

Fragmentation of Aromatic Heterocycles Following Resonant Core Excitation

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The C 1s resonant excitation spectrum of benzene (C₆H₆) is dominated by the C 1s → π* resonance, which exhibits vibrational structure when observed with sufficient resolution. Substitution of benzene at a single carbon centre, e.g., by replacement of CH with N to give pyridine (C₅H₅N), lowers the symmetry of the molecule from D_{6h} to C_{2v}, creating three types of chemically inequivalent carbon centres in the aromatic ring and splitting the degenerate e_{2u} (π*) unoccupied molecular orbitals of benzene into separate b₁ and a₂ (π*) orbitals. For pyridine, the C 1s ionisation threshold splittings are 0.4 eV and the b₁/a₂ splitting is 0.5 eV. An analogous splitting occurs in five-membered cyclic aromatics upon hetero atom substitution of the D_{6h} symmetry cyclopentadienyl to give, e.g., pyrrole (C₄H₄NH) or thiophene (C₄H₄S), each having two pairs of inequivalent carbon centres and again unoccupied π* orbitals of b₁ and a₂ symmetry.

The core excitation spectroscopy and subsequent ionic fragmentation of benzene and several aromatic heterocycles (pyridine, pyrrole, 1-methylpyrrole, thiophene) have been studied in the vicinity of the C 1s and N 1s edges using monochromatic synchrotron radiation and time-of-flight mass spectrometry. For each of the heterocycles studied, one or both of the C 1s core hole and π* splittings are sufficiently large to allow selective excitation either from a specific carbon centre or to a specific valence orbital.

Resonant excitation to vibrationally resolved core excited states was also investigated. In all cases, no dramatic site specific, electronic state specific, or vibrational state specific fragmentation pathways were observed for C 1s → π* excitation. In each molecule studied, enhancements in the parent ion yield were observed with core excitation to valence states but not upon excitation to Rydberg or continuum states, suggesting that participator Auger decay is a significant relaxation channel in the core → valence excited states of cyclic aromatic molecules. The obtained core excitation spectra and fragment ion yield spectra will be presented and contrasted.

The effect of the heteroatom on the electronic structure of the aromatic ring and on the ionic fragmentation processes occurring in these molecules will be discussed.