WHERE ATOMIC SPECTRA ARE DENSE AND COMPLEX: MILLIMETER WAVE SPECTROSCOPY AND MQDT ANALYSIS OF HIGH RYDBERG STATES OF XENON

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In the range 0–45 cm^{-1} below the ionization limit, the separation between adjacent electronic states Rydberg states (with principal quantum number $n > 50$) of atoms and molecules is smaller than 2 cm^{-1}. In order to resolve the fine or hyperfine structure of these states, very high resolution is needed. For most atoms and molecules, however, the direct access to Rydberg states from the ground state requires light in the UV or VUV range, and the spectral resolution is limited by the spectral bandwidth of the laser and the Doppler broadening. A significantly higher resolution can be obtained by combining a high-resolution laser system with millimeter wave radiation.[a] Such double-resonance experiments have been used to study the hyperfine structure of high Rydberg states of ^{83}Kr [b] or H_2 [c].

A phase-stabilized backward wave oscillator (BWO) tunable in the 240–360 GHz frequency range was combined with a UV laser system to record high-resolution spectra of high-n Rydberg states of xenon. The millimeter wave transitions at sub-MHz resolution between *n*s/*n*d and *n*p/*n*f Rydberg states of the isotopes ^{129}Xe, ^{131}Xe, and ^{132}Xe were detected by pulsed field ionization followed by mass-selective detection of the cations.

A multichannel quantum defect theory (MQDT) treatment of the hyperfine structure[d] was used to analyze the millimeter wave data in combination with the available data from the literature in order to obtain improved MQDT parameters and to determine the hyperfine structures of the $^2P_{3/2}$ ground electronic states of $^{129}Xe^+$ and $^{131}Xe^+$.

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