Appendix B

Rydberg wavepackets in Krypton

While looking for a 3+1' multiphoton photoelectron signature in Kr using ultrafast 266 nm and 800 nm pulses, we inadvertently stumbled across a long lived signal coming from a Rydberg wavepacket excitation. The energy level diagram of Kr is shown in Fig. B.1. Three photons of 266 nm light (black arrows) possess an energy which is slightly below the ionization threshold of Kr, with enough bandwidth to excite a large number of Rydberg levels. At t = 0, when the two pulses overlap, photoelectron signals are observed from a 3+1' (1), 3+2' (2), and 3+3' (3) (overlapped with a 4 photon signal from the 267 only) multiphoton ionization, (where the gray arrows represent the 800 nm photons in Fig. B.1). At long times, however, these photoelectron signals persist at a reduced count rate. An example of the photoelectron spectrum at long time delays ($\sim$500 fs) is given in Fig. B.2. The labels (1), (2) and (3) relate the photoelectron peaks in Fig. B.2 to the photon process in Fig. B.1. There are 3 sets of doublet peaks separated by $\sim$1.5 eV (the energy of an 800 nm photon). Each doublet represents the spin orbit splitting in the Kr^+ ion. The doublet labeled (1) results from ionization of the Rydberg wavepacket with one 800 nm photon. The second doublet peaks (labeled (2)) are photoelectrons from ionization of the Rydberg wavepacket with 2 photons of 800 nm. The photoelectron peaks labeled (3) do not change with pump-probe delay and are attributed to a 4-photon ionization of Kr with the 266 nm laser.

Taking the total photoelectron counts in the peak at 0.8 eV (leaving the Kr^+ ion in the high energy spin orbit state) from Fig. B.2 and plotting this versus pump-probe delay gives the

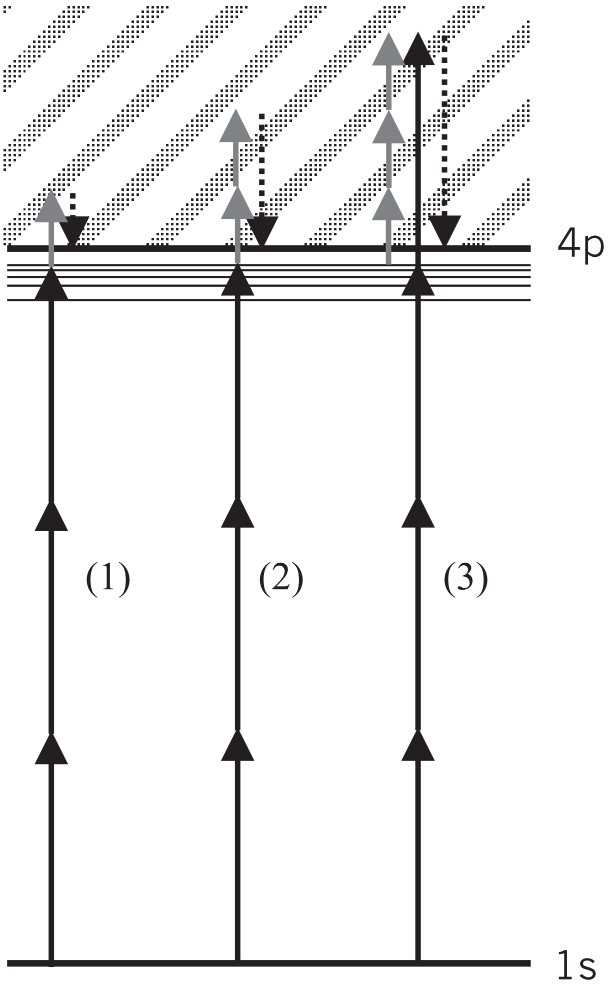

Figure B.1: An energy level diagram showing the excitation of a Rydberg wavepacket in Kr by a 3-photon absorption of 266 nm (black arrows). When an 800 nm pulse (gray arrow) is introduced, the Kr is ionized by a 1, 2, or 3 photon addition of the 800 nm photon. Note that the ionization of Kr with 4 photons of 266 nm is identical in energy to the 3+3’ multiphoton ionization at t = 0.

