St Petersburg University
www.spbu.ru

DFT modeling of the zwitterionic structure of alanine and its Raman spectrum

I. V. Krauklis, A.V. Tulub, A.V. Golovin, Yu. V. Chizhov

Faculty of Physics, St. Petersburg State University

** Kraukle@yandex.ru*

2021

DFT modeling of the zwitterionic structure of alanine and its Raman spectrum

Molecules of amino acids have a zwitterionic structure (NH_3^+–CHR–COO^-, where R is a radical; in the case of alanine R = –CH_3) in the water and in the crystalline state, which arises as a result of the proton transfer from the carboxyl group to the amino group.

The structural conformers of alanine (Ala). In this work 8 structural conformers of Ala were modeled and calculated at the level of DFT/B3LYP/6-311++G(3df,2p) in the gas phase and in the water environment. The zwitterionic conformer Ala-ZW was also calculated in the framework of the polarized continuum model (PCM) of the water.

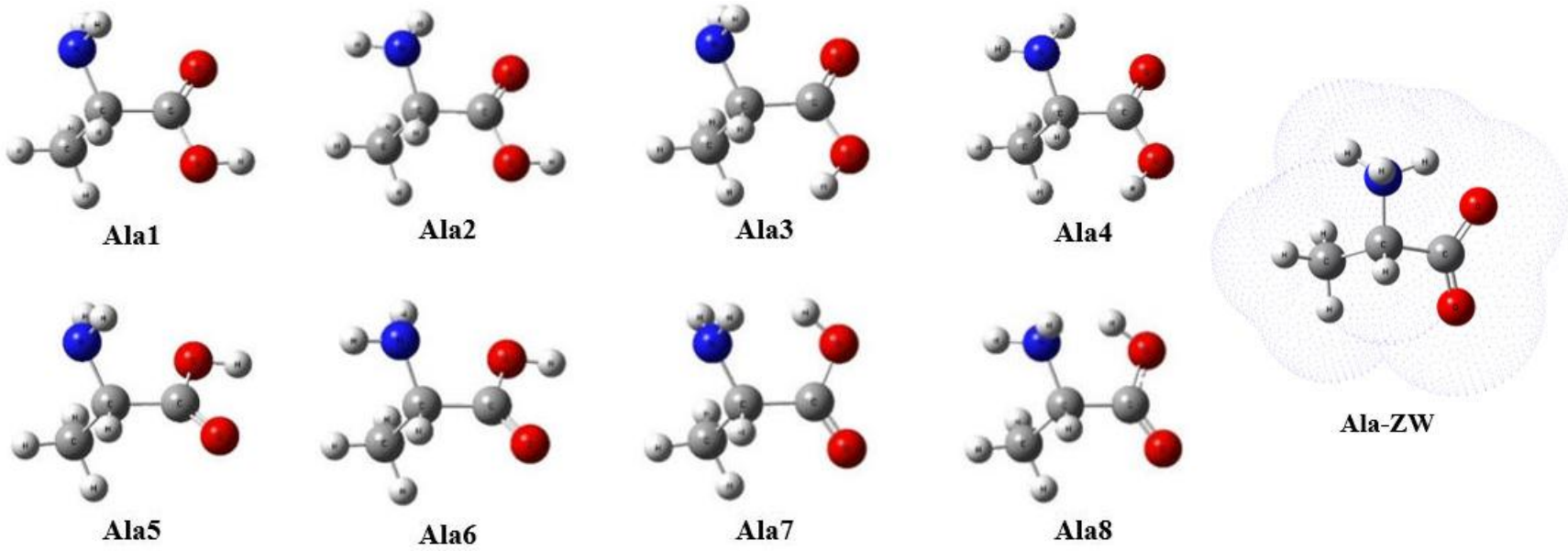


Fig.1. The structural cis–(Ala1- Ala4) and trans–(Ala5-Ala8) conformers of alanine in the gas phase. The zwitterionic conformer Ala-ZW is shown in the polarized continuum model (PCM) of the water.

