DISCRETE-CONTINUUM INTERACTIONS AND LINESHAPES IN THE AUTOIONIZATION SPECTRA OF BH

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The appearance of Rydberg spectra provides detailed information describing short range electron-core scattering dynamics in both atomic and molecular systems. We have applied three photon triple resonant ionization-detected absorption spectroscopy to probe rotationally resolved autoionizing Rydberg structure in the BH molecule converging to $X^2\Sigma^+$ BH^+ (ν^+ = 1 - 4). Third photon transitions originating from photoselcted levels of the $B^1\Sigma^+$ state excite autoionizing Rydberg states in $\Delta\nu = 0$ and $\Delta\nu = 1$ processes. Spectra exhibit discrete to discrete and discrete to continuum features, with transition intensities governed by Franck-Condon factors and continuum-discrete mixing of states. The spectra show asymmetric line profiles attributable to the phase interference between transition moments associated with competing ionization pathways. Lineshapes can be described using the Fano resonance formula. The two fitting parameters, q and Γ characterizing spectral lineshapes, model the photoionization cross section resulting from the interaction between a single discrete state and single continuum. Quantitative analysis of these parameters provides information about the continuum-discrete coupling of states and distribution of lifetimes in vibrational levels of BH. These insights together with the precise pattern of high-Rydberg states observed, probe differences between intermolecular electronic potentials.

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