Abstract Submitted
for the MAR12 Meeting of
The American Physical Society

Effects of Symmetry on Intense-field Ionization of Heterocyclic Organic Molecules[1]

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— We report on the ultrafast photoionization of pyridine, pyridazine, pyrimidine and pyrazine. These four molecules represent a systematic series of perturbations into the structure of a benzene ring which explores the substitution of a C-H entity with a nitrogen atom, creating a heterocyclic structure which remains isoelectronic with benzene. Other than pyridine, each molecule has the same molecular formula, with the only difference being the placement of the perturbing nitrogen atoms (ortho-, meta- or para-substitutions). Differences in the intense-field behavior of these molecules are caused by the symmetry of the perturbation to the benzene system, primarily influenced through the interactions of lone-pair states surrounding the nitrogen atoms. Data is recorded under intense-field, single-molecule conditions. 50 fs, 800 nm pulses are focused into the molecular vapor, and ion mass spectra are recorded for intensities of $\sim 10^{13}$ W/cm^2 to $\sim 10^{15}$ W/cm^2. We measure ion yields in the absence of the focal volume effect without the need for deconvolution of the data. For all targets, stable singly- and doubly-charged parent ions ($C_{6-n}H_{6-n}N_n^{+(+)}$) are observed with features suggesting resonance enhancement (REMPI).

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[1] This material is based upon work supported by the National Science Foundation under Grant Nos. PHY-0855675 and PHY-1005071.

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Date submitted: 10 Nov 2011 Electronic form version 1.4