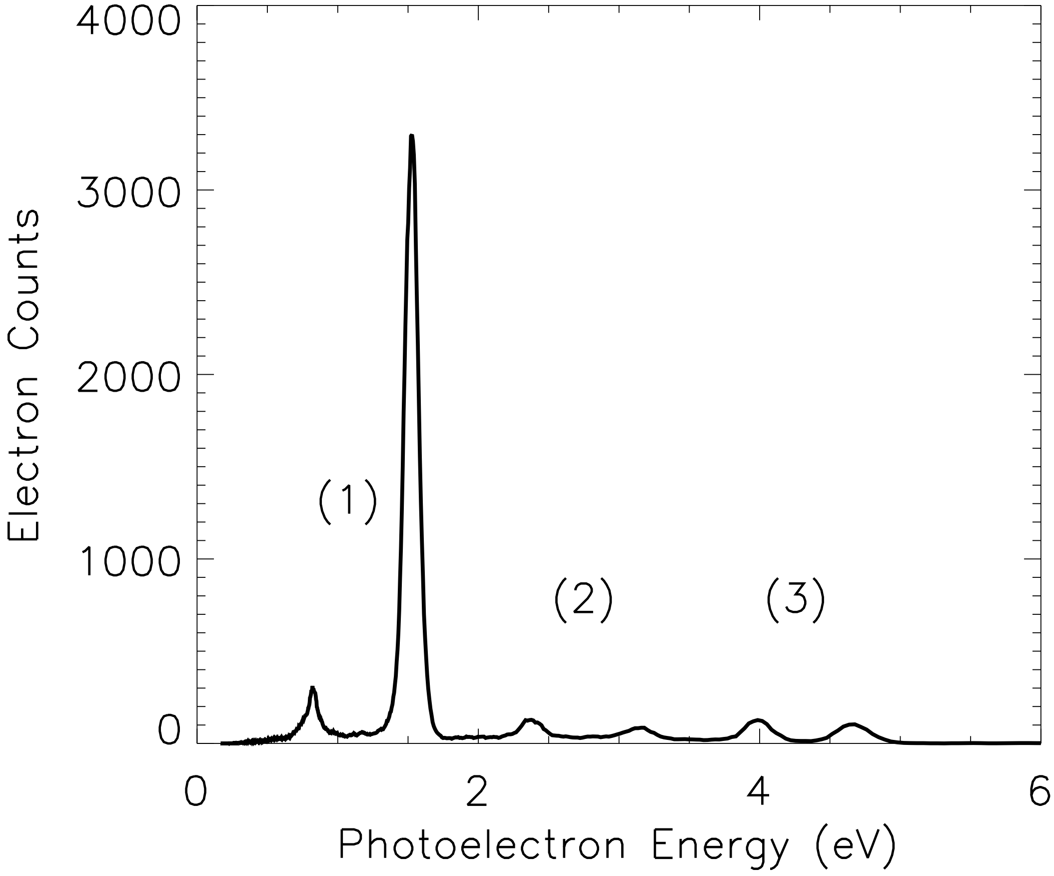

Figure B.2: Photoelectron spectrum of Kr with a time delay between the 267 nm pulse and the 800 nm pulse of 500 fs.

black curve in Fig. B.3. A fast oscillatory structure with a period of $\sim$60 fs is observed on top of a slower oscillation of about 2 ps. The peak at 1.5 eV (leaving the Kr^+ ion in the low energy spin orbit state) in Fig. B.2 shows primarily the slow 2 ps oscillation (shown as the dark gray line in Fig. B.3). When the black time trace is normalized to the dark gray time trace (effectively taking out the slow 2 ps oscillation), the light gray time trace results, showing only the fast oscillatory structure.

