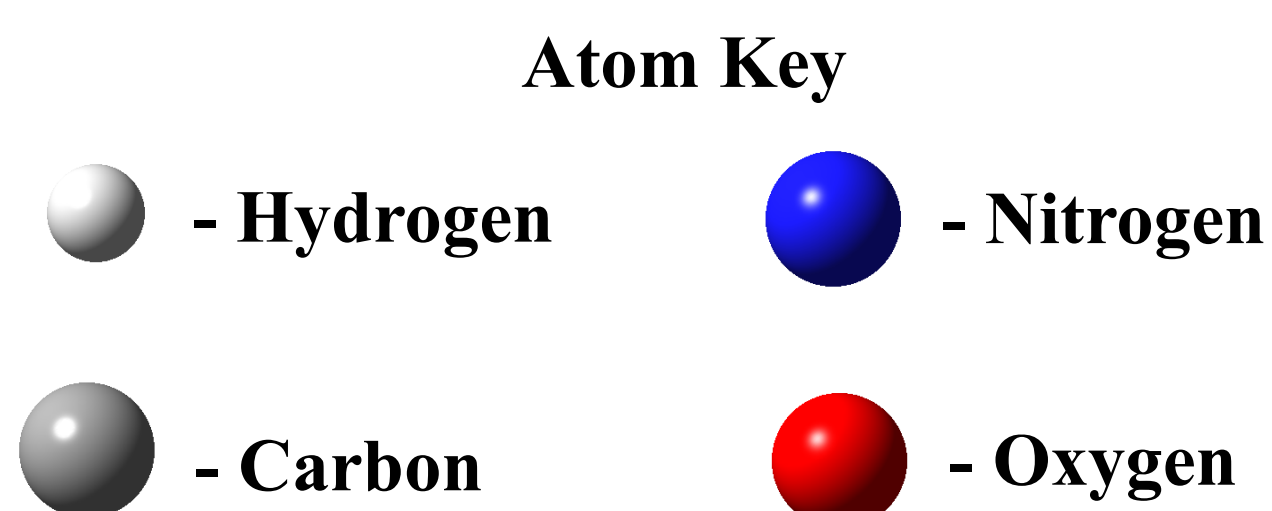


# Astrobiological Explorations of Amino and Methyl-Substituted Nucleobase Anions

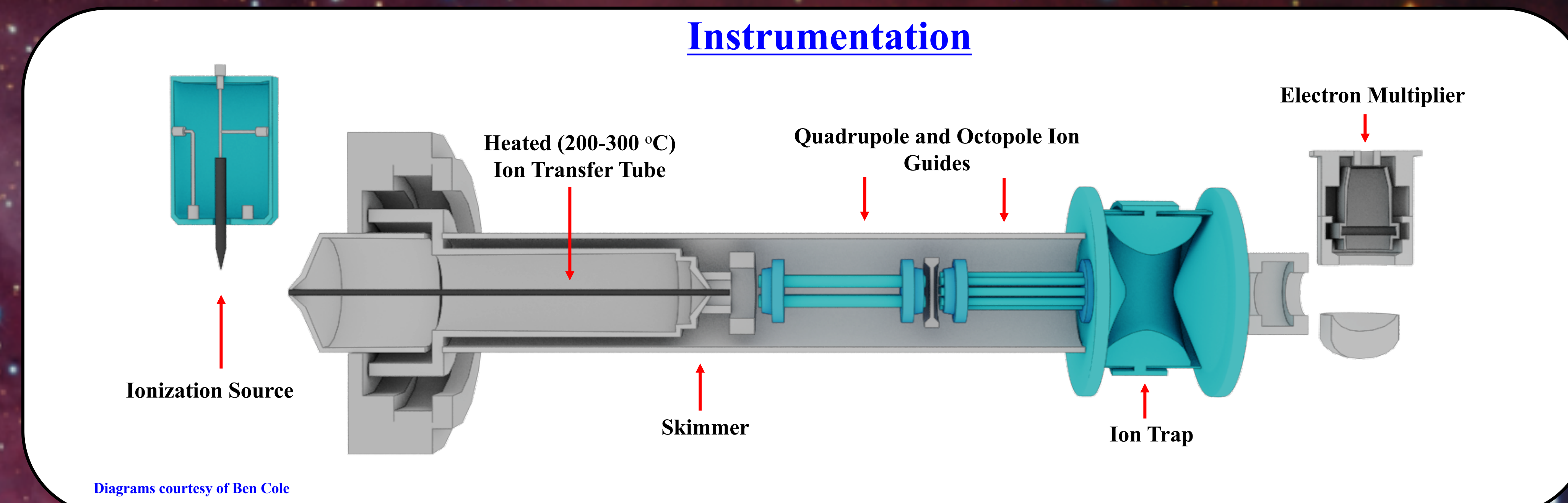
Alexandra A. Dobbs, Bryan E. Metz, Aaron R. Wegener, Diego T. Novoa, Callie A. Cole  
Department of Chemistry & Biochemistry, Fort Lewis College, Durango, CO.



