

Radiation Induced Decomposition of Glycine

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Introduction

Radiation damage of glycine as a result of soft X-ray irradiation is studied using X-ray absorption spectroscopy (XAS) measurements and density functional theory calculations. The shape of the π^* region is radically altered upon irradiation, and clearly shows contributions from several distinct compounds. To elucidate the experimental structural breakdown, the absorption spectra of glycine in both neutral and zwitterionic forms were

simulated and compared to the calculated spectra of several deprotonated and fragmented models.

Science

The damage that occurs when amino acids are subjected to intense soft X-ray radiation is a matter of concern to both the medical and molecular spectroscopy communities. Understanding the mechanisms that lead to such damage is vital if methods to avoid or repair it are to be developed. There are many synchrotron-based techniques that use soft X-rays to determine structural, electronic and magnetic properties. However, biological molecules such as proteins and DNA are prone to radiation damage, and the effects on the obtained data cannot be neglected. Amino acids are the building blocks of proteins, and their simplicity and availability makes them ideal candidates to study the effects of radiation.

By measuring several consecutive XAS spectra, each delivering a radiation dose of approximately 200–400 Gy, on the same spot on the sample, the effects of an increasing radiation dose can be observed. The N 1s XAS were measured at the SGM beamline 11ID-1, and models of the glycine and possible products of the breakdown were calculated using the StoBe-deMon DFT software [1].

Discussion

There is a clear evolution of the N 1s XAS as a function of radiation dose, particularly in the π^* region of the spectra. Surprisingly, the most significant changes are seen when the exposure time is relatively low, between the first and second spectra. This dramatic change is clearly visible in Figure 1a. The glycine N 1s XAS spectrum should not exhibit any π^* features in the 400–403 eV range due to the absence of any N double bonding or peptide bonding.

In order to better investigate the early stages of the damage processes, a second set of scans was performed over a smaller

window, encompassing only the π^* region from 398–404 eV, and these scans are shown in Figure 1b. It is clear from the changes in the peak ratios that there are time- or dose-dependent factors in the radiation damage process, and that several product molecules are involved.

Comparison of the measured N 1s XAS data to the spectra simulated using StoBe-deMon allows the peaks in the data to be assigned with some degree of confidence. The complexity of the leading edge (405–407 eV) of the first measured spectrum suggests that the initial state of the glycine sample was of mixed zwitterionic and neutral character. The surface-sensitivity of TEY suggests that the neutral glycine may represent a surface impurity in the expected zwitterionic ground state.

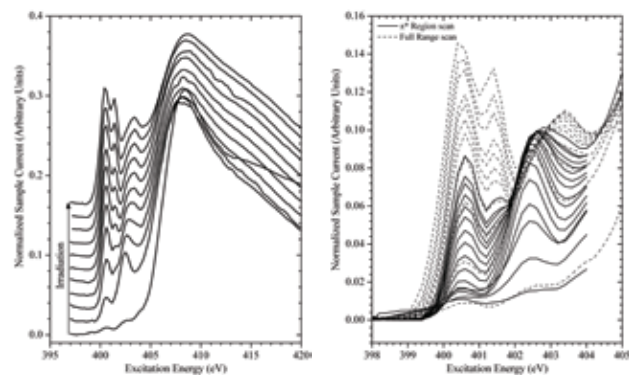


Figure 1. The full-range (a) and π^* only (b) N 1s XAS spectra of glycine, showing the effects of radiation damage that occur over a series of consecutive measurements.

The lowest-energy peak (400.5 eV) corresponds well in energy to the calculated peak for NH_3^+ . The next major feature, at 401.3 eV, is associated with a singly-protonated nitrogen site, likely HNCHCOOH , which could be produced by the decomposition of $\text{H}_2\text{NCHCOOH}$. This radical species ($\text{H}_2\text{NCHCOOH}$) is one of the expected products of glycine decomposition, [2,3] and its presence is clearly suggested by our study. The simulation of the spectrum of $\text{H}_2\text{NCHCOOH}$ produces a resonant absorption peak at 402.4 eV, the same location as the third lowest peak seen in the early-stage measured spectra. In Figure 2 this peak appears to migrate to higher energy as a function of time, finally appearing at an equilibrium position of 403.4 eV. This migration is an illusion, however, as close examination of the spectra show that it is in fact caused by the emergence of a competing, higher-energy peak. This peak can be attributed to $\text{H}_2\text{NCH}^{2+}$. The timing of its appearance suggests that it is not a direct product of the radiation-induced breakdown of glycine, but rather it is the result of the breakdown of radical species produced in this process.

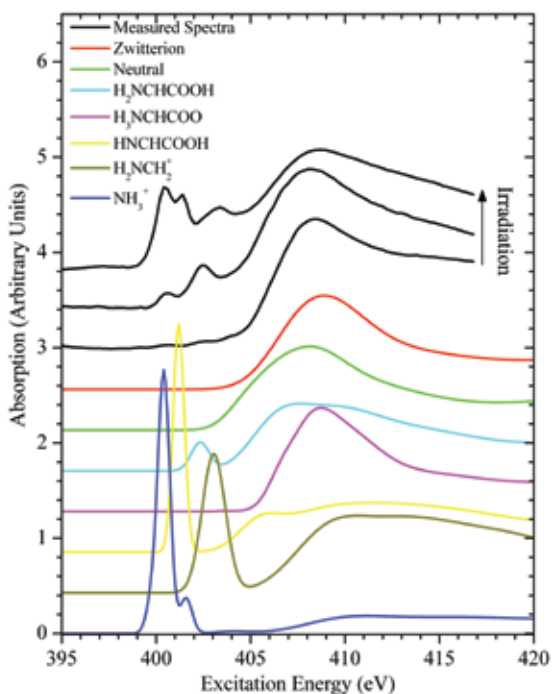


Figure 2. StoBe-deMon DFT simulations of glycine and the proposed products of the radiation-induced breakdown.

Conclusion

The results of the current study are in agreement with previous studies of radical species in glycine induced by X-ray irradiation. The glycine is largely zwitterionic at the outset of the experiment, with some neutral glycine mixed in. Soft X-ray irradiation causes deprotonation of the α -carbon almost immediately, leading to the production of $\text{H}_2\text{NCHCOOH}$ and H_3NCHCOO radicals. Other products that appear upon further irradiation are NH_3^+ , HNCHCOOH , CH_2COO^- , and H_2NCH_2^+ ; these molecules are the more prevalent products of the radiation-induced decomposition of glycine.

References

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Acknowledgements

Funding from NSERC and the Canada Research Chair Program is gratefully acknowledged.