Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

# Radical-Induced, Proton-Transfer-Driven Fragmentations in [$b_5$ – H]$^{\bullet+}$ Ions Derived from Pentaalanyl Tryptophan

*Declan Williams,*[a] *Justin Kai-Chi Lau,*[a,b] *Junfang Zhao,*[a] *Stefanie Mädler,*[a] *Yating Wang,*[a] *Irine S. Saminathan,*[a] *Alan C. Hopkinson,*[a] *K.W. Michael Siu*[a,b] *

[a]*Department of Chemistry and Centre for Research in Mass Spectrometry, York University, 4700 Keele Street,Toronto, Ontario, Canada M3J 1P3*

[b]*Department of Chemistry and Biochemistry, Windsor University, 401 Sunset Avenue, Windsor Ontario, Canada N9B 3P4*

## Supporting information

*Corresponding author

Email: kwmsiu@uwindsor.ca

Figure S1.Energy-resolved diagram of AAAWA*$_{\text{oxa}}^{\bullet+}$ where A* denotes the alanine having a $CD_3$ side chain. The formation of ion at *m/z* 240 is the dominant dissociation channel and the loss of AA$_{\text{oxa}}$ (*m/z* 328) is always more abundant than the loss of only one alanine residue (*m/z* 399).

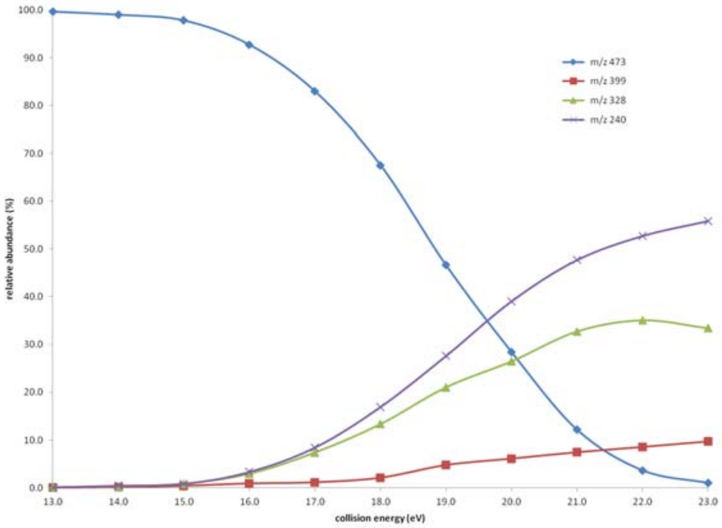
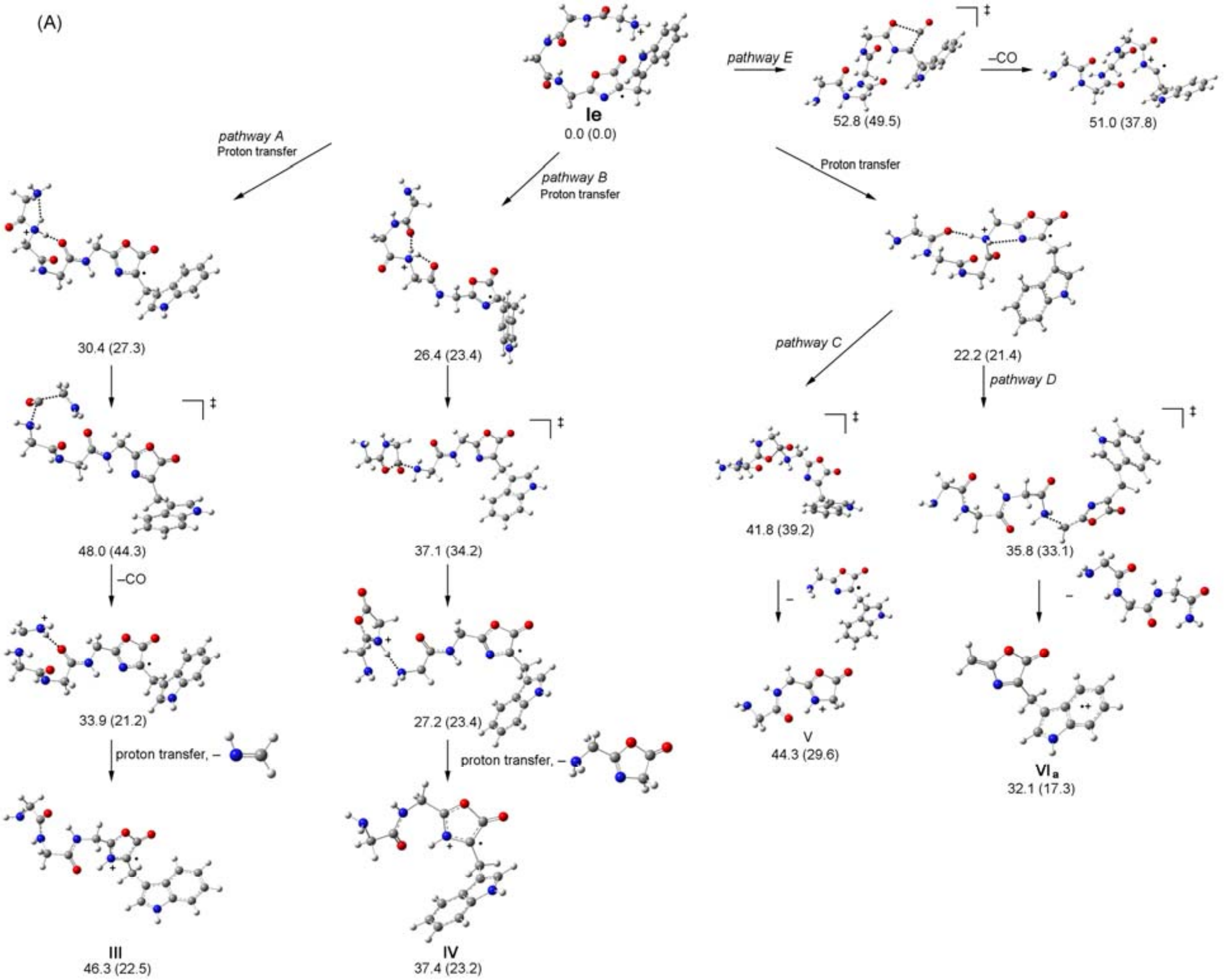
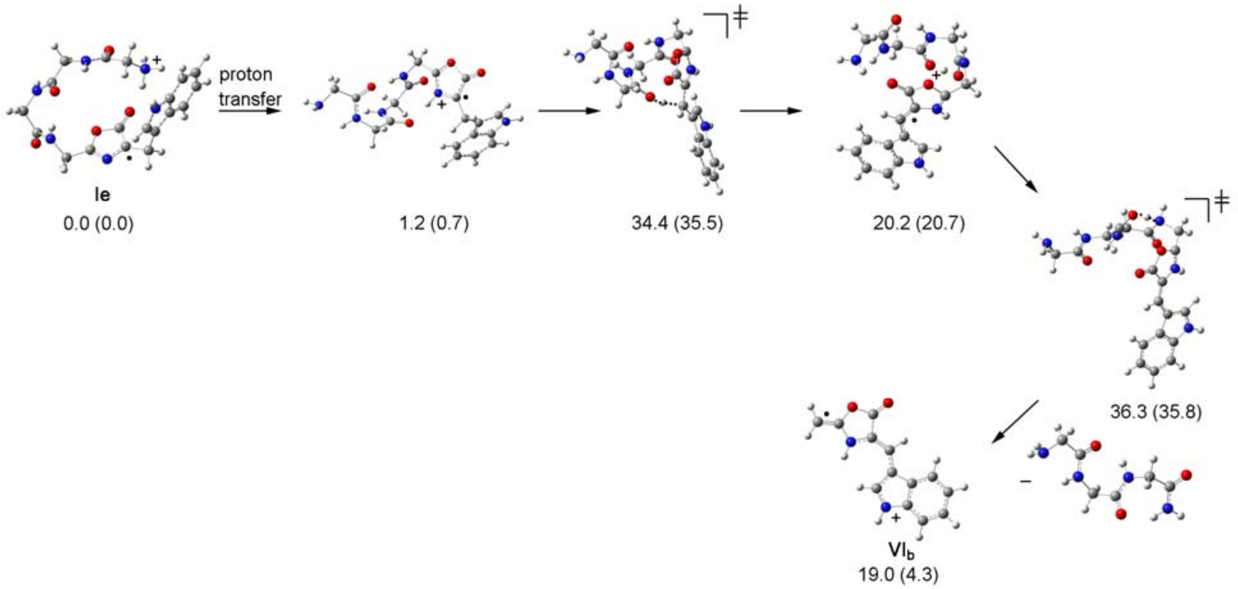


Figure S2. Mechanisms for the dissociation of $[b_5 - \mathrm{H}]^{\bullet+}$ ion induced by the migration of a proton (A) from the nitrogen of the oxazolone ring and (B) from the β-$CH_2$ group of the tryptophan side chain. Enthalpies ($\Delta H^{o}_{0}$, kcal mol$^{-1}$) and free energies ($\Delta G^{o}_{298}$, in parenthesis) are calculated at the B3LYP/6-31++G(d,p) level. All energies are relative to the global minimum structure **Ie**.



(B)


proton
transfer
Ie
0.0 (0.0)
1.2 (0.7)
‡
34.4 (35.5)
20.2 (20.7)
‡
36.3 (35.8)
VI$_b$
19.0 (4.3)
+
−