The energy/pulse of the 266 nm beam remained constant at $\sim$60 μJ, but the 800 nm beam was varied in an attempt to understand the oscillatory structure of the photoelectron signals. In Fig. B.3, the 800 nm power was held at 1.4 mJ/pulse. Fig. B.4, however, shows the same time traces as in Fig. B.3, but with the 800 nm beam reduced to 200 μJ/pulse by reducing the first iris inside the chamber (effectively blocking 85% of the beam). The difference between the time-correlation of the two photoelectron peaks (leaving the ion in two different spin-orbit states) is unclear, unless some coupling between spin orbit energy levels and the Rydberg energy levels exists. However, it is still the same 800 nm photon which ionizes the Rydberg wavepacket, and it would seem unlikely that the spin orbit states of the ion would yield different signals.

The Rydberg progressions leading up to the ionization threshold in Kr are given in Fig. B.5, calculated from Charlotte Moore's Rydberg equations. The probability of ionizing a Rydberg wavepacket is greater when the electron is near the nucleus, which is likely the cause of the fast oscillatory structure of the photoelectron signal. The period of the fast oscillation (60 fs or 555 cm^{-1}) could be due to a beating between two Rydberg energy levels. In other words, both energy levels are excited by the bandwidth of the laser and the frequency of recurrence of the wavepacket then becomes the difference in energy between these two states. The energy difference between the ns = 10 and 11 calculated Rydberg levels is 545 cm^{-1}, which is likely well within the error of the experimental measurement (perhaps properly fitting the data with a sin wave would give a more accurate number for the oscillation period with uncertainties, a Fourier transform of the data was attempted, but there are not enough points for a good result). The slow oscillatory structure is more puzzling. In the field of a high peak power laser, the Rydberg levels

