The inner shell excitation spectroscopy and subsequent photofragmentation of a number of aromatic molecules and their aliphatic analogues have been studied with vibrational resolution using synchrotron radiation and ion time-of-flight mass spectrometry. At the carbon edge, the excitation spectra of the aromatic molecules are dominated by the intense C 1s→π* bands, that exhibit complex structure arising from partially resolved vibrational excitations and, in the case of heteronuclear aromatic molecules such as pyridine, splitting both of the valence π* orbitals and of the C 1s inner shell orbitals of the inequivalent carbon centres. These excitations are of interest because of the contrast between the highly localised nature of the inner shell orbitals and the extensively delocalised π* orbitals. As a result of this contrast, inner shell excitation provides a probe of the character of the π* orbitals, information essential to an understanding of the chemical reactivity of aromatic molecules. Invariably, the core-excited state is short lived: electronic relaxation typically results in multiple ionisation and molecular fragmentation. The dependence of the ionic fragmentation processes on the site of inner-shell excitation and on the extent of vibrational excitation has been investigated by selective inner-shell excitation. The fragmentation pathways are found to be dictated by the delocalised nature of the π* orbitals rather than by the localised C 1s orbitals, such that the photoionisation branching ratios are invariant for promotion of an electron to the same π* orbital from C 1s orbitals of inequivalent carbon centres.

Details of the dynamics of the molecular fragmentation have been determined by coincident detection of multiple fragment ions. The relationship between aromaticity and the extent of selective fragmentation is determined by comparison of ionic fragmentation data of aromatic molecules (thiophene, 1-methylpyrrole) and aliphatic analogues (tetrahydrothiophene, 1-methylpyrrolidine). Furthermore, the C 1s spectroscopy of diphenylpropane has been investigated and compared with that of toluene and ethylbenzene to determine the extent of intramolecular π-π stacking interactions in diphenylpropane and the effect of such interactions upon the valence electronic structure.