High-Resolution Inner-Shell Studies of Free Radicals and Transient Species

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Third generation SR undulator beam lines allow low density and highly reactive species to be studied in the gas phase using high photon energy resolution. Core-excited states in the OH and OD free radicals and the CS transient molecule have been investigated for the first time. In the case of the lowest O 1s excited state ($^2\Sigma^+$) of OH and OD, vibronic components have been clearly observed in the total-ion-yield spectra using time-of-flight mass spectrometry. Relative transition probabilities, excitation energies, and core-hole lifetimes have been measured accurately for the vibronic components of this state. Excited states at higher energies have been also observed. The free radicals have been produced in situ by the fast atom-molecule reaction H (D) + $NO_2 \rightarrow$ OH (OD) + NO using a microwave technique to generate the H atom. In the case of CS, C 1s and S 2p excited states have been observed. Some of them display a resolved vibrational progression. As for the S 2p excited states, the extent of the vibrational progression, and therefore the change in molecular geometry, varies largely depending on the specific resonant state. Spin-orbit and molecular field splitting effects in S 2p excitation processes are observed for the first time in a diatomic molecule. The CS transient species has been produced in situ using the CS_2 precursor and the same microwave technique. Core-excited states of transient and radical species are often observed as "intermediate fragments" in studies of ultra-fast dissociation processes of core-excited molecules. Our experiments provide, for the first time, a direct information on the inner-shell spectroscopy of those fragments.