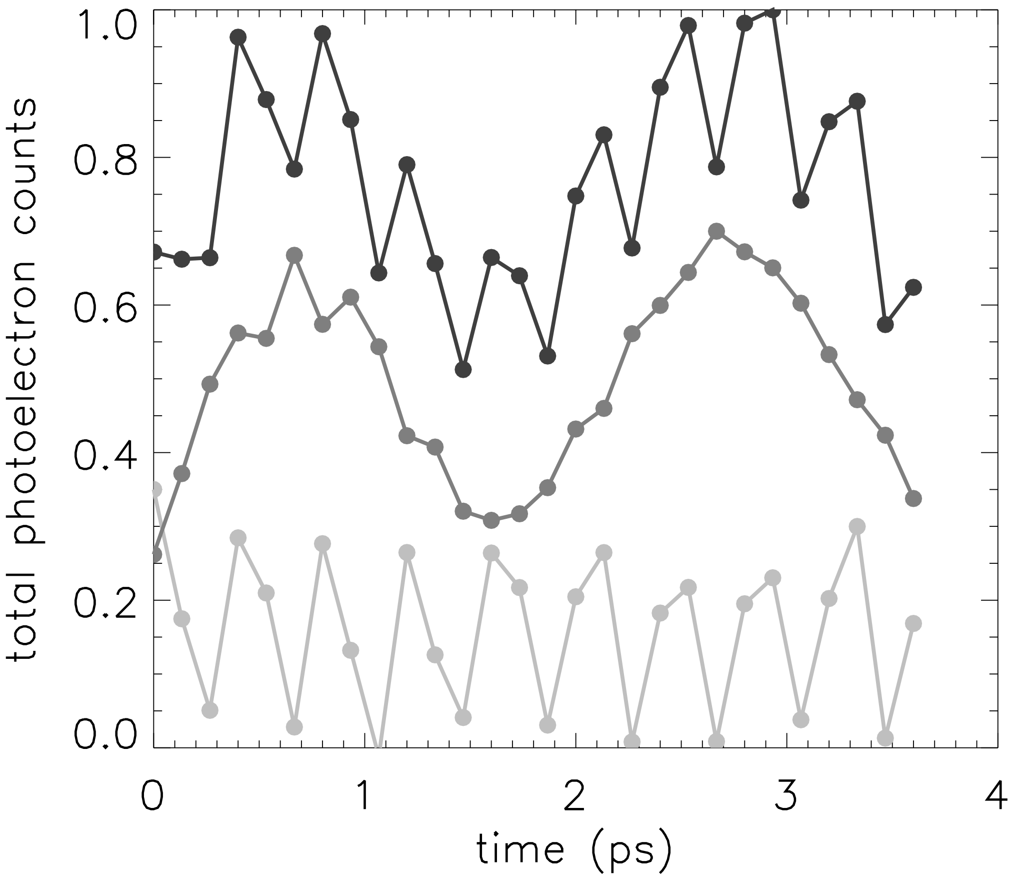

Figure B.3: Time traces of the photoelectron signal resulting from the ionization of a Rydberg wavepacket in Kr. The black trace represents the total counts in the photoelectron peak at 0.8 eV, and the dark gray from the photoelectron peak at 1.5 eV in Fig B.2. The light gray line is the black trace normalized to the dark gray trace, showing the fast oscillatory structure.

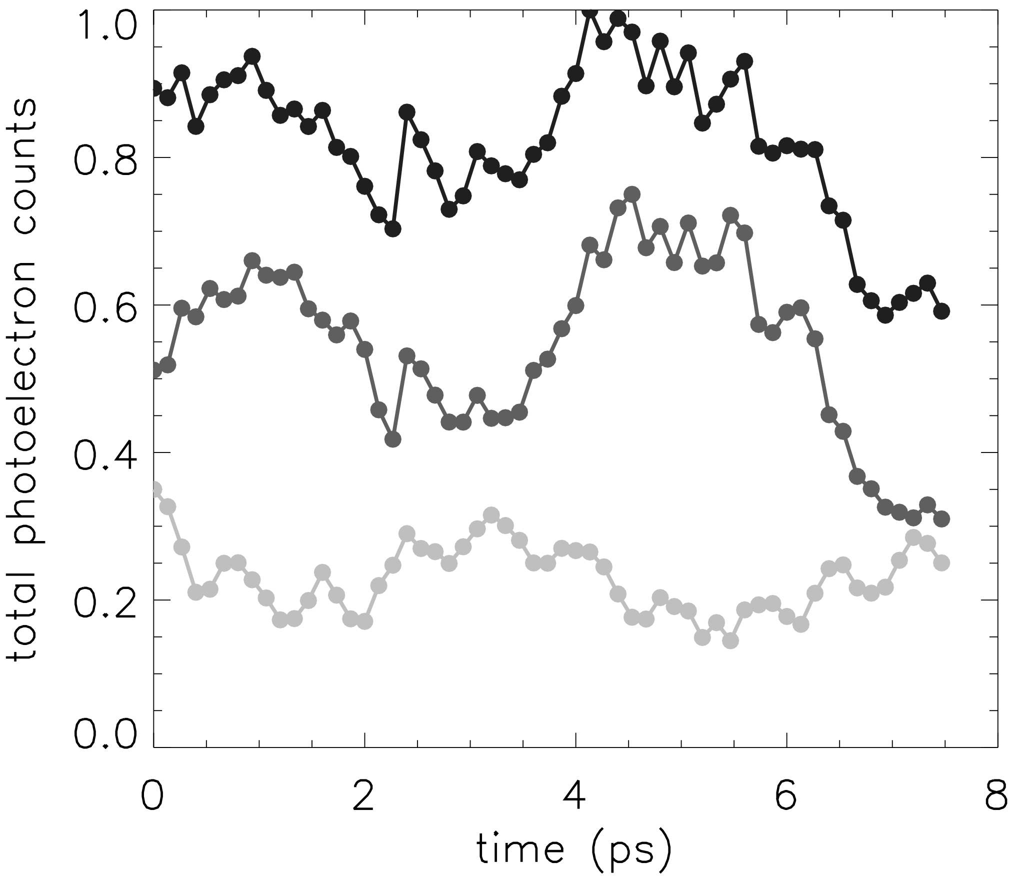

Figure B.4: The same time traces as in Fig. B.3, with the power of the 800 nm beam reduced to 200 mW average power.

