Supporting Information for:

Cis–Trans Isomerizations of Proline Residues are Key to Bradykinin Conformations

Nicholas A. Pierson,[†] Liuxi Chen,[‡] David H. Russell,[‡] and David E. Clemmer*[,†]

[†]*Department of Chemistry, Indiana University, Bloomington, IN 47405*
[‡]*Department of Chemistry, Texas A&M University, College Station, TX 77843*

Supporting Information section includes Figures S1 through S4 as discussed in the main text.

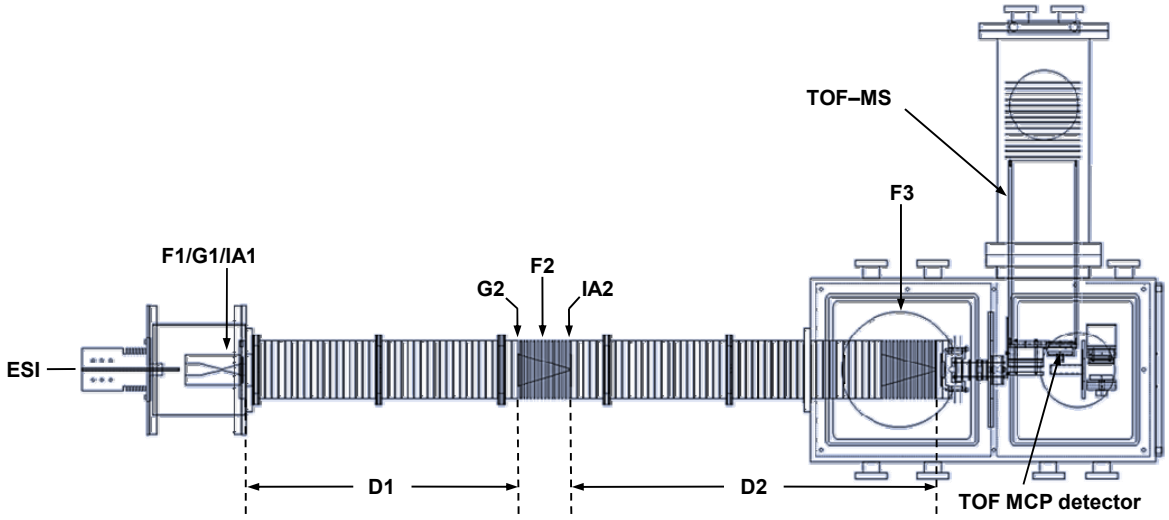

Figure S1. Schematic diagram of the home-built ion mobility – mass spectrometer at Indiana University, described in detail in the Experimental section.

