Relative Stability of Sequence Ions Generated by Tandem Mass Spectrometry

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Results and Discussion

We report the use of unimolecular dissociation by infrared radiation for gaseous multiphoton energy transfer to determine relative activation energy ($E_{a,laser}$) for dissociation of peptide sequence ions. The sequence ions of interest are mass-isolated; the entire ion cloud is then irradiated with a continuous wave CO_2 laser; and the first order rate constant, k_d, determined for each of a series of laser powers. Provided these conditions are met, a plot of the natural logarithm of k_d versus the natural logarithm of laser power yields a straight line whose slope provides a measure of $E_{a,laser}$ (see **Figure 1**). This method reproduces the E_a values from blackbody radiative dissociation (BIRD) for the comparatively large, singly and doubly protonated bradykinin ions (nominally y_9 and y_9^{2+}). The comparatively small sequence ion systems produce $E_{a,laser}$ values that are systematic underestimates of theoretical barriers calculated with density functional theory (DFT). However, the relative $E_{a,laser}$ values are in qualitative agreement with the mobile proton model and available theory. Moreover, novel protonated cyclic-dipeptide (diketopiperazine) fragmentation reactions are analyzed with DFT. FT-ICR MS provides access to sequence ions generated by electron capture dissociation, infrared multiphoton dissociation, and collisional activation methods (i.e., b_n, y_m, c_n, $z_m^{\bullet}$ ions).[1]

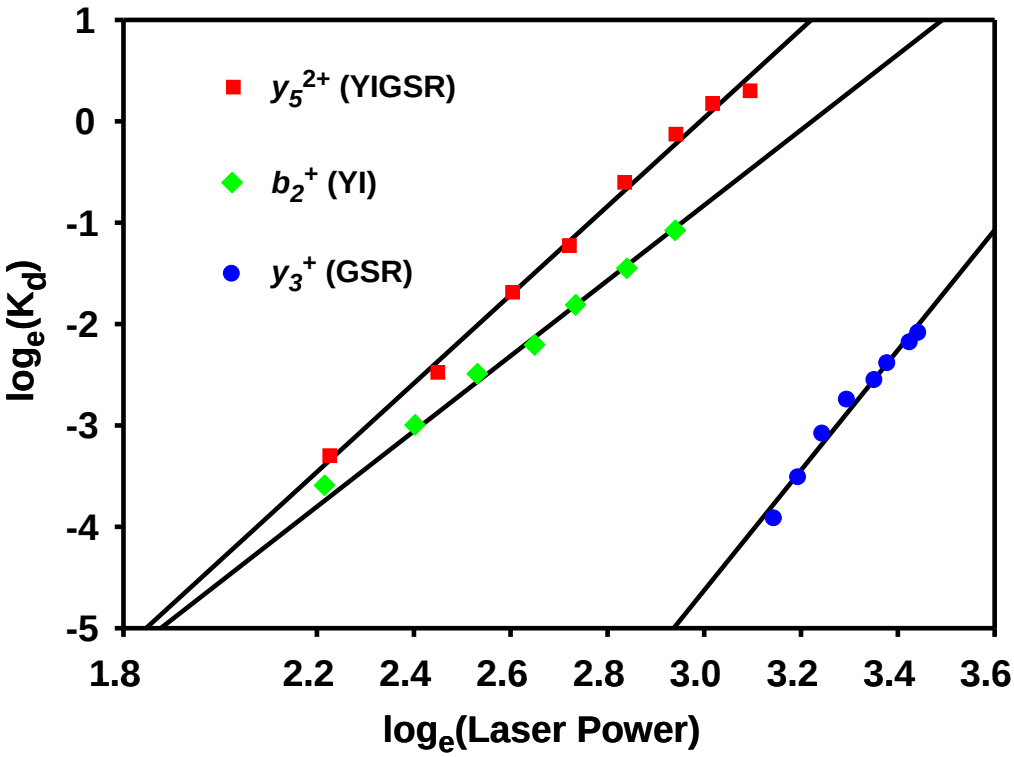

Figure 1. Log-log plot of dissociation constant vs. laser power, for each of three precursor peptide ions. The slope yields activation energy.

Acknowledgements

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References

[1] Bythell, B. J., *et al.*, J. Am. Soc. Mass Spectrom., **23**, 644-654 (2012).