Letter

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Infrared Multiple Photon Dissociation Spectroscopy of Potassiastated Proline

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The structure of proline in [proline + K]+ has been investigated in the gas phase using high level DFT and MP2 calculations and infrared photo dissociation spectroscopy with a free electron laser (FELIX). The respective FELIX spectrum of [proline + K]+ matches convincingly the calculated spectra of two structurally closely related and nearly iso-energetic zwitterionic salt bridge (SB) structures. An additional unresolved band at ~1725 cm⁻¹ matching with the characteristic CO stretching mode of charge solvation (CS) structures points toward the presence of a minor population of these conformers of proline in [proline + K]+. However, theory predicts a significant energy gap of 18.9 kJ mol⁻¹ (B3LYP/6-311++G(2d,2p)) or 15.6 kJ mol⁻¹ (MP2) between the lowest CS conformer of proline and the clearly favored SB structure.

TABLE 1: Relative Energies (ΔH\(^{\ddagger}\)) Including ZPE Corrections of the Gas-Phase Conformers Relevant for [proline + K]^+ conformer | B3LYP [kJ mol⁻¹] | MP2 [kJ mol⁻¹]
--- | --- | ---
SB1 | 0 | 5.5
SB1a | 4.3 | 0
CS1 | 18.9 | 15.6
CS1a | 20.5 | 17.6
CS2 | 26.0 | 22.3

In the present work, the molecular ion of proline with potassium has been investigated using infrared multiple photon dissociation (IRMPD) spectroscopy and theoretical calculations. Arbitrary CS and SB structures of [proline + K]^+ were chosen as input structures for a mixed low mode/Monte Carlo multiple minimum conformation search using MacroModel 8.1 (Schrodinger Inc., Portland, OR). 5000 LCMM steps were performed, each followed by minimization using the Merck Molecular Force Field (MMFF94s). Candidate structures with low MMFF energy were selected for subsequent higher level calculations. These were performed on the DFT and MP2 level of theory as implemented in Gaussian 03 applying the 6-311++G(2d,2p) basis set on all atoms. Harmonic frequency calculations verified that all structures corresponded to local minima on the potential energy surface. Optimized energies including zero point energy (ZPE) corrections of the B3LYP and MP2 calculations are given in Table 1. As shown by Russo et al., each isomer exists as a conformer pair differing by the puckering of the five-membered ring. Both the DFT and MP2 calculations predict a SB structure to be the energetic minimum. Figure 1 shows the most stable structures of [proline + K]^+. The energetically favored SB1 structure exhibits a nearly linear salt bridge, which obviously provides optimum stabilization of the charges (Figure 1). A complete list of all [proline + K]^+ structures identified with their corresponding energies are given in Table S1 in the Supporting Information.

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B3LYP calculations predict SB1 to be slightly more stable than the respective SB1a structure, whereas MP2 calculations predict an inverted ordering (Table 1).

The less intense band around 1590 cm$^{-1}$, corresponding to the NH$_2$ scissoring mode, calculated at 1620 cm$^{-1}$, also supports our assignment. Obviously, the signal intensities of the recorded FELIX spectrum differ from the intensities predicted by theory. Such discrepancies were experienced before and different reasons are noted to explain the significant deviations.\textsuperscript{20,22,23} Despite its relatively low intensity the band at 1475 cm$^{-1}$ matches well to that calculated at 1470 cm$^{-1}$ for the SB conformers. The wavenumber region 1250–1420 cm$^{-1}$ exhibits a clear similarity between the recorded and the calculated spectra for the SB structures, including the intense band at 1380 cm$^{-1}$. The measured spectrum exhibits a low-intensity band in the region of the characteristic CO stretches at $\sim$1725 cm$^{-1}$ which is not predicted for the SB structures of proline. The calculated spectra of the lowest energy CS conformer CS1 and its bended ring isomer CS1a show a band at 1735 cm$^{-1}$. This overlap hints toward the presence of CS conformers of potassiated proline, despite the significant energy gap (±16 kJ mol$^{-1}$) predicted by both DFT and MP2 calculations (see Table 1). No other bands characteristic for the CS conformers can be identified selectively, since these vibrations coincide with multiple absorption bands of zwitterionic SB structures.

In summary, the FELIX spectrum of [proline + K]$^+$ correlates convincingly with the calculated spectrum of the zwitterionic structure identified to be the most stable conformer (SB1) of proline. However, the unresolved band found at $\sim$1725 cm$^{-1}$ which is observed in both photo dissociation spectra of either sodiated\textsuperscript{12} or potassiated proline lead to different structure assignments. In the latter case we propose the presence of a mixture of SB and CS structures of proline conformers in [proline + K]$^+$, whereas Kapota et al. exclusively postulate a SB conformer for proline in [proline + Na]$^+$.\textsuperscript{12} Obviously, a proper scaling of the experimental data is crucial for correct structure assignments. A conclusive answer to this question awaits either the complete examination of all alkali metal complex ions of proline with photo dissociation spectroscopy or other experimental strategies, e.g., by ion mobility-MS. The results presented in this communication are integral part of a systematic and multidimensional study of gas-phase ion structures of a series of synthetic amino acid derivatives, which is currently conducted.

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**Supporting Information Available:** Figure 1S and Table 1S. This material is available free of charge via the Internet at http://pubs.acs.org.

**References and Notes**


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