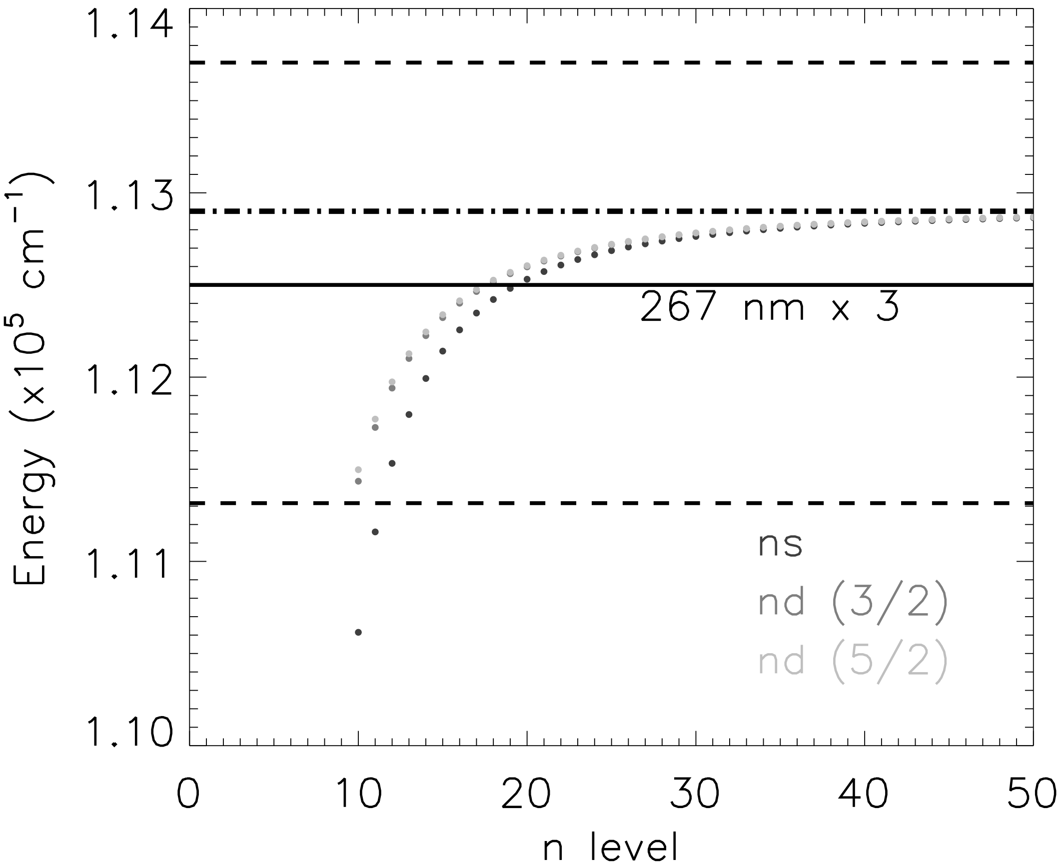

Figure B.5: Rydberg energy levels in Kr, showing the ns, nd3/2 and nd5/2 progressions. The energy of three 266 nm photons is designated by the solid black line. The dotted lines represent the energy bandwidth (FWHM) of the 266 nm pulse.

can be shifted in energy due to an AC stark effect. If a large number of energy levels (shifted to varying degrees) are populated, a slow oscillatory structure from the addition of many faster oscillations could result. The data was never fully analyzed, but some work was done by Ed Grant, which is summed up in a Microsoft Excel file named ’Kr Rydberg states(Ed).xls’. Some helpful references are [81, 82, 83, 84].