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13. ABSTRACT (Maximum 200 words)

Ultrafast laser excitation and probing is used to prepare Rydberg wave packets in atoms and molecules. Rydberg wave packets are achieved in Kr atoms and CO and lithium dimer molecules. Laser Stark field shifting of the states in the preparation of Rydberg wave packets by intense laser pulses is studied. Predissociation and autoionization of CO is investigated. Velocity map imaging of the angular distribution of photoelectrons is observed in time dependent wave packets for the first time. Entanglement of the core angular momentum and the outer electron angular momentum is determined.

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Ultrafast Laser Studies of Molecular Rydberg Wave Packets

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(4) Statement of the Problem Studied

The goal of this work is to investigate the formation and detection of Rydberg wave packets in molecules and to explore their possible use in quantum information processing. Very few coherent superpositions of molecular Rydberg states have been experimentally realized. Therefore this research focuses on several new ways to produce coherent superpositions of Rydberg states in molecules as well as innovative methods to detect them by kinetic-energy-resolved electron detection and photoelectron angular imaging. Two methods of preparation are developed: (1) pumping through intermediate launch states and (2) simultaneous three photon excitation. A number of important proofs of principle were carried out on atoms and then transferred to molecules. The culmination of this work is the observation of a pair of Rydberg states that exhibits entanglement between the core electron angular momentum and the Rydberg electron angular momentum as the Rydberg wave packet oscillates, causing the inner core angular momentum to follow the wave packet motion because of the entanglement.

(5) Summary of the Most Important Results

Initial efforts focused on forming electronic wave packets of low-lying Rydberg states ($n < 13$) in Krypton atoms. Three photons of tripled 266 nm light from an amplified 1 kHz Ti:Sapphire laser system are used to simultaneously excite multiple states in the Kr atom Rydberg region. A time-delayed photon of the fundamental 800 nm light is used to photoionize the excited atoms or molecules. A time-of-flight photoelectron spectrometer (TOF-PES) is used to measure the kinetic energy of the photoionized electrons. Given the well-characterized spectroscopy of Krypton, the experiments could focus on understanding the principles of the multiphoton excitation and detection of Rydberg wave packets as a new method of preparation. [paper published Physical Review A]

These results reveal that Stark-field shifting of the Rydberg levels is a large effect at the high fields of the 266 nm pulsed excitation. It is observed that Rydberg states are accessed successfully and that Rydberg wave packets, or coherent superpositions are formed. An important novel result is that Rydberg states can be accessed as much as 0.4 eV below the energy of the three-photon excitation energy. Intensities on the order of several TW/cm^{-2} are a consequence of the high photon flux needed in the three-photon process, causing a transient AC Stark effect primarily among the Rydberg levels and less so in the tightly bound ground state level of the Kr atoms. Remarkably, the coherence that is prepared during the excitation pulse is preserved after the large perturbative regime of the Stark shifting of the levels during the laser pulse. After the laser pulse the observed quantum beats faithfully reproduce the differences in energies between the unshifted levels.

By detecting the final electron kinetic energy in narrow bands of energy with the electron time-of-flight spectrometer, many individual quantum beats are assigned. This "post-filtering" of the complex multiple-state coherent superpositions is a breathtaking way to analyze a complicated system. A large number of states are excited all at once, but only a few final outgoing electron kinetic energies are analyzed by separating the data according to the electron energies. This permits weak quantum beats to be observed in the presence of a large number of other quantum beats, which typically obscures the information. A series of "g" orbital Rydberg states are observed and assigned for the first time, and different phases of the wave packets are observed when different final states are analyzed, indicating that the final states contain more detailed information about the mathematical signs of the transition matrix elements.

A direct transfer of this three-photon excitation method developed on the atomic system is applied successfully to a molecular case, the molecule CO. Coherent wave packet motion is observed for the CO Rydberg states. The data show two important new features compared to Kr: (1) the existence of mainly low frequency (<15 cm^{-1}) beats and (2) decays of the pump-probe ionization signals in time. The amplitudes of the low frequency quantum beat oscillations quickly decrease with the overall decay of the signal, indicating that the quantum beat superpositions have a short decoherence or de-excitation time. One quantum beat that is always present at ≈ 1.9 cm^{-1} beat is attributed to a coherence between two adjacent rotational levels and is assignable. Due to the high density of electronic levels in this energy region the rest of the beats are not accurately assigned. The decays of the signals are attributed to predissociation or autoionization mechanisms in CO. There is some evidence that different core vibrational states exhibit different timescales for decay. The timescales of the decays depend on the pump wavelength, which suggests a competition between these two mechanisms as a function of the excited states that are accessed. For the high-lying Rydberg states, the predissociation is much faster than the possible autoionization. The longer autoionization lifetime allows observation of wave packets with longer decoherence times.

