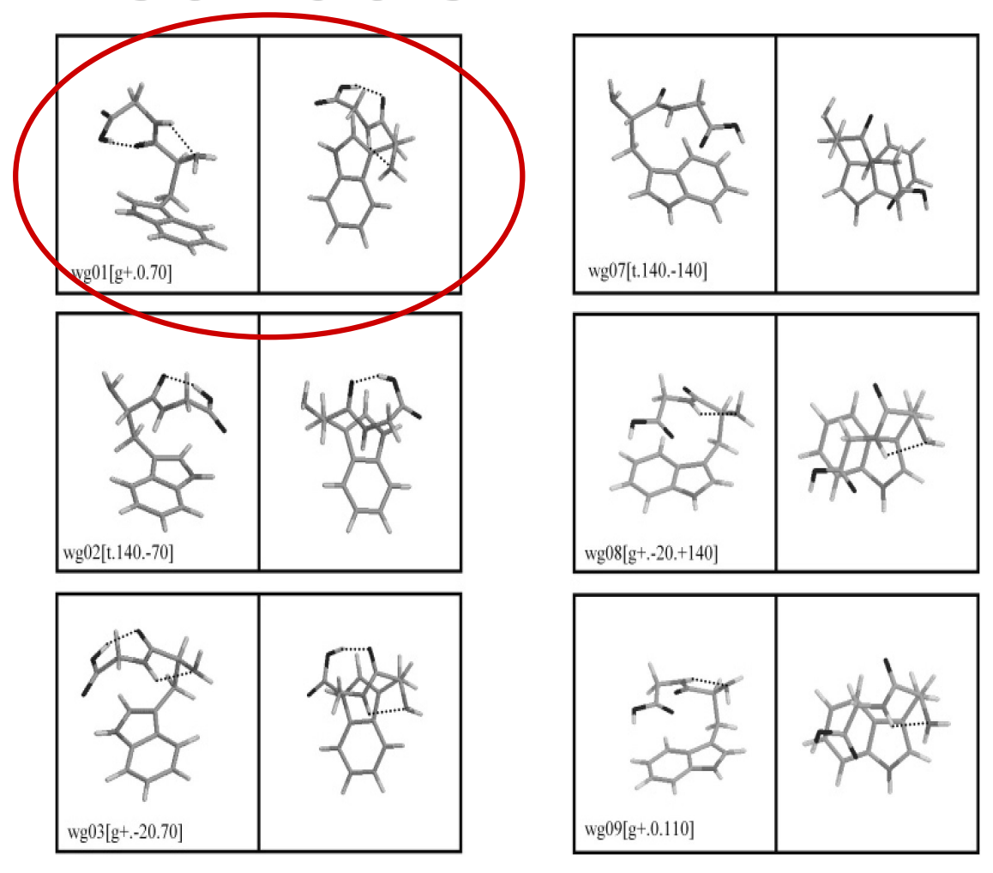
Conformationally Dependent Photodynamics of Glycine

Eva Muchová*, **Petr Slavíček†**, **Andrzej L. Sobolewski‡**, **Pavel Hobza***

*Center for Biomolecules and Complex Molecular Systems, Institute of Organic Chemistry and Biochemistry, Prague
†Institute of Chemical Technology, Prague
‡Institute of Physics, Polish Academy of Science, Warsaw