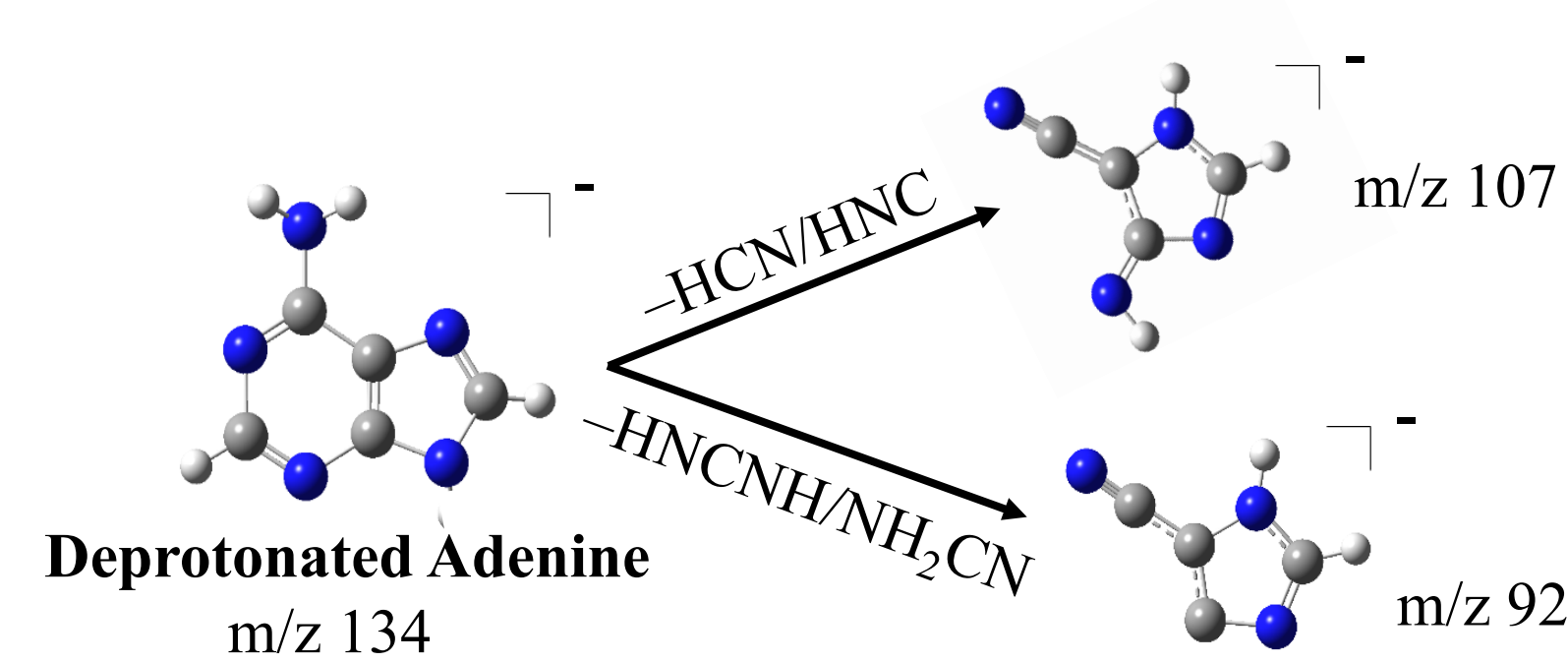
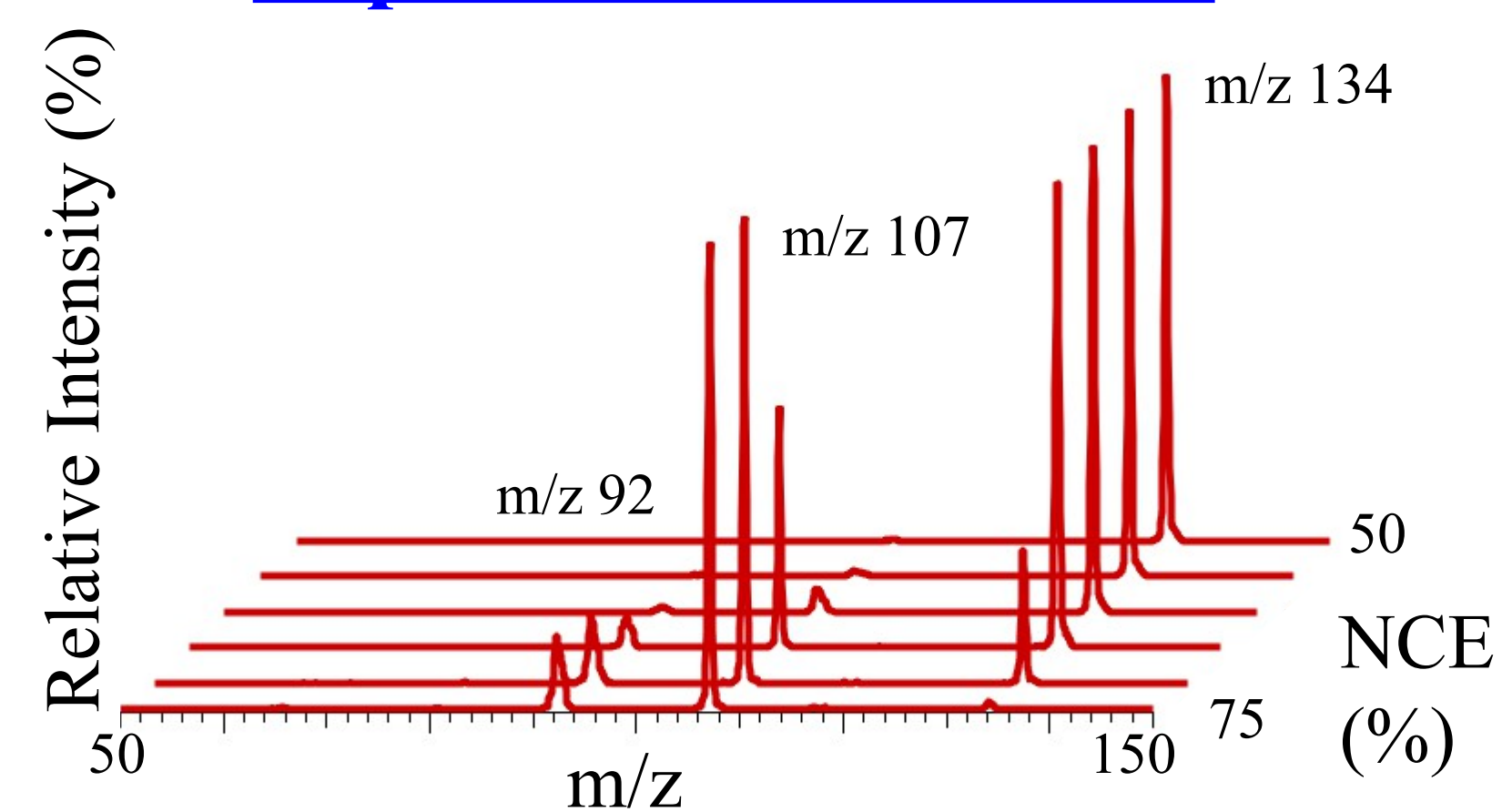
**Abstract:** The discovery of prebiotic molecules in the interstellar medium (ISM) provides incentive to investigate the extraterrestrial formation of biomolecules. This study aims to illuminate potential interstellar synthesis pathways of nucleobase analogs by analyzing their gas phase dissociation patterns. Purine analogs are of particular interest as the location of functionalization directly effects the conjugation of electrons around the ring (Beste et al., 2009), impacting fragmentation processes under CID. The products observed in these processes are possible ionic precursors to nucleobase formation and often yield interstellar species, such as HNCNH/ H<sub>2</sub>NCN and NH<sub>3</sub>.

