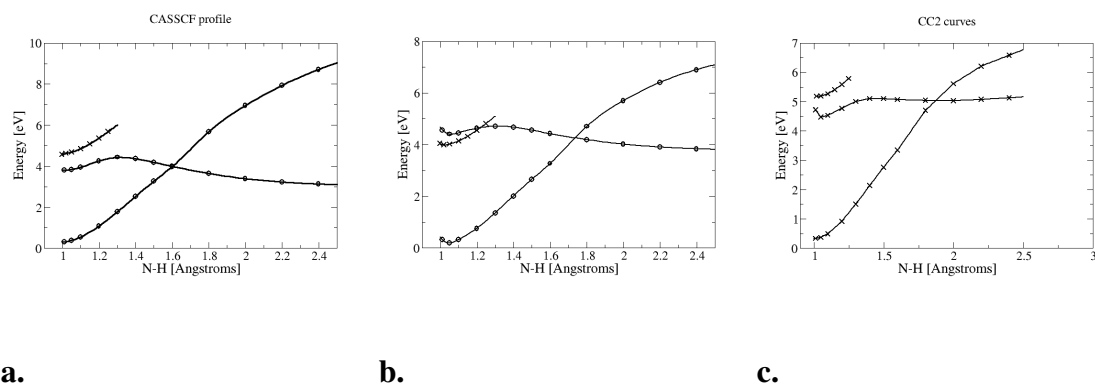


Fig. 1. Potential energy curves of the S0, ${}^1\pi\sigma^*$ and ${}^1\pi\pi^*$ states as a function of the NH stretching coordinate calculated at the CASSCF (a), CASPT2(b) and CC2 (c) levels.

Upon stretching the N-H bond, the ${}^1\pi\sigma^*$ potential energy intersects the ${}^1\pi\pi^*$ state resulting in conical intersection along the reaction path for hydrogen abstraction. Via these conical intersections, the populations of the bright ${}^1\pi\pi^*$ states can be efficiently transferred to the dark ${}^1\pi\sigma^*$ states on a very short time scale (≈ 20 fs). This explains the extremely low quantum yield of fluorescence.ⁱⁱ The repulsive ${}^1\pi\sigma^*$ PE function also cross the PE function of the ground state, providing a mechanism for ultrafast internal conversion to the electronic ground state, as well as hydrogen abstraction. The photoinduced detachment of fast hydrogen atoms indeed has been confirmed by experimental observations [i, ii].

We are presently extending our study by the characterization of two conical intersection seams. This requires the use of the COLUMBUS ab initio package. This package has been available to us only lately and we are presently testing its possibilities in this respect. We then plan to pursue this project within the COST framework by investigating the role of the triplet excited states. The results will be the subject of publications in international journals with acknowledgment of the COST grant.

Confirmation by the host institution of the successful execution of the mission:

Sabyashachi Mishra has been visiting Lille for three weeks in May 2005. During his stay, extensive calculations of the potential-energy surfaces of the aniline molecules have been performed with the aim to elaborate a comprehensive understanding of the ultrafast photochemistry of aniline. Aniline is an important model system of nitrogen atom contained aromatic molecules and its behaviour after UV excitation is of relevance for the understanding of radiation damage. We had many fruitful discussions on modelling aspects of vibronic coupling effects and theoretical modelling of photophysics and photochemistry. Through this STSM, the collaboration of the research groups in Lille and Garching has been substantially strengthened.

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