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COMPREHENSIVE STUDY ON THE METASTABLE NEGATIVE ION FRAGMENTATION OF INDIVIDUAL DNA COMPONENTS AND LARGER OLIGONUCLEOTIDES

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Abstract. Here we present a systematic study on the unimolecular decay pathways of the deprotonated building blocks of DNA and RNA to address the following questions:

1. Are the negative ion fragmentation patterns observed in the metastable decay of individual DNA components still evident when these are combined to larger oligonucleotides?

2. What is the significance of the charge location in determining the fragmentation pathways in the metastable decay process?

3. Are those metastable decay channels relevant in dissociative electron attachment to DNA components?

To address these questions we have studied the fragmentation patterns of the deprotonated ribose and ribose 5'-monophosphate, the fragmentation patterns of the individual bases, all nucleosides and all 2'-deoxynucleosides as well as the individual nucleotides and several combinations of hexameric oligonucleotides. Furthermore, to understand the significance of the charge location in determining the fragmentation path in the metastable decay process of these deprotonated ions we have also studied modified uridine and guanosine. These have been modified to block different deprotonation sites and thus to control the initial step in the in the fragmentation process i.e. the site of deprotonation. In addition to our experimental approach we have also simulated the metastable fragmentation of the deprotonated uridine and 2'-deoxyguanosine to clarify the mechanisms and fragmentation patterns observed.

Where data is available, the results are compared to dissociative electron attachment to DNA components and discussed in context to the underlying mechanism. Experiments on modified nucleosides where selected deprotonation sites have been blocked are used to verify the predicted reaction paths and imulations on uridine and 2'-deoxyguanosine are compared to the experimental results and used to shed light on the mechanisms involved.