

Quantum localization/delocalization of muonium in the glycine–K⁺ complex



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ABSTRACT

Previous electronic structure studies have revealed that the glycine–K⁺ complex has a low-barrier intramolecular proton-transfer pathway between zwitterionic and neutral forms. We have theoretically calculated quantum molecular structures of this complex including the proton-transfer process using a path-integral molecular dynamics technique on an interpolated potential energy surface developed at the B3LYP level of theory. When the transferring proton is substituted by muon, it was found that the muonium atom showed a broad distribution around the proton(muon)-transfer transition state region between the neutral and zwitterionic structures due to extreme nuclear quantum effects of a very light particle although the distribution peak is slightly deviated from the transition state. The present study demonstrates that Mu can be employed to probe transition-state regions of potential energy surfaces of proton-transfer chemical reactions.

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1. Introduction

Muonium (Mu) is an ultra-light isotope of hydrogen, consisting of a positive muon μ^+ and an electron e^- , since the mass of μ^+ is about one ninth of the proton mass. Although the lifetime of Mu is relatively short ($\sim 2.2 \mu\text{s}$), this timescale is long enough for studying the muonium chemistry experimentally [1,2]. In fact, Mu has long been used to understand nuclear quantum effects in chemical reactions including tunneling and quantized vibrations and there have been reported many studies showing very large isotope effects so far [3,4]. In particular, due to its extremely light mass and very large vibrational amplitudes, Mu-containing molecules frequently show a significantly delocalized character in molecular structures compared to hydrogen- and deuterium-containing molecules [5–15]. Alternatively, it has been reported that Mu can be localized in a very different region of the potential energy surface compared to hydrogen and deuterium cases due to multi-dimensional effects. In fact, it has been reported that Mu is sometimes localized around the saddle point region of the potential energy surface due to anomalously large zero-point energies at both reactant and product regions [16–19]. In this work, from a quantum mechanical point of view, we discuss localization/delocalization of Mu in the simplest glycine–metal cation complex having an intramolecular proton-transfer pathway between amino

group and carboxylic group. In particular, we are interested in whether Mu is localized around the proton-transfer transition state region between the neutral and zwitterionic forms due to its quantum mechanical nature.

There have been extensive studies on possible conformers of amino acid molecules in the past. It has been generally accepted that amino acids exist in their neutral form (with NH_2 and COOH groups) in the gas phase while they are found as the zwitterionic form (with NH_3^+ and COO^- groups) in aqueous solution [20–28]. This fact indicates that polar water environment significantly affects the stability of these different conformers. It is also known that metal-cation binding to amino acid molecules significantly affects the relative stability of various amino acid conformers [29–42]. In particular, there have been many theoretical studies on structures and stability of the complexes between metal-cation and glycine [29–42], the simplest amino acid molecule. Among various metal ions, we here focus on the glycine–K⁺ complex since previous electronic structure studies have shown that energy levels of the neutral and zwitterionic forms are comparable (nearly thermoneutral) and that the proton-transfer barrier height is known to be relatively low of a few kcal/mol. In addition, it should be pointed out that the interaction between potassium cation and protein plays an especially important role in the selective transport phenomenon across cell membrane. Although many structures of the glycine–K⁺ complex have been extensively studied in the past, we have also characterized the potential energy surface profile of this system using the GRRM (Global Reaction Route Mapping)

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computational algorithm [43–46] (which will be described below in detail), that can automatically find all possible local minima and transition states on a given multi-dimensional potential energy surface, to confirm the previous results [29–42]. Fig. 1(a) displays the schematic potential energy profile of the glycine–K⁺ complex showing eleven low-lying minimum structures and transition states between those minima obtained at the B3LYP/6-31+G(d) level of theory. It is seen that four structures (EQ₀, EQ₁, EQ₂, EQ₃) are more stable than other structures and have comparable relative energies at this B3LYP/6-31+G(d) level without zero-point correction. This result is in good agreement with

previous theoretical studies [29–42]. The EQ₂ structure is stabilized by the presence of the five-membered ring and by attractive electrostatic interactions between K⁺ and negative charges on carboxylic oxygen and the amine nitrogen. On the other hand, EQ₀, EQ₁, and EQ₃ are stabilized with attractive interactions between K⁺ and carboxylic oxygen. Notice that the EQ₃ structure takes the zwitterion form. It is interesting to notice that there exist large barriers between EQ₂ and the latter group (EQ₀, EQ₁, and EQ₃). Fig. 1(b) shows the schematic energy diagram with zero-point correction where harmonic zero-point vibrational energies were calculated with all the mass of five hydrogen atoms being 1.008 amu. It is

