CP-FTMMW SPECTROSCOPY OF HIGH-ℓ RYDBERG STATES OF NO

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Since the pioneering work of Miescher in the 1960s, the Rydberg states of nitric oxide have held the attention of spectroscopists due to the prototypical energy level structure and rich non-radiative dynamics, which have, in turn, confirmed and challenged existing theory. This work describes a new approach to investigate the relatively underexplored regime of high orbital angular momentum (ℓ) Rydberg states via chirped-pulse Fourier transform millimeter-wave (CP-FTmmW) spectroscopy. We have prepared high-n (n $\geq$ 27), high-ℓ ($\ell \geq 4$) Rydberg states of NO by a triple resonance laser excitation through the low-lying 4f state, followed by mmW excitation. The mmW field polarizes Rydberg-Rydberg transitions within the bandwidth of our spectrometer (220-330 GHz) and the free induction decay is phase-coherently detected and digitized on a fast oscilloscope. The observed transitions are interpreted in the framework of a long-range electrostatic model for the Rydberg energy level structure, resulting in improved determination of the electric structure (multipole moments, polarizability) of the NO^+ ion-core. In addition, we will discuss the role of electric fields, hyperfine structure, and non-radiative decay mechanisms – predissociation and autoionization – on the observed mmW spectra.