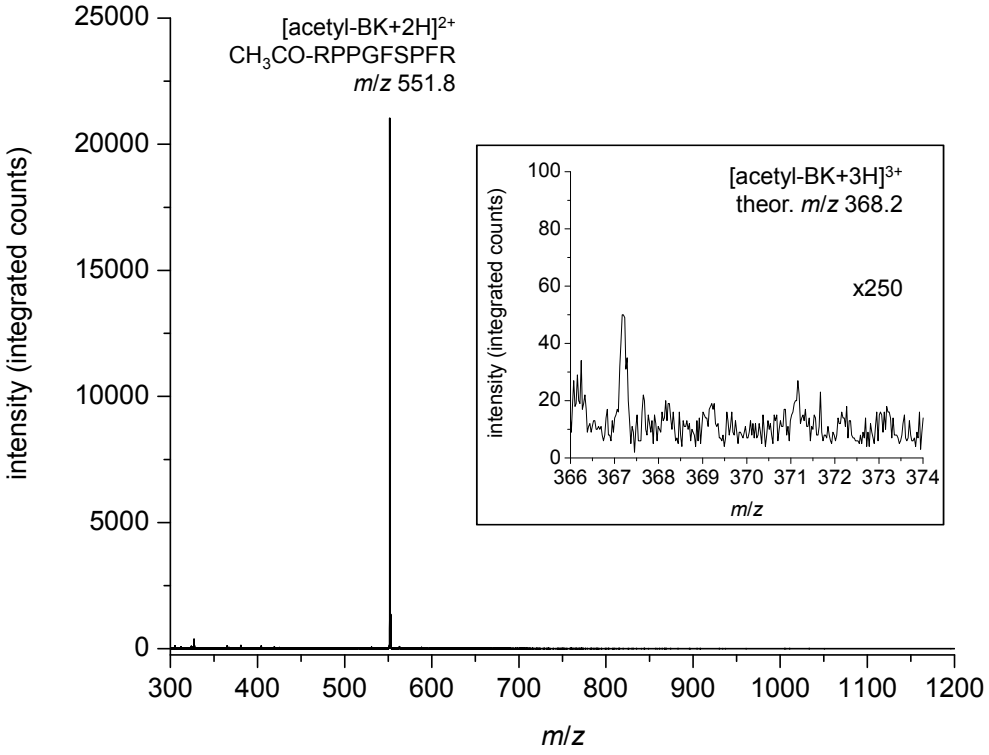

Figure S2. Mass spectrum of acetylated BK. The inset is a 250x blow up of *m*/*z* region 366–374, which shows there is no presence of the $[\text{acetyl-BK+3H}]^{3+}$ ion at *m*/*z* 368.2.