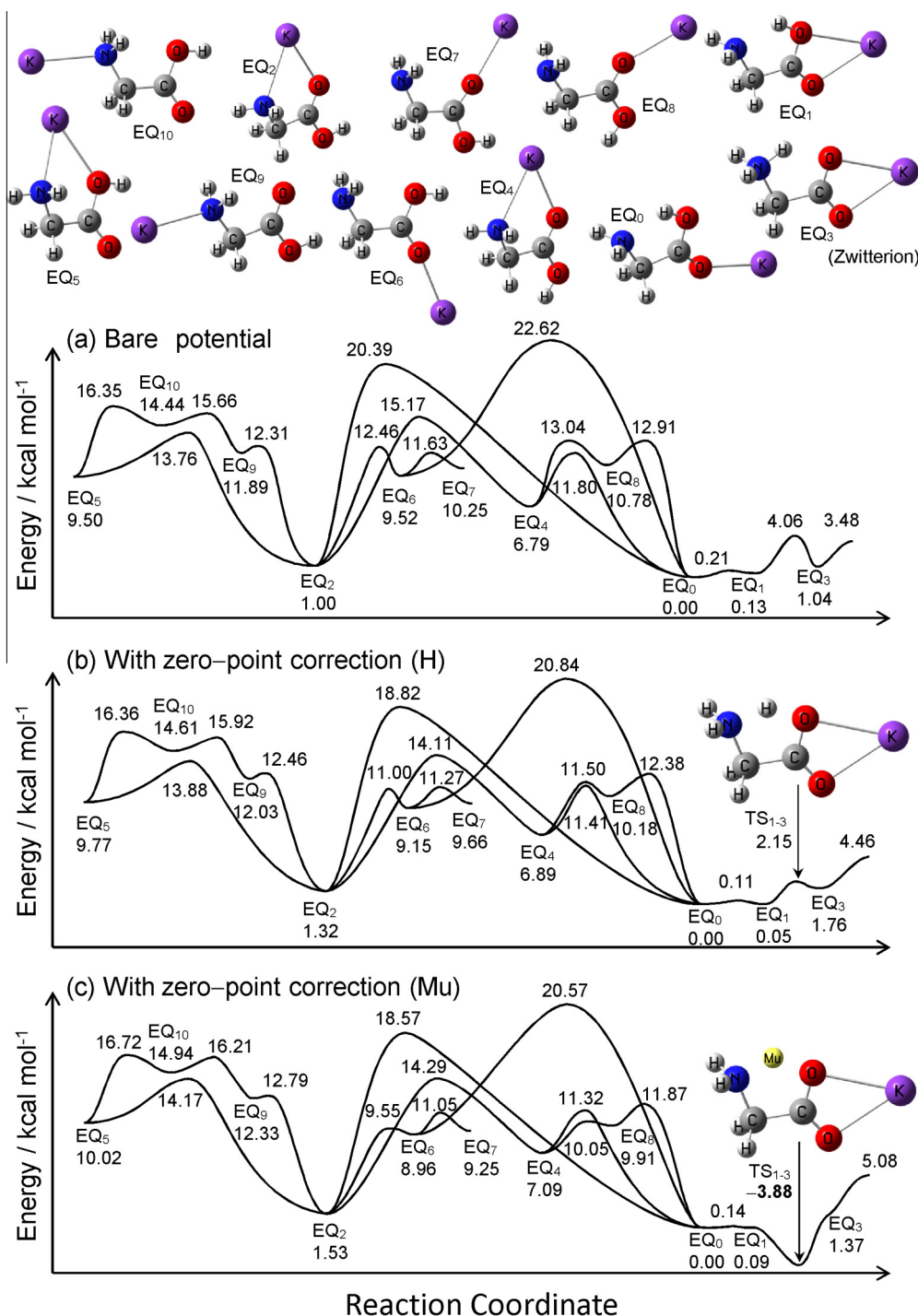


Fig. 1. Schematic potential energy profile of the glycine–K⁺ complex at the B3LYP/6-31+G(d) level of theory: (a) bare potential without zero-point energy correction, (b) with zero-point energy correction using harmonic frequency analyses, and (c) with zero-point energy correction but for the muonated glycine–K⁺ complex where one of the H atoms is substituted by Mu. Notice that all five hydrogen atom sites were examined and the most stable result is presented.

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