

Limitations on quantum ladder climbing in complex systems

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The use of cesium Rydberg atoms as a test system for quantum ladder climbing with chirped laser pulses is described. Quantum ladders can be used in the coherent control of chemical reactions; for instance, by exciting a specific molecular bond by climbing its vibrational ladder. A Rydberg atom is an easy test system because of the large transition dipole moments between Rydberg states. The Rydberg states are easy to access and to analyze. Picosecond far-infrared laser pulses around a wavelength of $50\ \mu\text{m}$, with peak intensities of $10^9\ \text{W}/\text{cm}^2$, from the free-electron laser for infrared experiments (FELIX) at Nieuwegein, The Netherlands, were used. It is found that the complexity of the system puts severe limits on the allowed intensities that are used to drive the ladder. At high intensity the ladder is distorted due to coupling with states outside the ladder. This distortion frustrates efficient climbing. [S1050-2947(97)10809-5]

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I. INTRODUCTION

Coherent transfer of population from one quantum state to the other, with controllable efficiency, is a major research topic in modern quantum physics. If, for example, a molecule could be manipulated into a particular rovibrational quantum state, one would be able to steer it into a chemical reaction that would not occur under statistical thermodynamic conditions. Mode-selective excitation of particular bonds may result in the breaking of molecules in places where they would normally never break.

In this field of research, the application of rapid adiabatic passage, in which two coupled energy levels are forced to cross in energy, has proven to be very successful [1] as a tool of efficient population transfer. A powerful way to controllably transfer population from one quantum state to another is by coupling levels with pulsed electromagnetic radiation of which the frequency is varied during the pulse [2]. Such light pulses are called chirped. If we describe the system in terms of its dressed energy levels the adiabatic evolution of the eigenenergies is easily visualized. Dressed energy levels are atomic levels to which the energy of a relevant number of photon energies is added. For example, in a two-level system, coupled by a radiation field with a photon frequency close to the energy difference between the two levels, the system can be described by looking at the lower level dressed with one photon energy and the upper level dressed by zero photon energies. If the radiation frequency is varied from red detuned to blue detuned with respect to resonance during the pulse, the two dressed levels cross in energy. At resonance the eigenenergies show an avoided crossing due to the coupling between the two levels. If the change of frequency is slow compared to the size of the avoided crossing, the population evolves adiabatically and a transition from one state to the other is made with 100% efficiency. In general the probability p to make a nondiabatic transition is described by the Landau-Zener formula for level crossings [3,4] (atomic units are used throughout),

$$p = 1 - \exp\left(-\frac{2\pi|H_{12}|^2}{\partial\omega/\partial t|_{\omega=0}}\right), \quad (1)$$

with H_{12} the coupling matrix element between the two crossing levels and ω the energy difference between the two levels.

It has been suggested [5,6] that the method of chirped pulse excitation could be a powerful tool in the excitation of multilevel systems. In particular this should be true for anharmonic systems; for example, a molecular vibrational potential well [7]. In that case, the chirped pulse not only ensures efficient population transfer between subsequent levels by adiabatic transfer, it also tunes the light to the next transition, which occurs at a slightly different frequency than the previous one. This idea has been tested for a three level system in rubidium [8,9]. The three levels were the $5s$ ground state and the excited $5p$ and $5d$ states. The second transition is slightly bluer than the first and, by chirping the pulses in the right way (red to blue, positive chirp), the atoms were excited with 100% efficiency to the $5d$ state, whereas the same pulse with opposite chirp resulted in virtually no transfer.

A next step in the development of this promising technique is its application to a ladder that more closely resembles the molecular system. Two important features of such a molecular system are (1) the high density of states and (2) transition energies that lie in the mid- to far-infrared. Molecular vibrational transitions typically occur for wavelengths between 1 and $100\ \mu\text{m}$. Intense coherent radiation in this wavelength region, especially the long-wavelength part, is currently available only from free-electron lasers. Furthermore, chirping these pulses requires pulse shapers built with all-reflective optical components, since transmissive components are not available for these wavelengths. The use of intense chirped far-infrared pulses, therefore, is a far less trivial matter than the use of similar pulses in the optical region.

