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Valence Photoionization of Thymine: Threshold Photoelectron Spectrum and Dissociative Photoionization studied with Photoelectron Photoion Coincidence (PEPICO) Spectroscopy

The radiation that enlightens complex structures also causes sample damage. Interestingly, DNA has been found to be relatively resistant to such damage. However, understanding the mechanism of radiation damage may help in lifting the sample damage limitations of crystallographic methods.
Besides the mutagenic and carcinogenic effects of photoinduced structural changes to DNA bases, their photophysical and –chemical properties are of interest to understand the molecular origins of life. The presence of purines and pyrimidines in Comet Halley suggests that these molecules were transported to Earth by cometary dust. The study of VUV radiation effects on DNA bases may thus shed light on their possible genesis and survival under extreme conditions.

We examined the valence photoionization of thymine (T) using synchrotron VUV radiation and imaging PEPICO spectroscopy after aerosol flash vaporization or bulk evaporation. The vaporization techniques were compared based on the photoelectron spectrum and the breakdown diagram (BD). We could confirm that aerosol vaporization is the milder approach but the difference in the rotational temperature of the gaseous T samples was smaller than expected at 38 ± 4 K.
The adiabatic ionization energies for the first four electronic states were found to be 8.922 ± 0.008, 9.851 ± 0.008, 10.30 ± 0.02 and 10.82 ± 0.01 eV. Vibrational features, including fundamentals, overtones and combination bands, have been assigned for the first three electronic states with the help of Franck–Condon factor calculations. The BD of T, as supported by composite method ab initio calculations, suggests that the main fragment ions are formed in sequential HNCO-, CO-, and H-loss dissociation steps from the T+ parent ion. The experimental rate curve and the breakdown curves were fitted using a statistical model to determine 0 K appearance energies of 11.15 ± 0.16, 11.95 ± 0.09, and 13.24 eV for the m/z 83, 55, and 54 fragment ions, respectively. The results allowed us to revise previously proposed fragmentation mechanisms and to account for the final, non-statistical H-loss step in the breakdown diagram, yielding the m/z 54 fragment ion.

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