Rotationally resolved high (n>100) Rydberg states in a polyatomic molecule

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High electronic valence states and low Rydberg states ($n < 5$) in molecules display very short lifetimes due to fast nonradiative relaxation processes. Typical time constants in these energy regions are found to be in the sub-picosecond range.
At very high excitation energies, close to the ionization continuum, however, electronic states resembling the Rydberg states of hydrogen are expected. They consist of electronic states with a single electron excited into a quasi classical orbit around the positively charged molecular core with high Rydberg quantum number n. These Rydberg states are long-lived due to their weaker interaction with the molecular core. In polyatomic molecules the energetic separation of neighbored high n Rydberg states with Energy E_n (s. eq.(**??**) becomes comparable or smaller than the spacing of vibrational or even rotational levels of the molecular core.
(In eq. (**??**) $R_{benzene}$ denotes the mass corrected Rydberg constant, $\mu(l)$ the quantum defect that is dependent on the angular momentum quantum number l of the electron, IE ionization energy and E_n the energy of the nth Rydberg state)

$$E_n = IE - \frac{R_{Benzene}}{(n - \mu(l))^2} \tag{1}$$

Using sub-Doppler double resonance excitation combined with pulsed field ionization techniques we were able to resolve *individual* high n Rydberg states in this interesting energetic region in a polyatomic molecule for the first time. It is shown that for a selected J_K intermediate rovibrational state in benzene, C_6D_6, several Rydberg series up to n>100 with nearly vanishing quantum defect are observed converging to different limits. The intensity of these series in the pulsed field ionization experiments depends strongly on applied electric fields in the range from 20 to 200 mV/cm. The pulsed field ionization signal has a "decay time" in the microsecond range which is longer than expected from extrapolations of measured lifetimes of low Rydberg states of benzene and is ascribed to l-mixing in the applied electric fields.