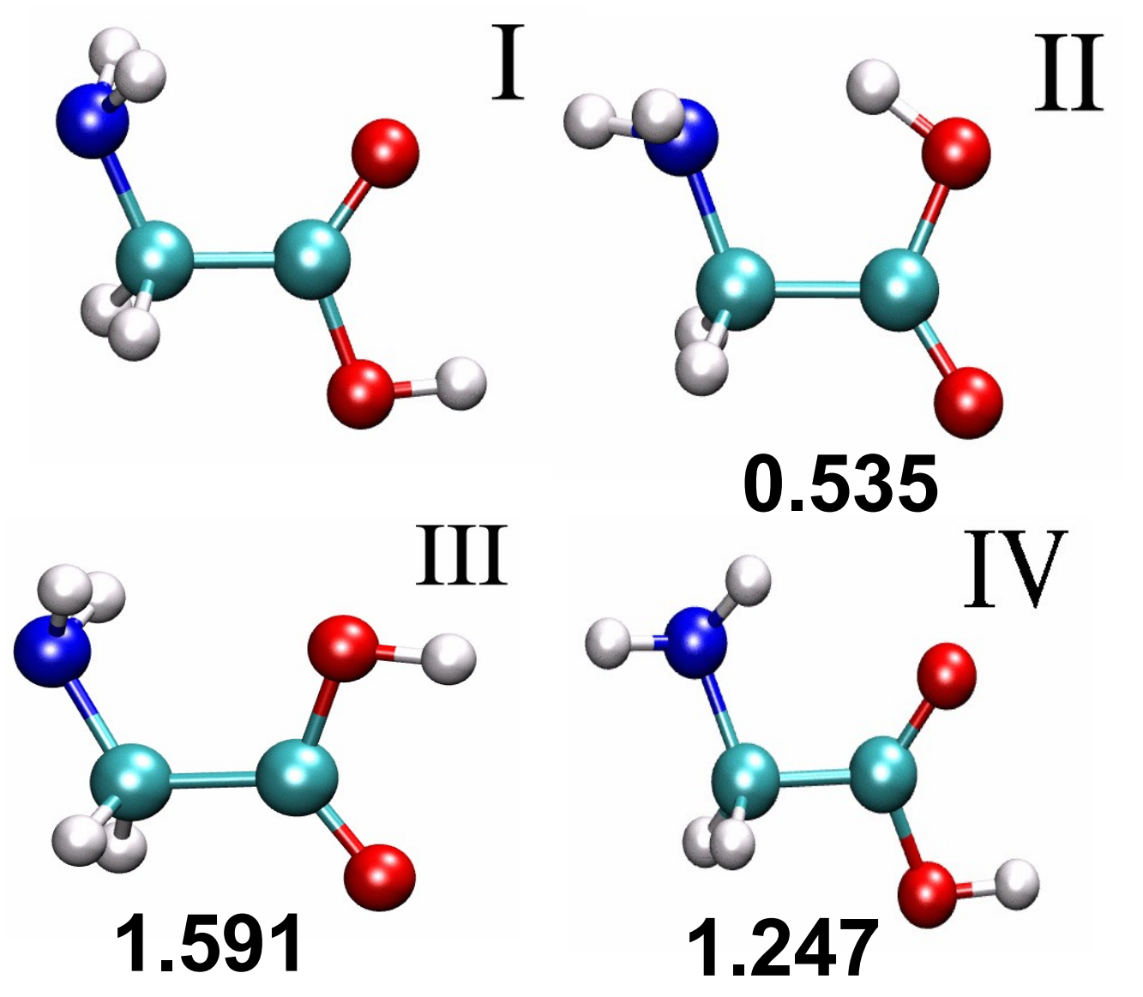
Motivation



1 H. Valdes et al J. Phys. Chem. B 110 (2006) 6385.

- Trp-Gly-Gly
the most populated structure in the gas phase is not observed experimentally (REMPI and UV-UV and IR-UV hole burning spectroscopy)
→ possible explanation is that very short lifetime of some conformers prevents them from being measured[1]
The difference among calculated conformers is due to various H bonding pattern in Gly-Gly part → glycine represents suitable starting point
- Addressing a general question about the possible role of ground state conformations on excited state dynamics.

Glycine in the ground state

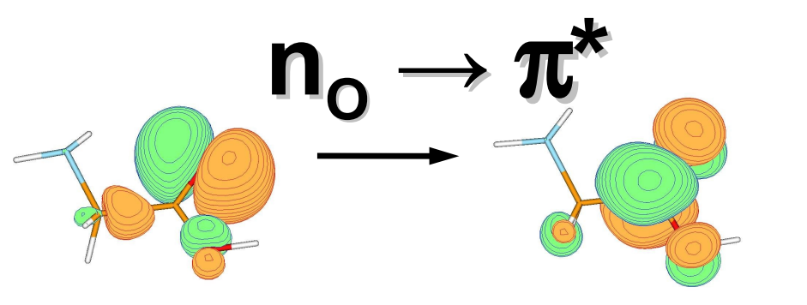
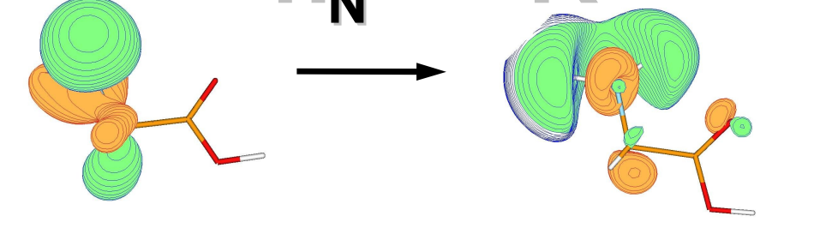


Glycine is a nonrigid (floppy) system → a large number of conformers
The minima are separated by small barriers that can be easily overcome (highest barrier is ~ 940 (III) and 740 (IV) cm^{-1} for interconversion to global minimum I)

4 energetically lowest structures in the gas phase plus relative energies in kcal/mol[2]

2 J. Chocholoušová et al. *J. Chem. Phys.* 113 (*2000*) 4629.

Vertical excitation energies (oscillator strength in parenthesis) for conformer 4.