A. Beste, A. C. Buchanan. *J. Org. Chem.* 2009, 74, 2837-2841.

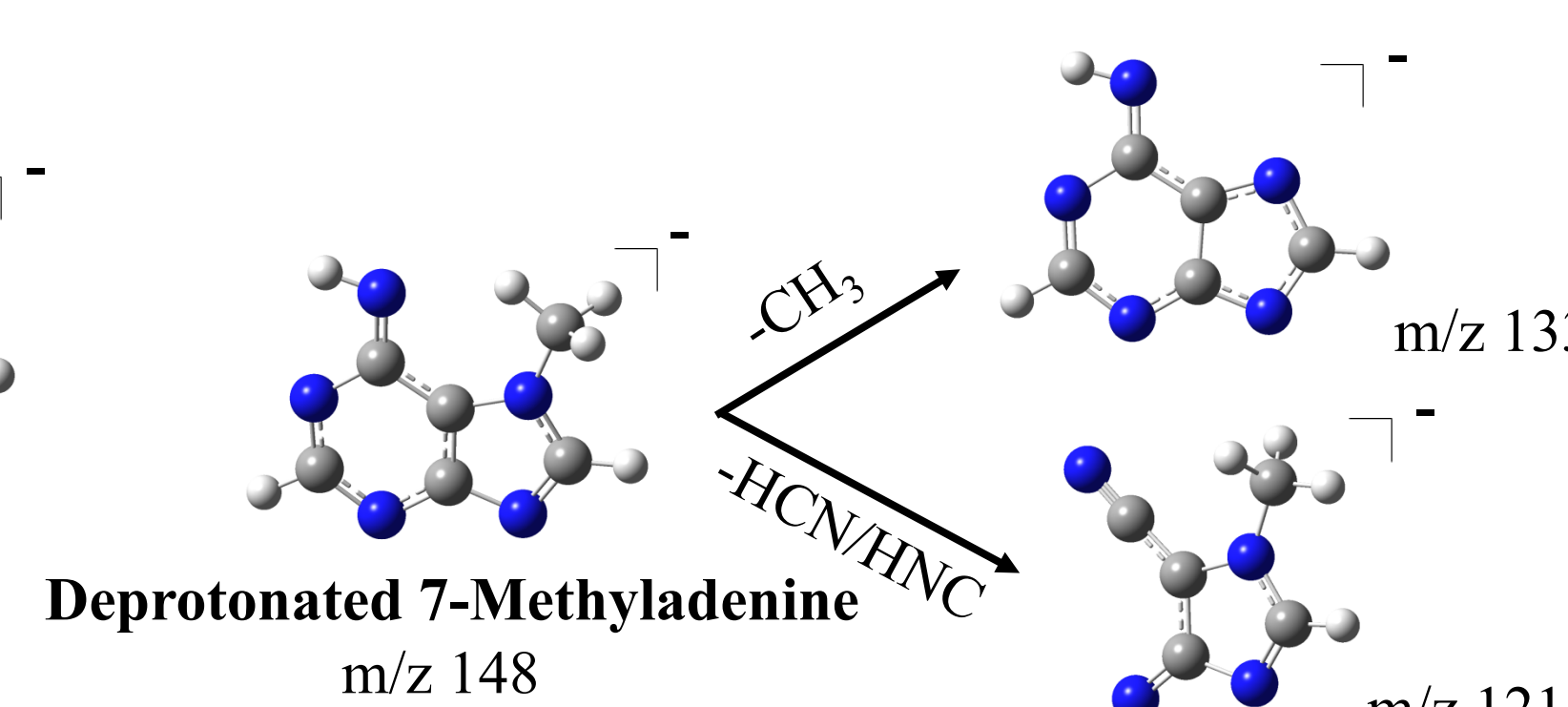
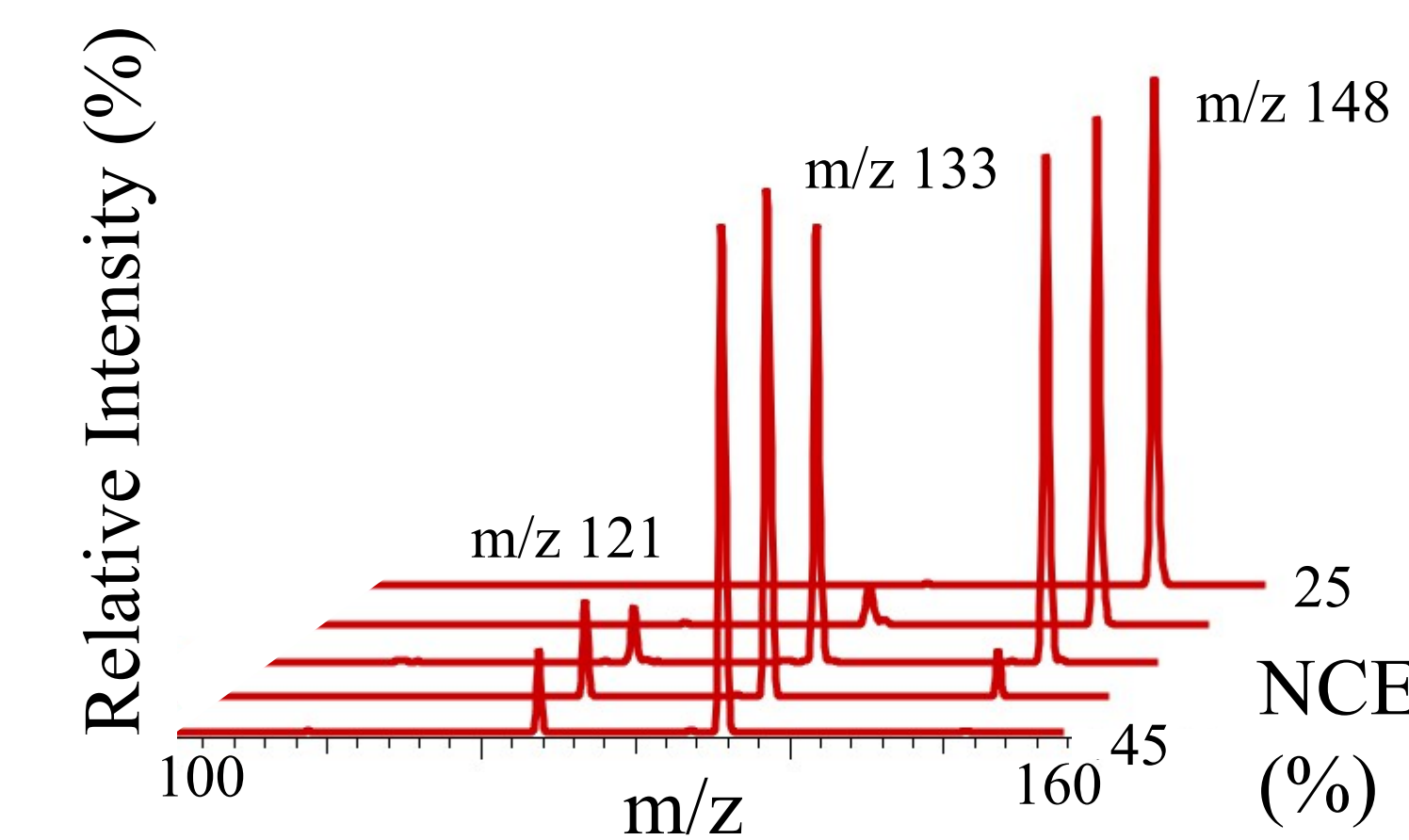
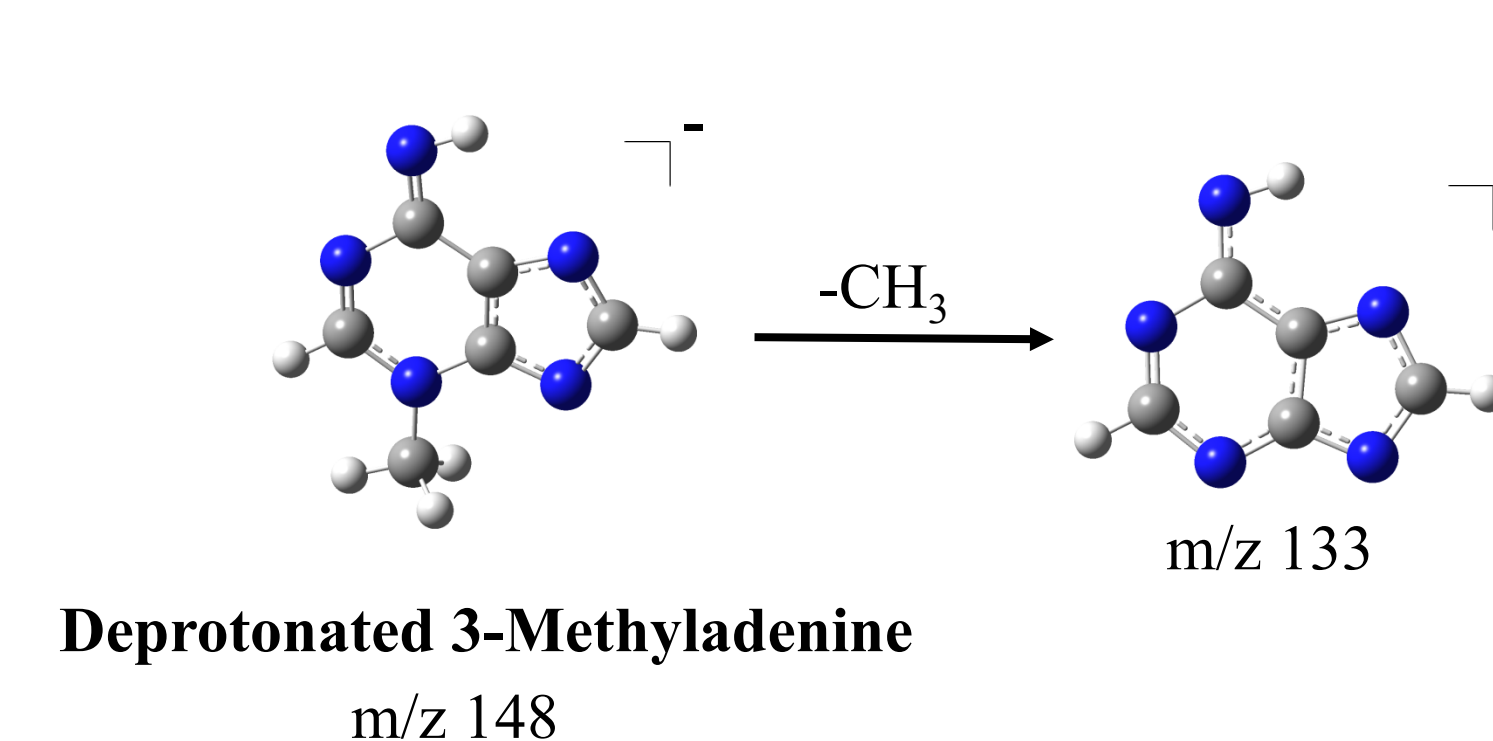
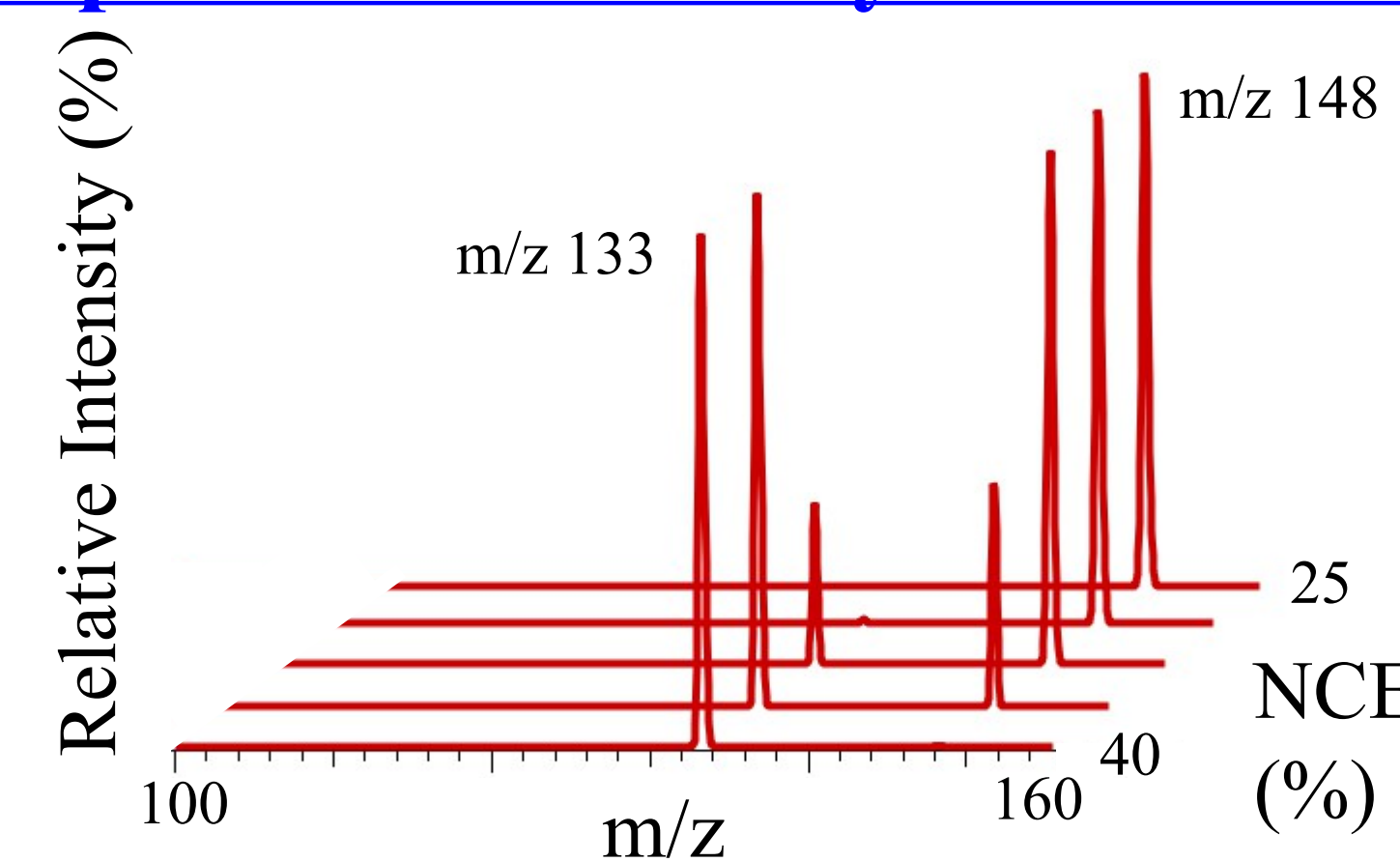