As a model system, with a high density of states and transitions in the far-infrared, we have chosen to study atoms in a highly excited Rydberg state. In Fig. 1 a graphic view of such a Rydberg ladder is given. The high density of states allows for the selection of a suitable subset of states to form a ladder. In addition the dipole matrix elements between Rydberg states are extremely large compared to dipole matrix

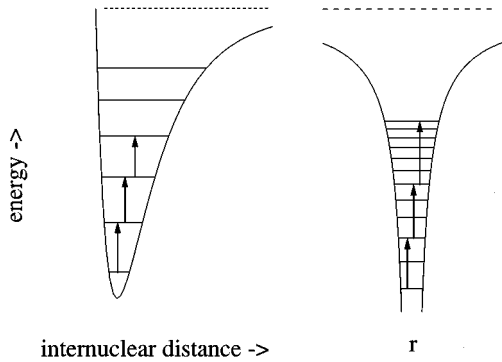


FIG. 1. Ladder systems in a molecule and in an atom. The final goal is to climb the vibrational ladder of a molecular bond. The Rydberg states of an atom allow for a model system that can be easily excited and analyzed.

elements between rovibrational states of a molecule. The radial extension of a Rydberg orbit is proportional to n^2 and consequently the dipole matrix elements are huge. Furthermore, the Rydberg states of alkali-metals atoms are easily prepared with optical radiation and can be analyzed state selectively with ramped field ionization.

This paper describes experiments with chirped far-infrared laser pulses, obtained from the free electron laser for infrared experiments (FELIX). These pulses are used to excite ladder systems in cesium Rydberg atoms. In Sec. II the choice of atom, cesium, and the choice of the subset of states that form the ladder system are discussed. In Sec. III the experimental configuration and synchronization with the free-electron laser radiation are discussed. We present the results of chirped excitation of Rydberg atoms in Sec. IV and give a qualitative theoretical analysis in Sec. V. Conclusions and an outlook to future experiments will be given in Sec. VI.

II. CESIUM RYDBERG STATES AS A LADDER SYSTEM

A Rydberg atom is a convenient model system for an infrared quantum ladder. Instead of climbing the ladder of vibrational states in a molecule, a ladder of increasing electronic excitation is used. It is not necessary to use transitions between neighboring states, which would suffer from the large anharmonicity of the Coulomb potential. By allowing $\Delta n > 1$ for each step, a ladder can be formed by finding a subset of states. The density of states is so high that a convenient subset of states can be found to match the characteristics of the exciting pulse, such as central frequency and bandwidth. The use of cesium atoms facilitates easy access into the Rydberg series since the ionization potential of cesium is only 3.89 eV. Therefore the relevant Rydberg states, which lie in a band of 30 meV below the ionization threshold, can easily be reached from the $6s$ ground state. Using the output of a dye laser around 640 nm, one can either drive a two-photon transition to the Rydberg s or d series, or first frequency double the radiation (in KDP) and access the p series with a single-photon transition.

One of the major advantages of using a Rydberg atom as a test ladder system is the possibility to analyze the population residing in each step of the ladder using ramped field

ionization [10,11]. Rydberg atoms can be ionized by a static electric field. The combined potential of the Coulomb field from the nucleus and the static electric field shows a saddle point that is lowered as the electric-field strength is increased. If the saddle point is depressed far enough, the bound electron is free to escape and the atom ionizes. Classically, one can calculate that for a state with principal quantum number n , ionization occurs if the field is larger than $\frac{1}{16}n^{-4}$ in atomic units.

Another consideration in choosing a specific ladder system is the output of the free-electron laser. The maximum power is generated around $50 \mu\text{m}$. In order to achieve maximum coupling between the atomic levels needed for a high transition efficiency, the wavelength for the experiment is chosen around $50 \mu\text{m}$. Three and two photons in energy below the ionization threshold lie the $n \approx 14$ and $n \approx 17$ Rydberg states, respectively. The density of states between the initial state and the ionization threshold is high enough to find a suitable three-step ladder. An example of such a ladder in cesium is

$$18p \rightarrow 22s \text{ at } 53.9 \mu\text{m},$$

$$22s \rightarrow 30p \text{ at } 54.4 \mu\text{m},$$

$$30p \rightarrow \epsilon s, d.$$

This ladder requires a pulse with a negative (blue to red) chirp and a bandwidth of some 3% of the central frequency. FELIX can easily supply a stable output of bandwidth-limited pulses with a bandwidth of up to 5% of the central frequency. While climbing this ladder with a negatively chirped pulse, first the initial $18p$ state becomes resonant with the $22s$ state, and at sufficient intensity the crossing is adiabatic: close to 100% is transferred into the $22s$ state. Then this state becomes resonant with the $30p$ state and again transfer takes place. Finally the remainder of the same pulse (partly) ionizes the population in the $30p$ state.

