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

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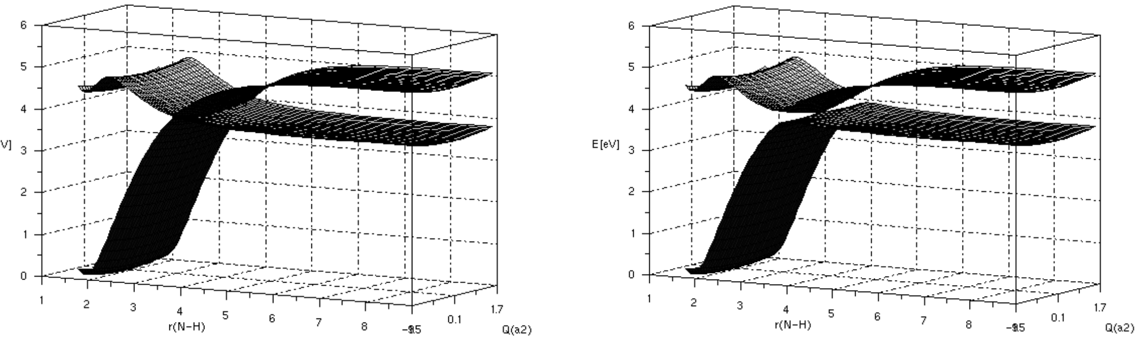
In cooperation with Prof Domcke in Munich, we have initiated the investigation of the photochemistry of aromatic amino acids, taking pyrrole and phenol as model molecules. The purpose of this ten-days visit to Munich was the extension of our study of the role of dark excited electronic states of $^1\pi\sigma$ character on the photochemistry of pyrrole by investigating the conical intersection of the lowest excited state, $^1A_2(\pi\sigma^*)$ with the electronic ground state, $S_0$. The photodissociation dynamics depends not only on the dissociative motion of the H atom, but also on the character of the coupling modes (i.e., the three modes of $a_2$ symmetry which couple the $^1A_2(\pi\sigma^*)$ state with the $S_0$ state at the intersection) and the coupling strength. The first and third $a_2$ modes have a weak dimensionless coupling strength $\lambda/\omega$ (0.45 and 0.42, respectively). For the present study, we have only considered the second $a_2$ coupling mode which has a rather large coupling strength, $\lambda/\omega = 1.33$. It essentially consists of out-of-plane screwing of the hydrogen atoms of the carbon ring. Involving mostly motion of the light hydrogen atoms, this conical intersection should result in an extremely fast internal-conversion process.

We have performed ab initio CASSCF calculations of the adiabatic potential-energy surfaces along the H dissociation coordinate and the $a_2$ coupling mode. We have used these data to construct a two-dimensional analytic diabatic two-state potential-energy surface by least-squares fitting. Figure 1 shows a plot of the diabatic and adiabatic potential-energy surfaces obtained in this manner.

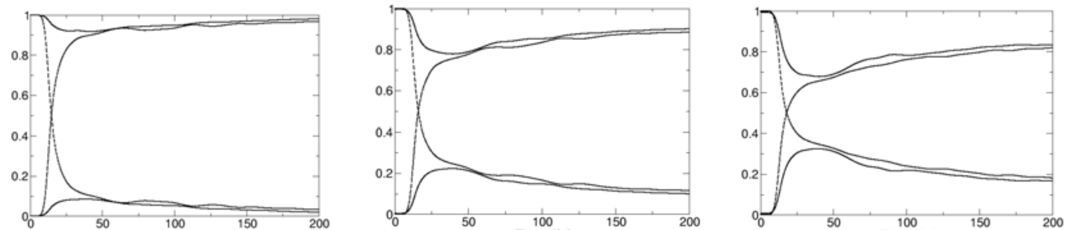


**a.** **b.**

**Fig. 1**. *Diabatic (a) and adiabatic (b) potential-energy surfaces of the $S_0$ and $^1\pi\sigma^*$ states as a function of the NH stretching coordinate r(N-H) and the $a_2$ normal mode.*

Next, we have investigated the non-adiabatic dynamical processes with time-dependent quantum wave-packet methods. Our goal was to develop an understanding of the behaviour of the wave-packet motion at the conical intersection, and the influence of mode-specific excitations on the branching ratio between the different reaction channels. We have therefore calculated the initial vibrational states of the molecule by relaxing the wave packet in the adiabatic ground electronic state. Invoking the Condon approximation, the initial photoexcited wave packets were prepared by vertical excitation of the different vibrational states. The wave packets are then propagated using the split-operator method and the fast Fourier transformation (FFT) method to evaluate the propagator of the kinetic-energy operator. The time dependence of the diabatic electronic populations is calculated to monitor population transfers between the two electronic states.

Our results, presented in Figure 2, show that the wave packet reaches the region of conical intersection very quickly (within 10 fs) and then splits into two parts. One part follows a diabatic path and moves towards the lower adiabatic dissociation limit, as illustrated by the diabatic and adiabatic populations shown in Figure 2. The other part is transferred to upper adiabatic surface, see Fig. 2a. The high-energy part of the wave packet dissociates directly, while the low-energy part, which does not have enough energy to dissociate, is trapped in the upper adiabatic cone as is seen by the oscillations in the diabatic populations in Fig. 2a. As observed previously for the $B_1$-$S_0$ conical intersection [1], excitation of the coupling mode favours adiabatic dissociation to the higher dissociation limit, see Fig. 2a-c. This finding indicates that a control of the photodissociation dynamics of pyrrole via mode-specific IR excitation should be possible for pyrrole. A publication of these results is in preparation.



**a.** **b.** **c.**

**Fig. 2.** Diabatic (full lines), adiabatic (dashed lines) population probabilities of the diabatic $^1\pi\sigma^*$ state and ground state for the initial conditions $(1, n_\gamma)$ ($n_\gamma = 0, 1, 2$ in (a), (b), and (c), respectively).

A shortcoming of the present low-dimensional model is that we do not observe internal conversion to the electronic ground state. We have to extend our model by including additional modes to observe vibrational damping of the modes actively involved in the photodynamics. We plan to pursue this project within the COST framework with the aim to include the other two coupling modes of $a_2$ symmetry. Our goal will be to systematically increase the number of degrees of freedom explicitly included in our model to investigate their effect on timescale of the photodissociation and their influence on the internal-conversion mechanism.

[1] V. Vallet, Z. Lan, S. Mahapatra, A. L. Sobolewski, W. Domcke, Time-dependent quantum wave-packet description of the photochemistry of pyrrole, *Faraday Discuss.* **127**, 283-293 (2004).

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

Dr. Valerie Vallet has been visiting here for ten days November-December 2004. During her stay, extensive calculations of potential-energy surfaces and time-dependent wave-packet dynamics have been performed with the aim to elaborate a comprehensive understanding of the ultrafast photochemistry of pyrrole. Pyrrole is an important building block of biological matter and its behaviour after UV excitation is of relevance for the understanding of radiation damage. We had many fruitful discussions and Valerie interacted strongly with several members of the group. Through this STSM, the collaboration of the research groups in Lille and Garching has been substantially strengthened.