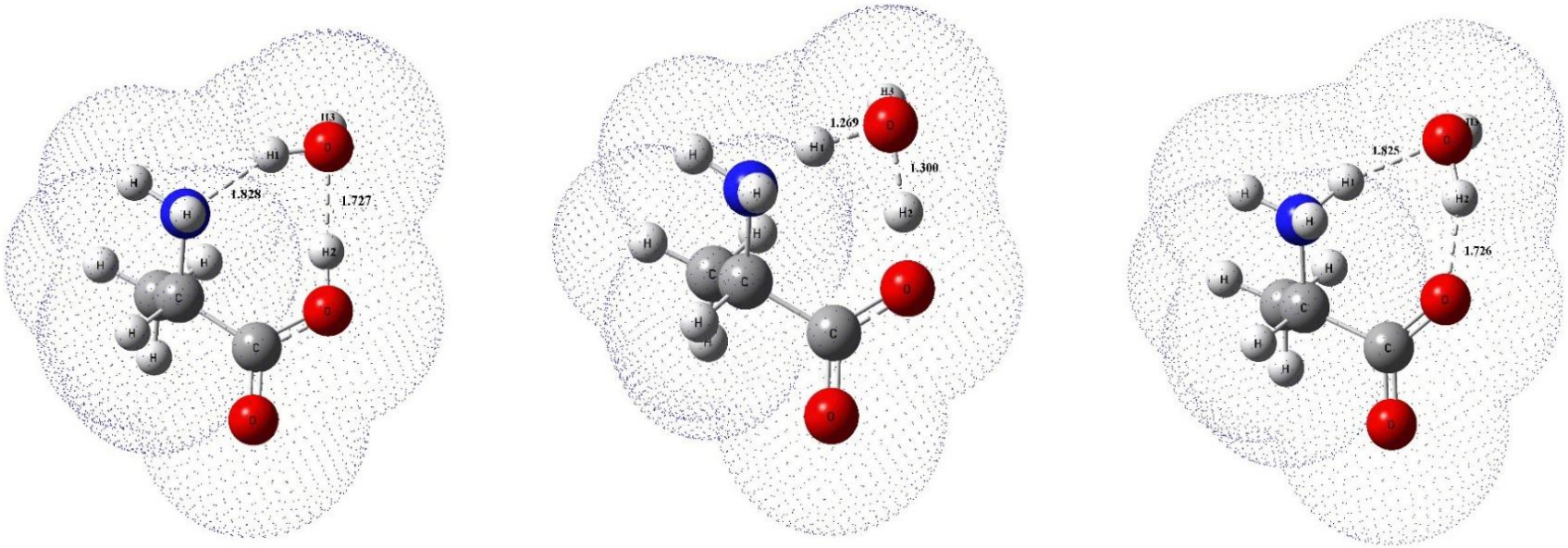
DFT modeling of the zwitterionic structure of alanine and its Raman spectrum

We were interested of the stabilization energy and the dipole moments of conformers during the transition from the gas phase to the water (PCM). According to our calculations, the zwitterionic state of alanine is less stable than the Ala8 conformer. Why? And how to correctly model the zwitterionic state of amino acids?

Conformer	gas		water (PCM)		Stabilization energy, ΔE, kJ/mol
	E, a.u.	μ, D	E, a.u.	μ, D	
Ala1	**-323.877207**	**1.314**	-323.886439	1.820	-24.239
Ala2	-323.875389	2.173	-323.885175	3.240	-25.693
Ala3	-323.869185	3.248	-323.882956	4.262	-36.156
Ala4	-323.867557	4.265	-323.881630	6.129	-36.949
Ala5	-323.875361	1.653	-323.884993	2.289	-25.289
Ala6	-323.873599	2.569	-323.883827	3.342	-26.854
Ala7	-323.868771	4.168	-323.883084	5.204	-37.579
Ala8	**-323.877140**	**5.376**	**-323.890634**	**7.146**	-35.428
Ala-ZW			**-323.887967**	**12.860**	

DFT modeling of the zwitterionic structure of alanine and its Raman spectrum

Modeling of the zwitterionic state of alanine. We showed that the formation of the zwitterionic state (ZW) occurs from the most stable conformer (GS) with the participation of a single water molecule, which is responsible for the proton transfer from the –COOH group to the $–NH_2$ group through the transition state (TS) with the hydroxonium ion $(H_3O)^+$ (Fig.3).



Ala + H_2O (GS) **Ala + H_3O^+ (TS)** **Ala + H_2O (ZW)**

Fig.3. The optimized at level method B3LYP/6-311++G (3df,2p) geometry of the molecular system Ala + H_2O in the ground (GS), transition (TS), and zwitterionic (ZW) states.

DFT modeling of the zwitterionic structure of alanine and its Raman spectrum

Also we calculated the internal coordinate of this reaction (IRC). The potential barrier of transition is $\Delta E = E(TS) - E(GS) \approx 13,9$ kJ/mol, and taking into account the zero-point energy only $\Delta E \approx 0,8$ kJ/mol.