	CASPT2 6-31G**	CASPT2 ANO-L[3]	EOM-CCSD aD(T)[4]	experiment[5]
$n_O \rightarrow \pi^*$ 	5.76 eV	5.65 eV (0.001)	5.88 eV (0.0005)	~5.8-6.0 eV
$n_N \rightarrow R$ 	6.68 eV	6.09 eV (0.005)	6.32 eV (0.0124)	

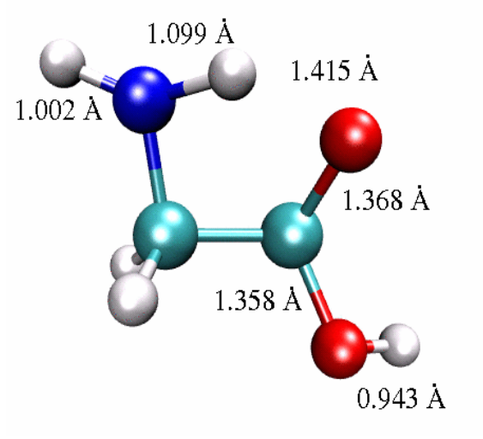
the vertical excitation energies are similar for all confromers, the ordering of states is the same.

3 L.-S. Andres *J. Am. Chem. Soc.* 118 (*1996*) 12200. 4 A. Osted et al *J. Phys. Chem. A* 109 (2005) 1430. 5 Inagaki, T. *Biopolymers* 12 (*1973*) 1353.

Possible photophysical pathways

Localization of conical intersection CASSCF/6-31G** SA3(6,8), in cases of H-atom loss the s and p diffuse functions were added (with exponent 0.02)
The energies and the character of excited states was checked by using the RICC2 method with cc-pVTZ and aug-cc-pVDZ on N and O basis set with added diffuse s and p functions on H atom (with coefficient 0.02) on the geometries of the conical intersections
Dynamic correlation included by using CASPT2 method (level shift 0.3 Hartree)

