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Conformational Analysis of Alanine, its Radical Cation and Anion.

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More than 70 amino acids have been identified in meteorites collected in Earth coming from interstellar medium (ISM) and alanine [$CH_3CH(NH_2)CO_2H$] is one of the most abundant among them [1]. In the ISM, amino acids are found in solid phase, covered by icy mantle and the presence of water molecules seems to be essential for their survival [2]. However, due to some high energy phenomena of the hostile ISM, amino acids may undergo to gas phase, not only in their neutral form but also as radical cations and anions. These desorbed (transient) specie may produce characteristic fragments, which are commonly detected in the ISM [2]. This work aims to the conformational analysis of alanine, in its neutral, cationic and anionic forms ($CH_3CH(NH_2)CO_2H$, $[CH_3CH(NH_2)CO_2H]^{\cdot+}$ and $[CH_3CH(NH_2)CO_2H]^{-}$) described as an isolated system, and also in its neutral and zwitterionic ($[CH_3CH(^{+}NH_3)CO_2^{-}]$) forms, in aqueous solution. The collection of the geometries corresponding to the possible stationary points will be useful for simulating the high energy phenomena in space and evaluating the possible decomposition and formation paths of alanine in the ISM and in its way to Earth. The conformational analysis is extended to its radical cation and anionic forms. Theoretical calculation have been performed at the B3LYP/6-311++G(2d,2p) level for optimizations and additional single-point calculations have been performed at the CCSD(T)/6-311++G(2d,2p) level in order to achieve more accurate electronic energies. Results suggest the location of 12 conformers for alanine as R stereoisomers, and, consequently, 12 S stereoisomers, in neutral form, in gas phase. Here, the conformers have been denominated following their dihedrals angles. The dihedral angles of the lowest energy conformers (031) are D(HOCO)=-178.4º, D(OCCN)=-13.9º and D(CCNH)=-94.4º. These conformers can be seen in Figure 1. The population of the most stable conformer have been calculated as 58.6%, at 300K, while the second (112) and third (011) have been predicted as 16.5% and 10.5% respectively. Other conformers account for approximately 15%. CPCM calculations, simulating the icy mantle in which amino acids are frequently found in ISM, have been performed using the Pauling atomic radii for building up the molecular cavity and explicitly including the solute cavitation energy and solute-solvent dispersion and repulsion interaction energies in the total energies. Eleven conformers (in S stereochemistry) have been located and characterized as local and global minima. Among those geometries, the 112 has been observed as the most stable in aqueous solution, showing a population of 96%. In aqueous phase,

however, the zwitterionic form is predominant and the predicted tautomerization Gibbs free energy (112 → ZW) is -5.00 kcal mol^{-1}.

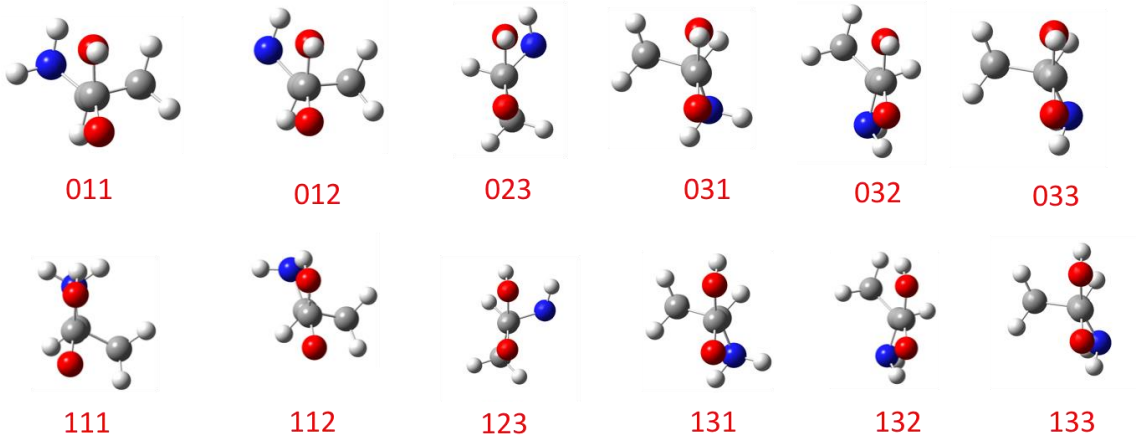

Figure 1. Conformational spectrum of neutral alanine in gas phase, calculated in B3LYP/6-311++G(2d,2p) level of theory.

A conformational spectrum for cation radical form reveals 6 conformers. The lowest energy geometry shows dihedral angles of D(HOCO)=-1.5º; D(OCCN)=35.5º and D(CCNH)=-69.2º and account for a population of 73.2% at 300K, while the second lowest energy conformer accounts for 26.2% (population of the other conformers is less than 1%, at 300K). Adiabatic ionization energy (including the vibrational zero-point .energy corrections) is predicted as 8.74 eV, in agreement with experimental data, 8.88 eV [3]. The possibility of electron capture due to the ISM phenomena is not rare, and encouraged the search for possible geometries for the corresponding anions. Five conformers for $[CH_3CH(NH_2)CO_2H]^-$ have been characterized. The characterization of geometries in different forms, in gas and aqueous phase, for alanine, indicates that the lowest energy conformer represents a first contribution for this amino acid behavior in interstellar medium.

Key-words: alanine, B3LYP, interstellar, astrochemistry, amino acid
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