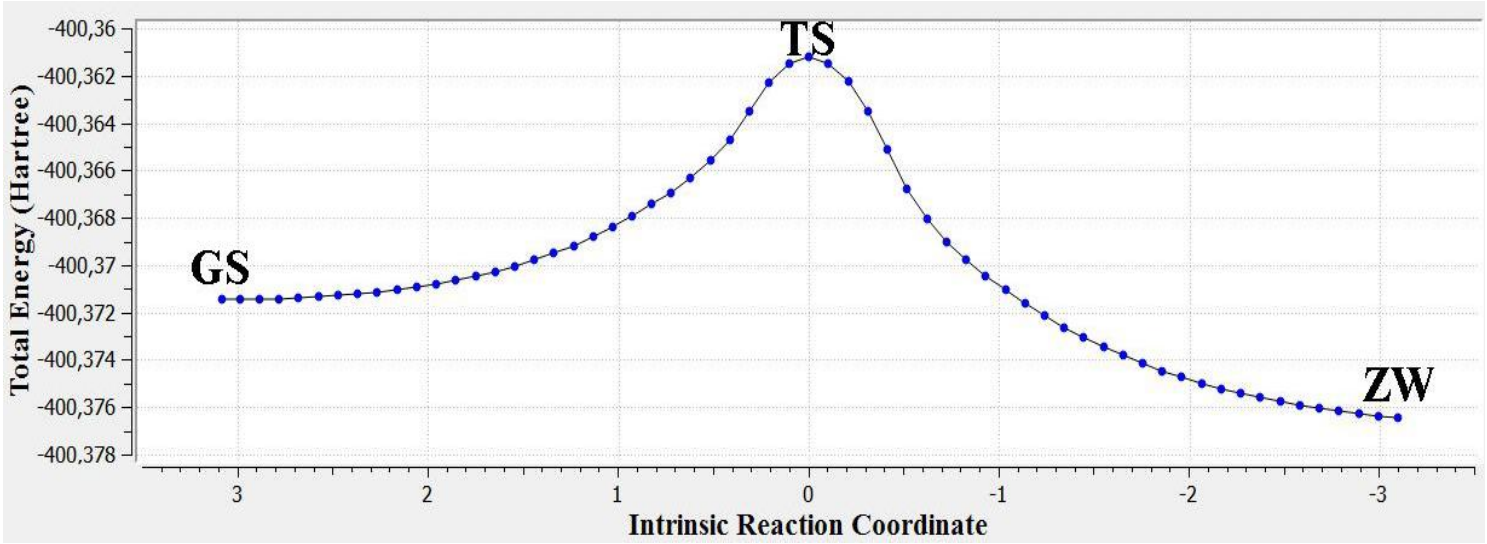


Fig. 4. The internal coordinate of the proton transfer reaction from the group –COOH to the $–NH_2$ group.

DFT modeling of the zwitterionic structure of alanine and its Raman spectrum

To test this discrete-continuum model of the zwitterionic state, the Raman spectra of alanine were calculated and compared with the experimental data. As the calculations showed, the inclusion of a single water molecule allowed a good description of the experimental Raman spectrum. The addition of two more water molecules to the **Ala + n·H_2O** complex improves the agreement with the experiment.

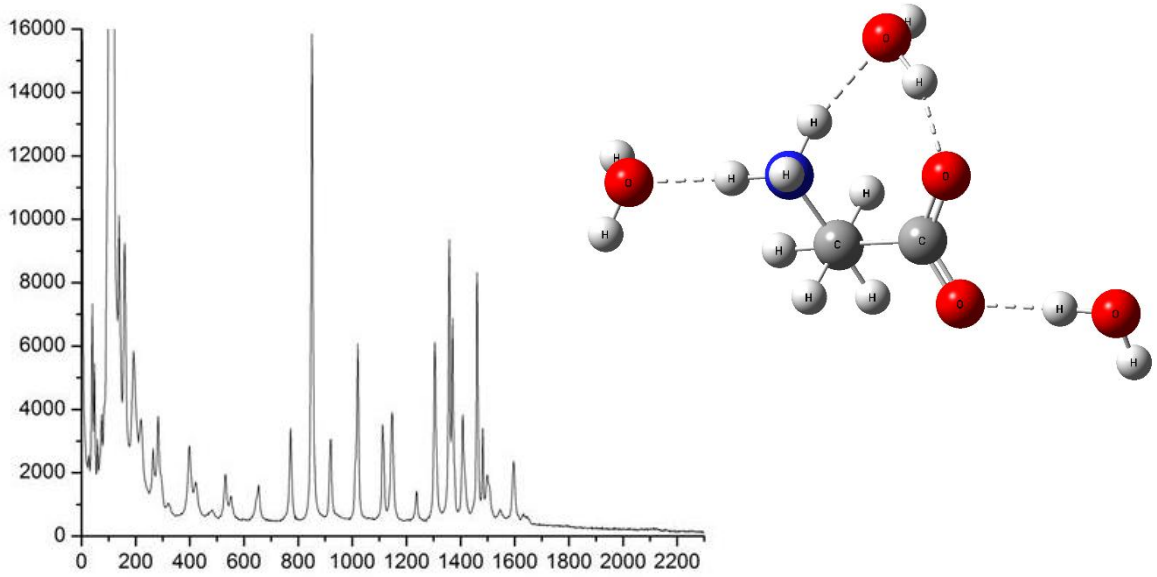


Fig. 5. The Raman spectrum of alanine in water and the model system Ala + 3H_2O.

Thank you for attention!