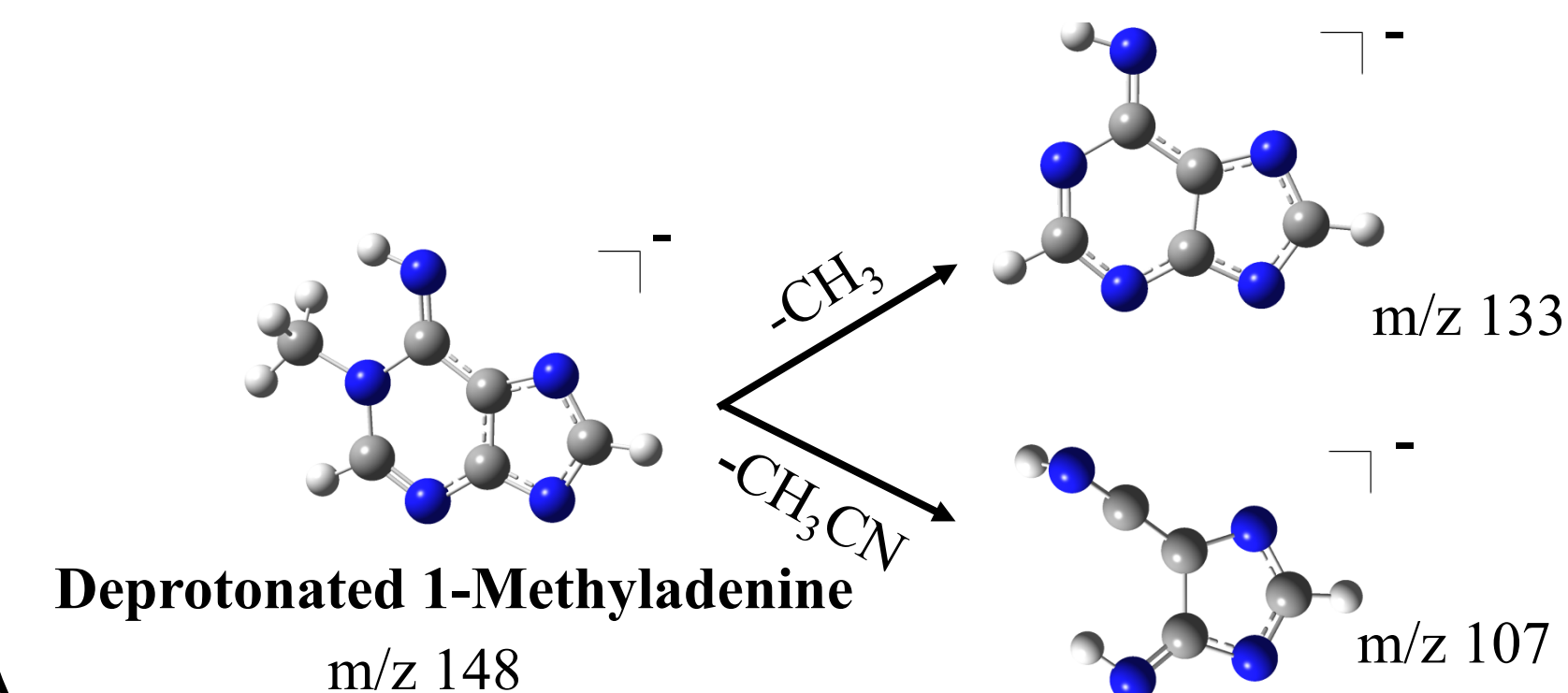
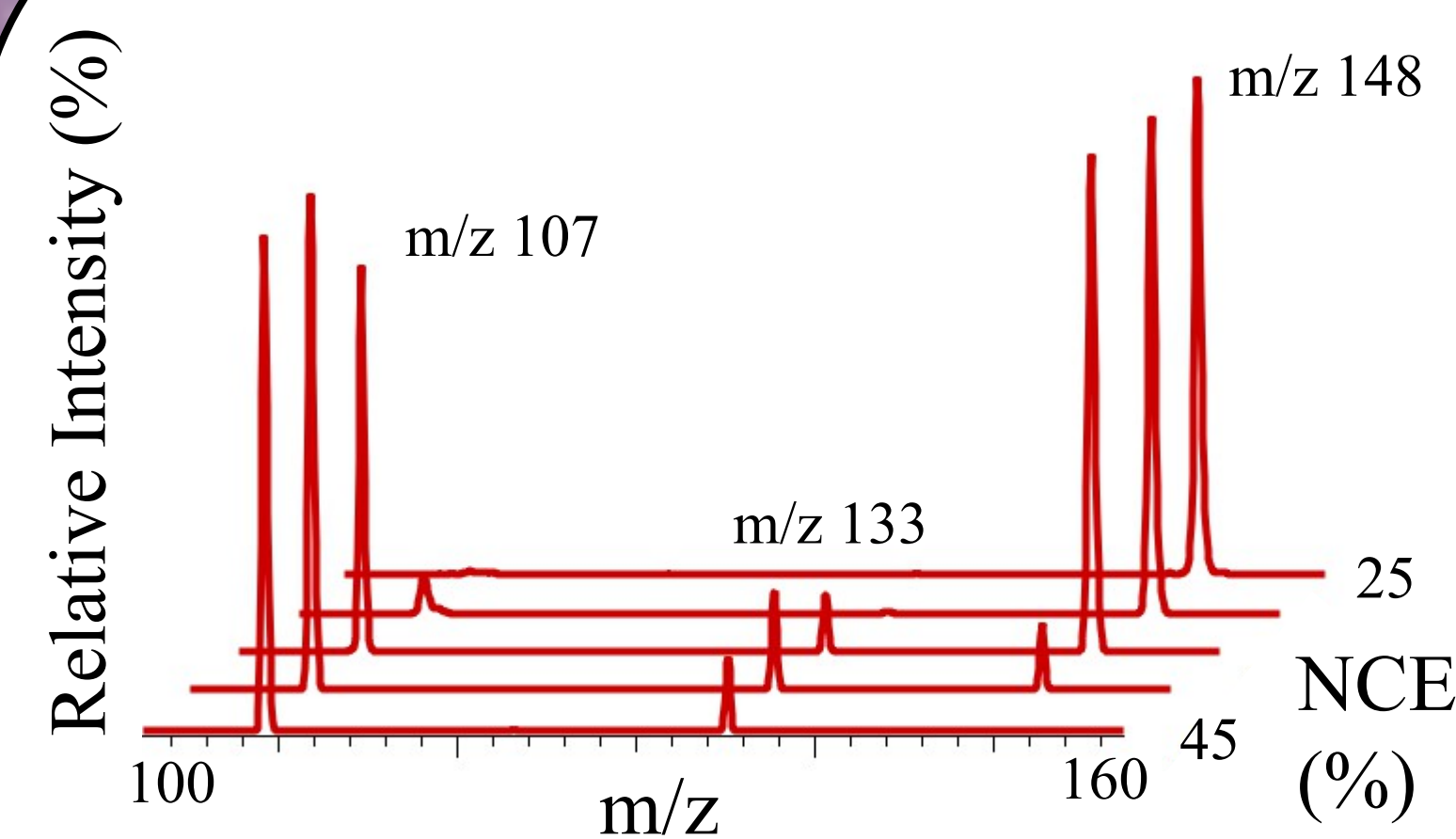
**Methods:** Electrospray ionization (ESI) was employed to create anions with a Thermo LCQ Deca XP Plus ion trap mass spectrometer for these experiments. The mechanisms and energetics of experimental observations are calculated using density functional theory (B3LYP/6-31+G(d,p)). These experiments and quantum chemical calculations provide relevant insights into the synthesis and destruction of amino-substituted purines in the ISM, contributing to the ongoing exploration of prebiotic molecules in extraterrestrial environments.



