

Impulse driven fragmentation of biomolecules

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Synopsis We have studied collisions between biomolecular ions and He or Ne at center-of-mass energies around 100 eV. We find that impulse driven prompt atom knockouts is an important destruction mechanism.

Recent experimental and theoretical studies have shown that prompt knockouts of atoms in Rutherford-like scattering processes may be important steps in the fragmentation of complex molecular systems such as Polycyclic Aromatic Hydrocarbons (PAHs) [1, 2, 3, 4], hydrogenated PAHs [5, 6] and fullerenes [4]. It was then also found that knockout processes often lead to the formation of more reactive species [7] than thermally driven (statistical) fragmentation processes, and thus also to more efficient molecular growth processes in molecular clusters [1]. However, this type of fragmentation is difficult to observe directly in biomolecular systems as these systems and their sub-systems resulting from knockout or statistical fragmentation often have low dissociation energies. This means that the fingerprint of knockout, unlike in the cases of the PAHs, very often is washed out by subsequent fragmentation events for biomolecules.

Porphyrin molecules are important for many biological functions and for a range of applications [8]. Here, we will present results for collisions between Tetraphenylporphyrin (TPP) cations (see Fig. 1) and He or Ne in the 50-110 eV centre-of-mass energy range. For these experiments, we used the single pass collision set-up at the DESIREE facility [2, 4], at Stockholm University, Sweden. The interpretations of the experimental results are aided by Density Functional Theory (DFT) calculations of dissociation energies and classical Molecular Dynamics (MD) simulations of TPP+He/Ne collisions, yielding the minimum energies needed to remove a single C, N, or H atom from TPP, *i.e.* the displacement energies. We found that the probability to knockout one heavy atom from these molecules is high under the present experimental conditions, as was also the case in similar experiments on PAHs [2]. These similarities are related to the similarities in dissociation and displacement energies for porphyrins and PAHs [1, 9]. Although such direct identifications are much more difficult for more fragile biomolecules, knockout processes must still be important for these systems influencing the fragment distributions and secondary fragment reactivities.

To further investigate these intriguing issues, we have recently carried out pilot studies of impulse driven fragmentation of protonated and deprotonated DNA bases such as *e.g.* adenine (see Fig. 1). The results from these studies will be presented and discussed at the meeting in view of results from molecular structure calculations and molecular dynamics simulations.

We also plan to study the effect of embedding biomolecular ions in a cluster or solvent environment. The surrounding environment may then protect (highly reactive) knockout fragments from secondary fragmentation processes and thus favour intracuster molecular growth processes [1].

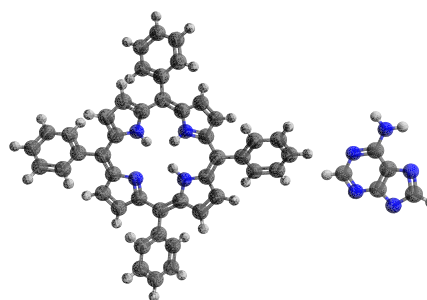


Figure 1. Molecular structures of protonated Tetraphenylporphyrin (left) and deprotonated Adenine (right).

References

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