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A semi-empirical and ab initio combined approach for the full conformational searches of gaseous lysine and lysine–H_2O complex

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Abstract

A full structural search of the canonical, zwitterionic, protonated and deprotonated lysine conformers in gas phase is presented. A total of 17,496 canonical, 972 zwitterionic, 11,664 protonated and 1458 trial deprotonated structures were generated by allowing for all combinations of internal single-bond rotamers. All the trial structures were initially optimized at the AM1 level, and the resulting structures were determined at the B3LYP/6-311G* level. A total of 927 canonical, 730 protonated and 193 deprotonated conformers were found, but there were no stable zwitterionic structures in the gas phase. The most stable conformers of the canonical, protonated and deprotonated lysine were further optimized at the B3LYP/6-311++G** level. The energies of the most stable structures were determined at the MP2/6-311G(2df,p) level and the vibrational frequencies were calculated at the B3LYP/6-311++G** level. The rotational constants, dipole moments, zero-point vibrational energies, harmonic frequencies, vertical ionization energies, enthalpies, Gibbs free energies and conformational distributions of gaseous lysine were presented. Numerous new structures are found and the lowest-energy lysine conformer is more stable than the existing one by 1.1 kcal/mol. Hydrogen bonds are classified and may cause significant red-shifts to the associated vibrational frequencies. The calculated proton affinity/dissociation energy and gas-phase basicity/acidity are in good agreement with the experiments. Calculations are also presented for the canonical lysine–H_2O and zwitterionic lysine–H_2O clusters. Interaction between lysine and H_2O significantly affects the relative conformational stabilities. Only one water molecule is sufficient to produce the stable zwitterionic structures in gas phase. The lowest-energy structure is found to be zwitterions when applying the conductor-like polarized continuum solvent model (CPCM) to the lysine–H_2O complexes.

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1. Introduction

The knowledge of thermochemical parameters of a molecule is of fundamental importance for the elucidation and interpretation of its reactivity. There is a growing interest in measuring and predicting the thermochemical parameters of amino acids both with experimental techniques and theoretical methods. Experimentally, these thermochemical data can be obtained by bracketing determinations [1], thermokinetic [2] or kinetic as well as other methods [3–5]. Early literature on the protonation chemistry of amino acids was reviewed by Harrison [6]. Recently, the proton affinity (PA) of lysine was reexamined by both kinetic and thermokinetic methods [2,4,5,7]. However, not all the obtained PAs of Lysine are equally reliable. For example, Tabet and coworkers [4] applied the simplest variant of the kinetic method without considering entropy corrections that are necessary to deal with multifunctional compounds like amino acids according to recent consensus in the community [5,8–10]. Bouchoux's PA for lysine [2] were derived from GB determined by the thermokinetic method, with the entropies used to convert GB to PA taken from variable temperature equilibrium studies on similar molecules.

Theoretically, the most stable canonical, protonated and deprotonated lysine conformers are prerequisite for reliable

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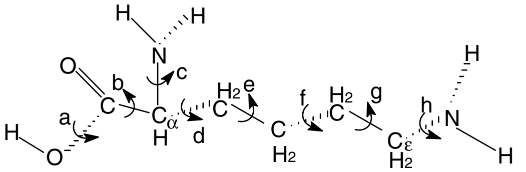
computations of thermochemical parameters like proton affinity, gas-phase basicity, proton dissociation and gas-phase acidity. Extensive ab initio calculations have been performed for proton affinities of several amino acids [11–16]. Maksic and Kovacevic calculated the PA of Lysine at the MP2/6-31+G(d,p)//RHF/6-31G(d) level, but no details were reported on the canonical and protonated structures used to obtain the final protonation energetics [12]. To avoid the defect of the Hartree–Fock theory for the molecular geometries with hydrogen bonds [17], Paizs and coworkers calculated the PA of lysine at the G2(MP2)//B3LYP/6-31+G(d,p) level [14]. Due to the large number of possible lysine conformations, they optimized a set of probable structures selected by simulated annealing techniques in conjunction with the AMBER force field. However, simulated annealing techniques are not efficient for sampling the potential energy surface with many local minima with stabilities only slightly inferior to the global minimum. Similarly, recent ab initio calculations by Poutsma and coworkers [18] on the lowest-energy structures of lysine located by the GMMX algorithm in PCModel are likely to miss some important low-energy conformers. As the most stable structures are dominant in equilibrium ensemble and are critical for explaining not only the PAs, but also many other experimental observations such as the measurements for dipole moments [19], rotational constants [20], NMR [21], IR and UV spectra [22], ionization potentials and dissociation energies [23], two-photon circular dichroism [24], etc., it is vitally important to determine the most stable structures in a more reliable way. In this paper, we report a systematic search of the full conformational spaces of gaseous lysine and its protonated and deprotonated species, with the finding of several lysine conformers that are more stable than the existing one as well as some new protonated and deprotonated lysine conformers.