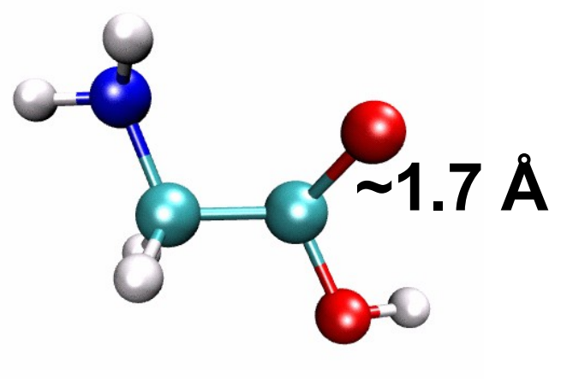
S3/S2



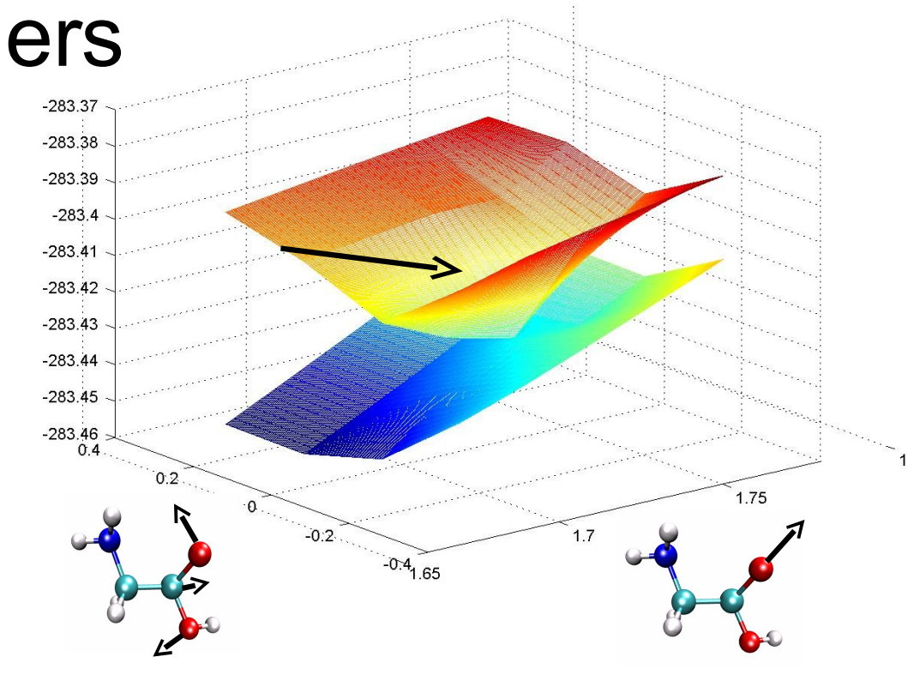
For all conformers the S3/S2 conical intersection is connected with NH2 group planarization and moderate elongation of N-H bond (from 1.099 Å for conformer 4 to 1.210 Å for conformer 2, 3).
The character of S3 state is changed to $n_N \rightarrow \pi^*$ when slightly moving the hydrogen atom → the basis set used is not excellent but should be sufficient

S2/S1

- **C=O bond stretching** – found for almost all conformers

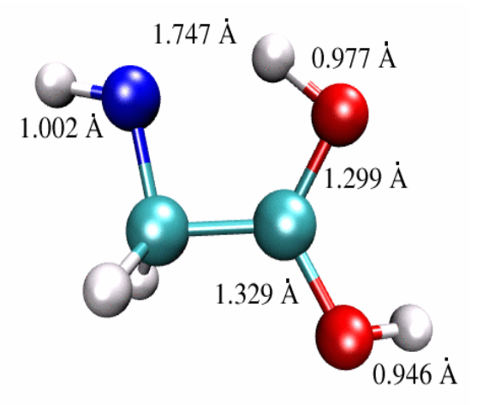


- the deexcitation process leads to **vibrationally excited molecule** in the ground state.



ground and excited state surfaces (CASPT2 energies) in respect to g and h vector that can be projected to C=O bond stretching and -CO2 bending

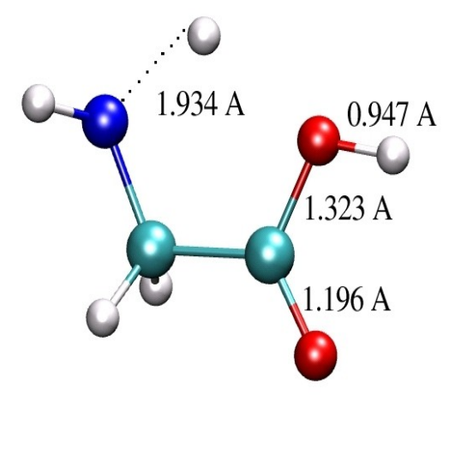
- **H-atom transfer** – found only for conformer 4



- the energy of the CI is lower than in the case of C=O bond stretching (~ 1.1 eV)
- **question** – the stability of dihydroxyisomer in the ground state.

the H-atom transfer was observed in the case of β-turn studied by A. L. Sobolewski

- **H-atom loss** – found for conformers 2 and 3



- energy of the CI is approximately the same as in the case of C=O bond stretching
- the channel leads to a **fragmented molecule** in the ground state

the dissociation along the N-H coordinate was observed for in neutral biological aromatic molecules experimentally as well as described theoretically[6]

3 A. L. Sobolewski, W. Domcke et al Phys. Chem. Chem. Phys. 4 (2002) 1093.

Ab initio non adiabatic molecular dynamics

Full Multiple Spawning[7]

Time-dependent Schroedinger equation is solved

Wave function ansatz $\Psi = \sum_I \chi_I(R;t)\phi_I(r;R)$

time-dependent nuclear wavefunction associated with *I*th state

electronic wavefunction

Nuclear wavefunction – superposition of frozen Gaussian basis functions

time-dependent coefficients

$$\chi_I(R;t) = \sum_{j=1}^{N_I(t)} C_j^I(t)\chi_j^I(R, R_j^I(t), P_j^I(t), \gamma_j^I(t), \alpha_j^I)$$

