WHERE MILLIMETER WAVE SPECTRA ARE SENSITIVE TO SMALL ELECTRIC FIELDS: HIGH RYDBERG STATES OF XENON AND THEIR HYPERFINE STRUCTURES

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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, it is necessary to combine high-resolution vacuum ultraviolet (VUV) laser radiation, which is required to access the Rydberg states from the ground state, 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], H_2 [c], or D_2 [d].

Millimeter wave transitions (240–350 GHz) between $n\ell$ ($52 \leq n \leq 64, \ell \leq 3$) Rydberg states of different xenon isotopes were detected by pulsed field ionization followed by mass-selective detection of the cations. Because of the high polarizability of high-n Rydberg states ($\propto n^7$, $\sim 10^4$ MHz cm^2 V^{-2} for $n \approx 50$), it is necessary to reduce the electric stray fields to values of the order of mV/cm (or less) in order to minimize the (quadratic) Stark shift of the millimeter wave transitions. Some p and d Rydberg states of Xe are nearly degenerate and efficiently mixed by small stray fields, making it possible to observe transitions forbidden by the $\Delta\ell = \pm 1$ selection rule or transitions exhibiting a linear Stark effect, which is typical for the degenerate high-ℓ Rydberg states.

Multichannel quantum defect theory (MQDT) was used to analyze the millimeter wave data and to determine the hyperfine structures of the $^2P_{3/2}$ ground electronic states of $^{129}Xe^+$ and $^{131}Xe^+$.

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