Amino acids are well known to exist as zwitterions in aqueous solution, while the canonical form is much more stable in the gas phase [25–29]. In fact, no stable zwitterionic structures have been found for gaseous amino acids except arginine, the most basic amino acid. The most stable zwitterionic arginine is about 15 kJ/mol less stable than its canonical counterpart [13]. It is interesting to know if stable zwitterionic forms can be found for gaseous lysine, the second most basic amino acid. The question is addressed here also by a full conformational search. In addition, systematic searches are also performed for canonical and zwitterionic lysine–H_2O complex in gas phase.

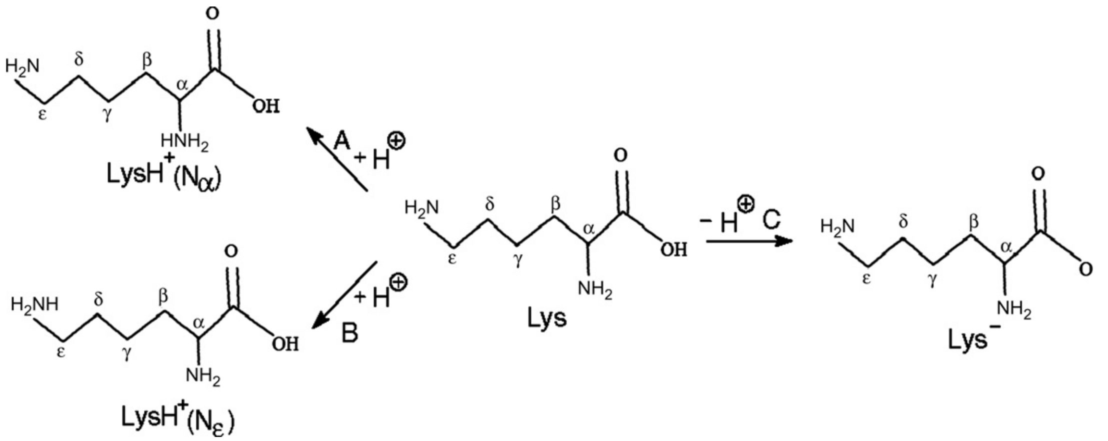
2. Computational methods

2.1. The canonical, zwitterionic, protonated and deprotonated lysine

The structures of the canonical (lys), protonated (lysH$^+$(N$_\alpha$) and lysH$^+$(N$_\varepsilon$)) and deprotonated (lys$^-$) lysine are illustrated in Scheme 1. The conformational spaces of the canonical, protonated and deprotonated lysine were explored by allowing for all combinations of the internal single-bond rotators as shown in Scheme 2. The total numbers of trial structures thus generated for lys, lysH$^+$(N$_\alpha$), lysH$^+$(N$_\varepsilon$) and lys$^-$ were 17,496, 5832, 5832 and 1458, respectively. These trial geometries were fully optimized at the AM1 level, resulting respectively 2625, 1284, 1070 and 292 unique structures. These structures were subjected to further optimization at the B3LYP/6-311G* level and the numbers of unique structures were reduced to 927,



Scheme 2. Schematic illustration of the degrees of freedom of rotamers of canonical, deprotonated and protonated lysines. (a) 2-fold: 0, 180 (except Lys$^-$); (b) 6-fold: 30, 90, 150, 210, 270, 330 (except Lys$^-$ 2-fold: 0, 90); (c) 3-fold: -120, 0, 120 (except LysH$^+$ (N$_\alpha$)); (d) 6-fold: −120, −60, 0, 60, 120, 180 (except Lys$^-$ 3-fold: −120, 0, 120); (e) 3-fold: 60, 180, 300; (f) 3-fold: 30, 150, 270; (g) 3-fold: −120, 0, 120; (h) 3-fold: −60, 60, 180 (except LysH$^+$ (N$_\varepsilon$)).



Scheme 1. Gaseous lysine and its protonated and deprotonated species as linked by the respective reactions.

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