N_{2} Valence Photoionisation in the Presence of a Core Hole

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The strong enhancement of molecular valence lines on the inner shell resonant excitations to discrete anti-bonding orbitals opens up the question, whether inner shell continuum (shape) resonances have an influence on valence photoionisation as well. To contribute to that question we have recorded photoelectron spectra of the valence lines of N₂ from far below the N 1s- π^* resonance to deep into the 1s ionization continuum. While we find some enhancement of the A ($1\pi_u$ ⁻¹) state on the σ_u shape resonance the strong coupling of the B ($2\sigma_u$ ⁻¹) state to it, which was seen in earlier fluorescence work, cannot be observed to that extent. From our measurements we can also extract the Fano parameters of the valence single hole states on the 1s- π^* resonance.

Our photoelectron work is compared with wavelength dispersed fluorescence yield spectra of the B-X final state decays. We can show, that on the shape resonance an indirect mechanism leads to an enhancement of the fluorescence yield, which has no counterpart in the photoelectron spectrum. Possible candidates for this mechanism are fluorescence cascade decays, either by K-V X-ray photons or after spectator decay of neutral doubly excited states.