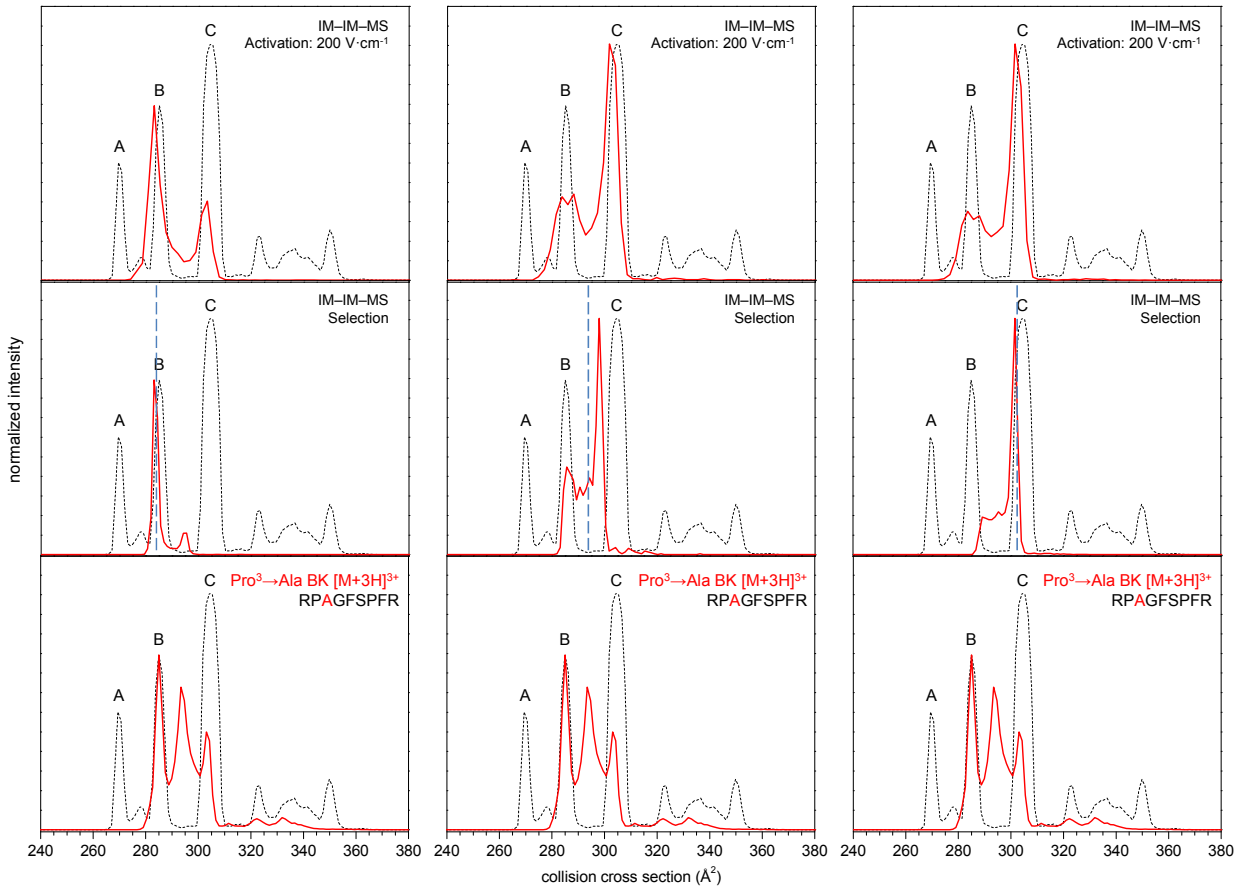

Figure S3. IM–IM–MS studies of Pro^3→Ala BK (RPAGFSPFR) (red traces), where the IM–MS cross section distribution of $[M+3H]^{3+}$ ions is shown across the bottom, three different IM–IM–MS selections in the middle (vertical dashed line represents where the selection pulse was applied), and IM–IM–MS distributions obtained from collisional activation of the three selections on top. The $[BK+3H]^{3+}$ cross section distribution (dashed traces) is shown in all panels for comparison with the analogue peptide. The IM–IM–MS selection and activation results indicate the middle peak in the IM–MS distribution of Pro^3→Ala BK $[M+3H]^{3+}$ is not a stable conformation. Cross section values for the analogue peptide were shifted to compare with BK according to amino acid size parameters in ref. 33.

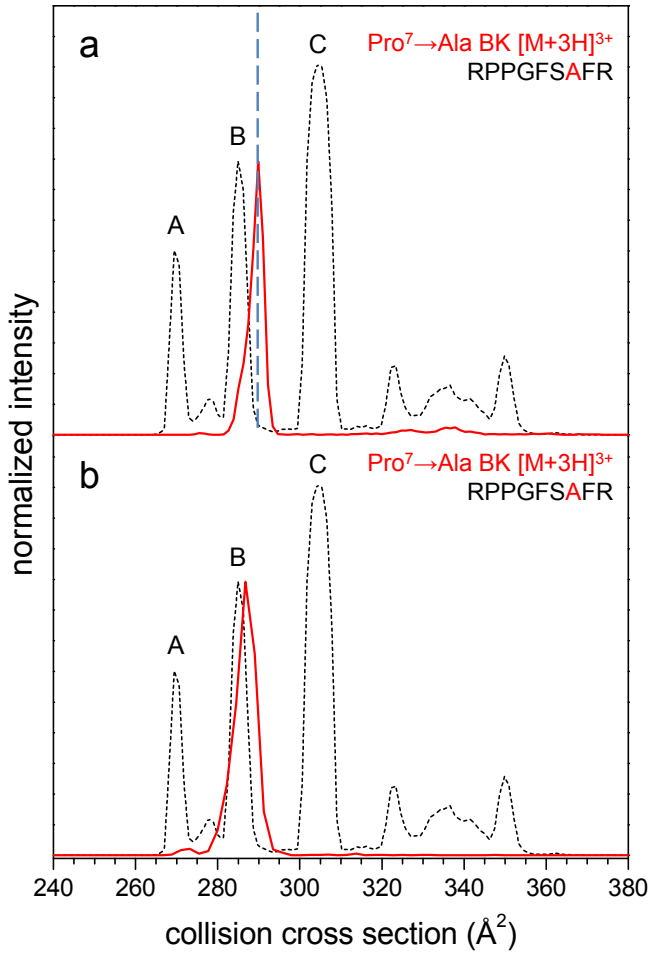

Figure S4. IM–IM–MS (a) selection of $[Pro^{7}\rightarrow Ala\ BK+3H]^{3+}$ and (b) activation by application of 60 V (200 $V \cdot cm^{-1}$) in IA2 region. The vertical dashed line represents where across the distribution the selection pulse was applied. Upon activation, the distribution shifts to a higher mobility. Cross section values for the analogue peptide were shifted to compare with BK according to amino acid size parameters in ref. 33.