Vibration Frequencies Shifts of Naphthalene and Anthracene as Caused by Different Molecular Charges

Hassan H. Abdullah, Rehab M. Kubba, and Muthana Shanshal

Department of Chemistry, College of Science, University of Baghdad, Jadiriya, Baghdad, Iraq

Reprint requests to Prof. M. S.; Fax: 009 641-7763 592

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Semi-empirical SCF-MO calculations were carried out for the naphthalene and anthracene radical cations and anions. For all ions D_{2h} symmetry was obtained. All 3N-6 vibration frequencies for all species were calculated and assigned, applying the Herzberg convention. The valence assignment of the vibration modes was possible applying graphical pictures of each mode and the so called atomic partial participation (APP) values. Interesting relations between the frequencies of the ions were obtained, e. g. for the radical cation of naphthalene $\nu_{sym}(CH_\beta\ str.)^{\cdot+} > \nu_{asym}(CH_\beta\ str.)^{\cdot+} > \nu_{sym}(CH_\alpha\ str.)^{\cdot+} > \nu_{asym}(CH_\alpha\ str.)^{\cdot+}$, and for its anion $\nu_{sym}(CH_\alpha\ str.)^{\cdot-} > \nu_{asym}(CH_\alpha\ str.)^{\cdot-} > \nu_{sym}(CH_\beta\ str.)^{\cdot-} > \nu_{asym}(CH_\beta\ str.)^{\cdot-}$, as well as for both ions ν_{sym} ring (C_β-C_β) str. > ν_{asym} ring C_α-C_β) str. > ν_{sym} ring (C_9-C_{10}) str. Similar correlations were detected for the anthracene ions. Interionic correlations could be observed for the frequencies of similar modes for the ions and neutral molecules, e. g. for naphthalene $\nu_{sym}(CH_\beta\ str.)^{\cdot+} > \nu_{sym}(CH_\beta\ str.) > \nu_{sym}\ (CH_\beta\ str.)^{\cdot-}$ and $\nu_{sym}(CH_\alpha\ str.)^{\cdot+} > \nu_{sym}(CH_\alpha\ str.) > \nu_{sym}(CH_\alpha\ str.)^{\cdot-}$. Generally the calculated frequencies for the radical anions were nearer to those of the neutral molecule than those of the radical cations.

Key words: Vibration Frequencies; Naphthalene; Anthracene; Ions.