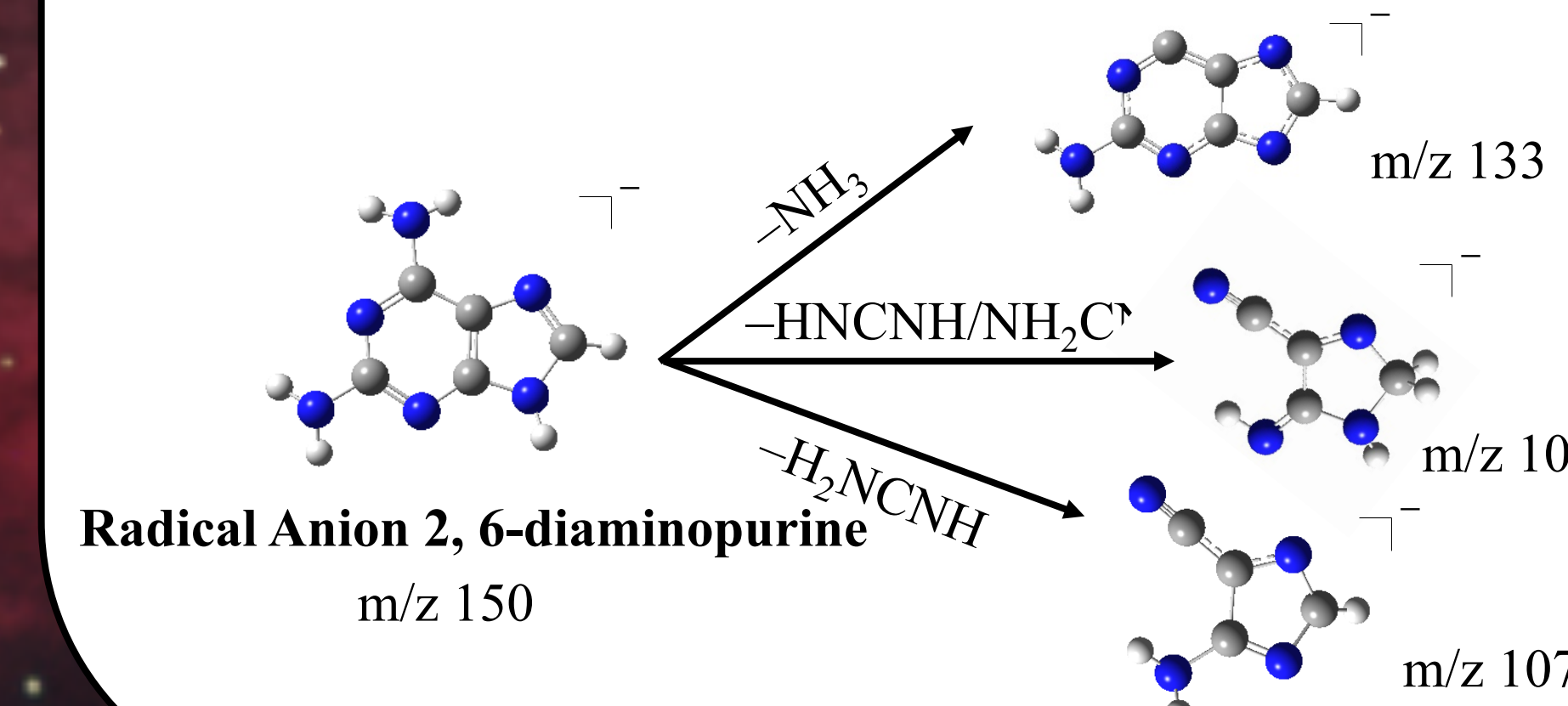
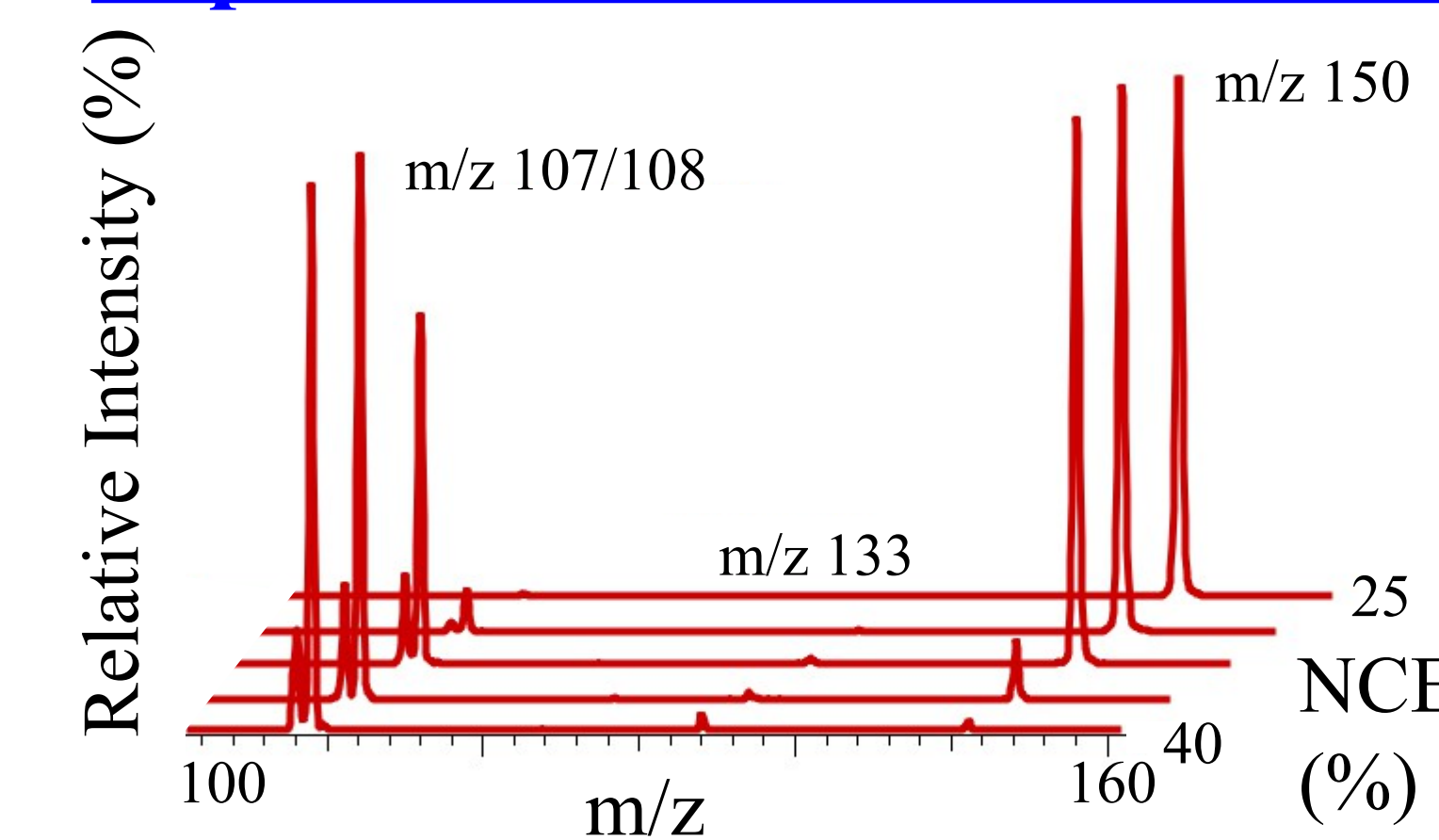
## Experimental: Adenine



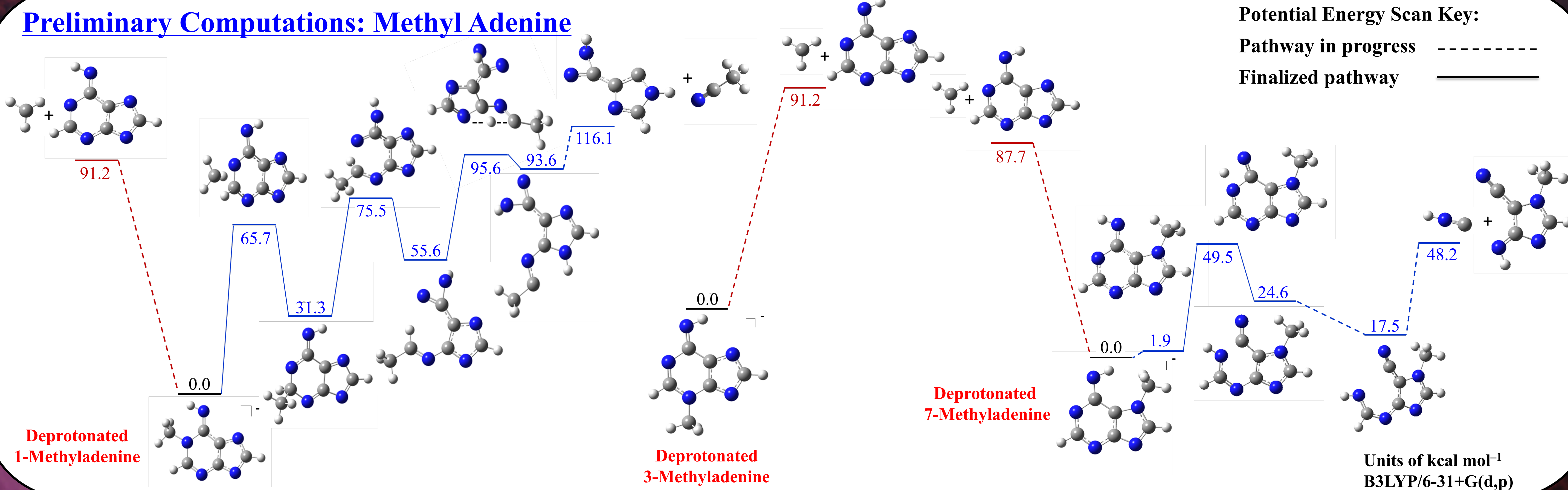
## Experimental: Methylated Adenine



## Experimental: Aminated Adenine



## Preliminary Computations: Methyl Adenine



## Conclusions

- The addition of an amino group on adenine stabilizes the most acidic proton and produces a radical anion in addition to the deprotonated species upon electrospray ionization.
- Both amino and methyl substituted adenine create a fragment similar to that of HCN/HNC loss on pure adenine with the exception of 3-methyladenine. This is likely due to methyl's behavior as an electron donor on N3.
- The energetics of HNC loss on 7-methyladenine are lower than that of the analogous loss of -CH<sub>3</sub>CN on 1-methyladenine, likely because the methyl stabilizes the 5 membered ring.
- CID experimentation reveals how the position of a methyl or amino group around adenine alters its fragmentation patterns.