Individual, multidimensional nuclear basis functions - one-dimensional Gaussian basis functions:

$$e^{\gamma_j^I(t)t}\prod_{\rho=1}^{3N}\left(\frac{2\alpha_{\rho j}^I}{\Pi}\right)^{1/4} exp(-\alpha_{\rho j}^I(R_{\rho j}-R_{\rho h}^I(t))^2+iP_{\rho j}^I(t)(R_{\rho j}-R_{\rho h}^I(t))$$

nuclear phase propagated semi classically

time-independent width

position and momentum propagated classically

Substituting the wavefunction ansatz into nuclear Schrodinger equation - evolution of the coefficients

$$\frac{dC^I(t)}{dt} = -i(S_{IJ}^{-1})\left((H_{II}-i\dot{S}_{II})C^I + \sum H_{IJ}C^J\right)$$

The new basis functions are “spawned” in region of high non-adiabatic coupling

7 M. Ben-Nun, J. Quenneville, T. J. Martinez *J. Phys. Chem. A* 104 (*2000*) 5171.

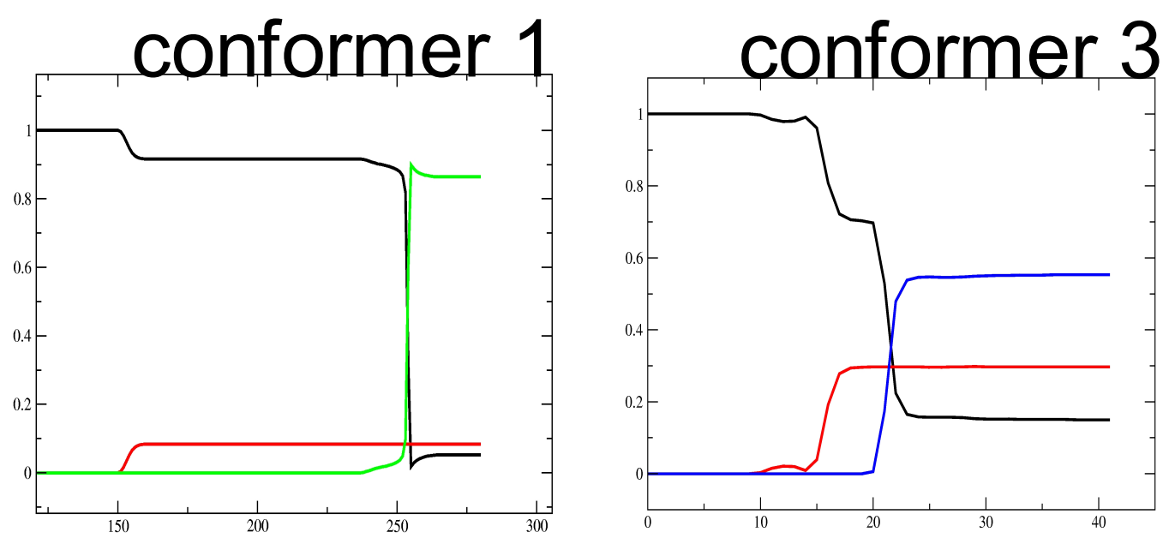
Simulation details

Electronic structure
CASSCF wavefunction – SA3(4,4) with 6-31G** basis set

Dynamics
Initial trajectories sampled according to Wigner distribution function computed for the initial vibrational ground state
Timestep 10 a.u. (0.24 fs)
Dynamics started on S3 using for each conformer its ground state minimum geometry

Results – work in progress

S3/S2



The AIMS data show almost complete population transfer from S3 to S2 in tens of femtoseconds.

Conformers 1 and 4 behave equally they are interconverting faster that the population transfer to S2 takes place → they are **indistinguishable**

S2/S1 - observed channels

Channels observed - C=O bond stretching and H-atom transfer (only for conformers 1 and 4). The H-atom loss channel was not found due to small basis set used in the simulations (there was only extensive N-H bond stretching (~1.2 Å)).
No rotation around C-C bond was observed before the S2/S1 interconversion takes place → conformers 1,4 and 2,3 are **distinguishable** in respect to H-atom transfer.

Outlook

the basis set used is not suitable for all photophysical pathways (does not allow H-atom loss). More trajectories also need to be calculated to get relevant of information about photophysics in the S2 state.

Acknowledgement

Project LC512 of Ministry of Education
Project 203/05/H001 of Grant Agency of ČR
FMS-Molpro Ben Levine