A second method to prepare electronic wave packets is accomplished in lithium dimer, Li_2. Using a cw laser to first excite an intermediate bound electronic state on a single rovibronic transition (launch state), followed by an ultrafast laser pulse at 800 nm to launch wave packets between the $G^1\Pi_g^+$ and $F^1\Sigma_g^+$ electronic levels, highly selected superposition states are produced. In this case, simultaneous electronic, vibrational, and rotational wave packets are prepared for the first time. Thus three degrees of freedom are controllable simultaneously to produce coherent superpositions and possible entangled states that might target vibration or rotation as the control qubit to switch the electronic degree of freedom, for example. In this work, a detailed assignment of the levels is made and accurate measurements of the quantum beat frequencies faithfully reproduce the spectroscopic states. [paper published Chemical Physics Letters]

A new experimental method is developed to measure photoelectron angular distributions of time-resolved coherent superpositions for the first time. The method not only obtains angular information, but also kinetic energy resolution simultaneously. A way to think about this method is that the angular information provides an additional filter for the wave packets that are detected. There can be multiple wave packets that have the same outgoing electron kinetic energies in the final state, but these can be separately probed by analyzing the angular information of the

photoelectrons. The measurements are accomplished by velocity map imaging of the ejected photoelectrons as a function of time delay between the formation of the coherent superposition and the probe ionization pulse. Each electron is observed on a two-dimensional map, where kinetic energy is radially outward and the angular pattern is also recorded.

The method is first applied to Kr atoms where a well-defined beam of atoms can be formed and the excitation step and the states involved are already well-assigned. Many pairs of Rydberg states are studied to obtain their photoelectron angular distributions as a function of time. Most of the pairs show the same outgoing electron angular pattern, but that pattern is modulated in intensity as the wave packet recurrences occur. However, one studied pair exhibits an alternating change from a $Y_{3,0}$ spherical harmonic of the outgoing electron wave to a $Y_{3,\pm1}$ outgoing wave. An analysis of the states involved shows that the transfer from one outgoing wave to the other is accompanied by a change in the inner core angular momentum, indicating that the inner core angular momentum is entangled with the time dependent outer electron's superposition state. The system of states represents the well-known Bell states, and the results indicate that when the electron is removed, the system must remain entangled. This exciting result indicates that it is possible to find entanglement among the states involved in coherent superpositions of Rydberg states and therefore it may be possible to control and alter the entanglement at different points in the Rydberg electron time-dependent motion. [publication submitted to Phys. Rev. Lett. The publication received favorable reviews, but the reviewers suggested that the results should be sent to another journal. We are in the process of making minor changes so that we can request the referee reports be transferred to Phys. Rev. A.]

(6) List of Publications:

(a) Papers Published in Peer-Reviewed Journals

J. B. Ballard, X. Dai, A. N. Arrowsmith, L. Hüwel, H. U. Stauffer, and S. R. Leone, "Observation of wave packets with simultaneous electronic, vibrational, and rotational degrees of freedom in Li_2, Chem. Phys. Lett. **402**, 27-31 (2005).

S. Gilb, V. Nestorov, S. R. Leone, J. C. Keske, L. Nugent-Glandorf, and R. R. Grant, "Kr(n=5-10, s, d, g) electronic wave packets: Electron time-of-flight resolution and the ac-Stark shift during wave-packet preparation," Phys. Rev. A **71**, 042709 (2005).

(d) Manuscripts Submitted, but not published

S. Gilb, E. A. Torres, and S. R. Leone, "Time-Dependent electron orbital alignment in krypton: conservation of angular momentum and the associated Bell states," Phys. Rev. Lett. (submitted – referee reports received – undergoing revision for Phys. Rev. A)

(7) Paticipating Scientific Personnel

Stephen R. Leone – Principal Investigator

Stefan Gilb – Postdoctoral Fellow

Vilen Nestorov – Postdoctoral Fellow

Elva Torres – Postdoctoral Fellow

Alan Arrowsmith – Graduate Student

Dalziel Wilson – Undergraduate Student

(8) Report of Inventions

None