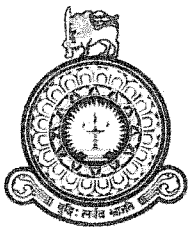

Theoretical Investigation of Ionization Energies of Polyaromatic Hydrocarbons (PAHs)

A thesis submitted to the Faculty of Science,
University of Colombo
for the Degree of M.Sc. in Analytical Chemistry

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September 2010

ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are fused ring aromatic hydrocarbons which are distributed among all the phases of the environment contributing to the environmental pollution. PAHs in the atmosphere are susceptible for photoionization which is the crucial step in photodegradation of PAHs after the absorption of radiation. Therefore, the ionization energy (IE) of PAH species is regarded as the stability index of PAH in the atmosphere. The experimental determination of ionization energies is expensive, time consuming, and requires sophisticated instrumentation. With the advancement of computer technology and the introduction of various computational chemistry software, computational calculation of physical properties of chemical species (i.e., ionization energy) is becoming more and more accurate and straight forward. Therefore these calculated properties are now more representative to experimentally determined properties. The ionization energies of selected PAH species are calculated using Gaussian computational software package. The suitable level of theory for the calculation is selected after performing geometry optimization and energy calculation at HF, B3LYP, and MP2 level of theories for benzene, anthracene, acenaphthylene, and naphthalene. The B3LYP level of theory is selected for the calculations of higher order PAHs after comparing calculated results with available experimental results. The geometry optimization is performed using B3LYP 6-31G* level of theory and the energy calculations were performed using B3LYP 6-311+G(2d,2p) level of theory. The calculations indicate the systematic decrease of ionization energies with the increasing size of the PAH molecule. Calculations also suggest that ionization energy values obtained for smaller (less than four rings) PAH molecules in agreement with the experimental results. However for higher order PAHs, systematic deviation of IE values from the experimentally determined values was found. This suggests that higher order PAH molecules requires factoring of IE values in order to be more representative to experimental IE values. It is also found that the IEs for linear PAHs may unusually low compared to their nonlinear counterparts.