# **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 <sup>†</sup>Institute of Chemical Technology, Prague <sup>‡</sup>Institute of Physics, Polish Academy of Science, Warsaw

#### Motivation

 Addressing a general question about the possible role of ground state conformations on excited state dynamics – the photochemical properties of amino acids are very sensitive

not only to environment but also to conformation.



Recently reported experimental study of conformer-dependent S<sub>1</sub> lifetime of L-phenylalanine suggests that lifetimes of S<sub>1</sub> differ by a factor of three for different conformers.

#### Ab initio non-adiabatic molecular dynamics

Time-dependent Schroedinger equation is solved using Full Multiple Spawning algorithm<sup>6</sup>

Wave function ansatz  $\Psi$ 

$$\Psi = \sum_{I} \chi_{I}(R;t) \phi_{I}(r;R)$$
 electronic wavefunction

time-dependent nuclear wavefunction associated with Ith state

Nuclear wavefunction – superposition of frozen Gaussian basis functions Substituting the wavefunction ansatz into nuclear Schroedinger equation evolution of the coefficients  $\frac{dC^{I}(t)}{dt} = -i(S_{IJ}^{-1})\left((H_{II} - i\dot{S}_{II})C^{I} + \sum H_{IJ}C^{J}\right)$ 



→ N-H....O=C

arrangement

#### **Glycine** • $S_0$ Glycine is a nonrigid (floppy) system $\rightarrow$ a large number of conformers – 2 main types The minime are concreted by small barriers

The minima are separated by small barriers that can be easily overcome (highest barrier is ~ 940 (III) and 740 (II) cm<sup>-1</sup> for interconversion to global minimum I)<sup>2</sup>

• 
$$S_1$$
  
 $n_0 \rightarrow \pi^* 6.00 \text{ eV}$  (experiment<sup>3</sup> ~ 5.8-6.0 eV)  $\swarrow$ 

The new basis functions are "spawned" in the region of high non-adiabatic



Time  $\rightarrow$ 

#### Simulation details

coupling

Π

Electronic structure:

CASSCF wavefunction – SA3(6,6) with 6-31G\* and 6-31+\* on N 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  $S_1$  using for each conformer its ground state minimum geometry. 10 trajectories for each group of conformers.

#### **Results**

conformers having N-H...O=C arrangement – conformers I and II



The values are for conformer II, CASPT2/6-31G\*, 6-31+G\* on N atom

### **Possible photophysical pathways**

Localization of conical intersection: CASSCF/6-31G\* and 6-31+G\* on N; SA3(6,6) (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: using CASPT2 method (level shift 0.3 Hartree)

#### S<sub>1</sub>/S<sub>0</sub> intersection

 $n_{N} \rightarrow R + \sigma^{*} 6.65 \text{ eV}$ 

#### C=O bond stretching $(n\pi^*/S_0)$

1.7 Å

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



#### S<sub>2</sub>/S<sub>1</sub> intersection

- NH<sub>2</sub> planarization and
   N-H bond stretching
   energetically very
   close to the Franck Condon region
- Energetics





In the first **50~100 fs** – population transfer to  $S_2$ through the CI  $S_2/S_1$  between  $n\pi^*$  and  $n\sigma^*$  states

In ~125-250 fs – population transfer to  $S_0$  through the CI  $S_1/S_0$  between the dissociative no\* and the ground state (structure a and b).

The main channel is **H-atom loss** (structure a and b)

conformers having N-H...O-C arrangement – conformer III
 In the first ~25 ps – no population transfer from S<sub>1</sub> to S<sub>0</sub> was observed.

The rotation along the C-C bond does not take place.

#### Conclusion

• The main process is photofragmentation of glycine leading to the release of H-atom from NH<sub>2</sub> group.

the channel leads to a **fragmented molecule** in the ground state

the dissociation along the N-H coordinate was observed for neutral aromatic molecules<sup>4</sup>

#### H-atom transfer $(n\pi^*/S_0)$

the channel leads to a diol – unstable on  $S_0$ the H-atom transfer was observed in  $\beta$ -turn<sup>5</sup> energetically lowest CI **S**₁/**S**₀ 4.60(4.80) H-atom loss

> $S_1/S_0 4.01(3.81)$ H-atom transfer

**S**<sub>1</sub> min\* 3.44(3.37)

# S<sub>0</sub>

CASSCF energies (CASPT2 are given in parenthesis) in eV \*for conformer II

• The lifetimes for conformers having **N-H...O=C** arrangement is much shorter than for conformers having **N-H...O-C** arrangement (the difference is at least 2 orders of magnitude)

 $\rightarrow$  glycine conformers close in energy in the ground state show significantly different photodynamics

#### Acknowledgement

Project LC512 of Ministry of Education Project 203/05/H001 of Grant Agency of ČR

FMS-Molpro Ben Levine, Todd J. Martinez

#### References

<sup>1</sup>T. Hashimoto; Y. Takasu; Y. Yamada; T. Ebata *Chem. Phys. Lett.* 421(2006) 227.
 <sup>2</sup>O. Bludský;J. Chocholoušová;J. Vacek;J. Huisken;P. Hobza *J. Chem. Phys.* 113(2000) 4629.
 <sup>3</sup>Inagaki, T. *Biopolymers* 12(1973) 1353.
 <sup>4</sup> A. L. Sobolewski; W. Domcke et al. *Phys. Chem. Chem. Phys.* 4(2002) 1093.

<sup>5</sup> A. L. Sobolewski, W. Domcke et al. *Phys. Chem. Chem. Phys.* 4(2002) <sup>5</sup> A. L. Sobolewski, W. Domcke Chem. Phys. Chem. 7(2006) 561.

<sup>6</sup> M. Ben-Nun, J. Quenneville, T. J. Martinez *J. Phys. Chem.* A 104(2000) 5171.

