Conformationally Dependent Photodynamics of Glycine

Eva Muchová*, Petr Slaviček†, 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
- 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 S1 lifetime of l-phenylalanine suggests that lifetimes of S1 differ by a factor of three for different conformers.

- Glycine is the simplest amino acids that could serve as a good starting point

Glycine
- S1
Glycine is a nonrigid (floppy) system → a large number of conformers – 2 main types

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

- S1, n` → π* 6.00 eV (experiment) ~ 5.8-6.0 eV

- S2, nπ → R + σ* 6.65 eV

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 atom; SA3(6,6)

C=O bond stretching (nσ*/S1)

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

H-atom loss (nπ*/S2)

the channel leads to a fragmented molecule in the ground state

H-atom transfer (π*/S3)

the channel leads to a diol – unstable on S2

The H-atom transfer was observed in β-turn energetically lowest CI

Energies
FC S1, 6.00(6.00)* S1/S2, 6.05(6.02) S2/S3, 5.17 C=O stretch

S2/S3, 4.60(4.80) H-atom loss

S1/S2, 4.01(3.81) H-atom transfer

S1, min* 3.44(3.37) S0

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

S1, nσ* 6.00 eV

Ab initio non-adiabatic molecular dynamics
Time-dependent Schrödinger equation is solved using Full Multiple Spawning algorithm

Wave function ansatz

Nuclear wavefunction – superposition of frozen Gaussian basis functions Substituting the wavefunction ansatz into nuclear Schrödinger equation - evolution of the coefficients

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

Simulation details
Electronic structure: CASSCF wavefunction – SA3(6,6) with 6-31G* and 6-31+G* 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 S1, 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

- conformers having N-H...O-C arrangement – conformer III

In the first ~25 ps – no population transfer from S1 to S2, 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 NH2 group.

- 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)

→ glycine conformers close in energy in the ground state show significantly different photodynamics

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References