III. EXPERIMENTAL SETUP

Figure 2 gives a schematic view of the experimental setup. The far-infrared radiation needs to be propagated in a vacuum with a background pressure of better than 10^{-4} mbar to avoid absorption by the numerous water absorption lines that are present in the $50\text{-}\mu\text{m}$ region. The experiment contains three vacuum systems that are connected to each other. The first vacuum system is the FELIX beam line. The second vacuum system contains the pulse shaper. The radiation enters this system and propagates through the shaper. The chirped beam is reflected into the third vacuum system containing the atoms and focused into the interaction region using a parabolic mirror.

The pulse shaper is an all-reflective pulse shaper built for shaping far-infrared laser pulses. It has been described in detail elsewhere [12]. The shaper is similar to shapers commonly used to shape optical pulses [13], and based on a grating and a folded $1\times$ telescope. It has been shown to produce chirped pulses with a stretch factor of up to 25, both with a negative and with a positive chirp [12]. It has been explicitly verified that the pulses are linearly chirped, and

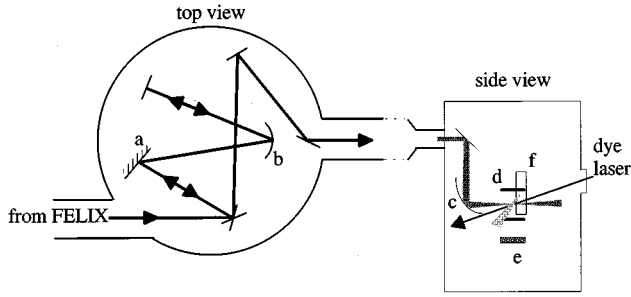


FIG. 2. Experimental setup. The incoming far-infrared radiation is reflected to the grating of the shaper (a) and focused by the spherical mirror (b). After exiting the shaper the radiation is reflected into the next section of the vacuum system, which is shown from a side view. The (chirped) pulses are reflected onto a parabolic mirror (c) ($f/d=6.4$ cm/1 cm) and focused into the interaction region. The cesium atoms emerge in an effusive beam from a resistively heated oven (f). A dye laser beam crosses the far-infrared beam under a small angle and excites the atoms to the desired Rydberg state. Both lasers are linearly polarized. The dye laser is vertically polarized and the far-infrared laser deviates 10° from vertical polarization (due to experimental circumstances). Emitted electrons are accelerated by an electric field applied between the two field plates (d) and are detected by a multi-channel-plate detector (e).

that higher orders of chirp are negligible at these stretch factors.

The third vacuum system is differentially pumped to achieve a background pressure of better than 10^{-6} mbar. The cesium atoms are obtained from a resistively heated oven, which produces atoms in a thermal beam that is directed between two field plates on which a static or pulsed electric field can be applied. The atoms are excited to the desired Rydberg state with the output of a neodymium-doped yttrium aluminum garnet (Nd:YAG) pumped Quantel dye laser that is spatially overlapped with the FELIX beam. Electrons emitted from ionization events are accelerated from this interaction region to a multichannel-plate detector, which detects the electrons with nanosecond time resolution.

For an extensive description of the free-electron laser FELIX we refer to Oepts *et al.* [14]. The output of FELIX has a very characteristic temporal structure. The radiation comes in so-called macropulses that are repeated at 5 Hz. A macropulse typically lasts a few microseconds. It consists of a train of picosecond pulses, separated by 40 ns. The micropulse train complicates experiments in which a single-pulse effect is studied. In the case of quantum ladder climbing this complication is severe. This can easily be seen by considering a two-level system in which rapid adiabatic passage from the lower to the upper state is made during one of the micropulses with 100% efficiency. The next micropulse, 40 ns later, will pump the population back to the ground state with the same efficiency. By examining the population distribution after a train of hundreds of micropulses, no information is obtained about the single-pulse interaction. It is therefore crucial to develop a method to analyze the single pulse response before subsequent pulses can interfere. The first requirement is that the dye laser be synchronized with FELIX on a nanosecond time scale. Furthermore, detection of the final atomic state needs to take place in a way that selects the

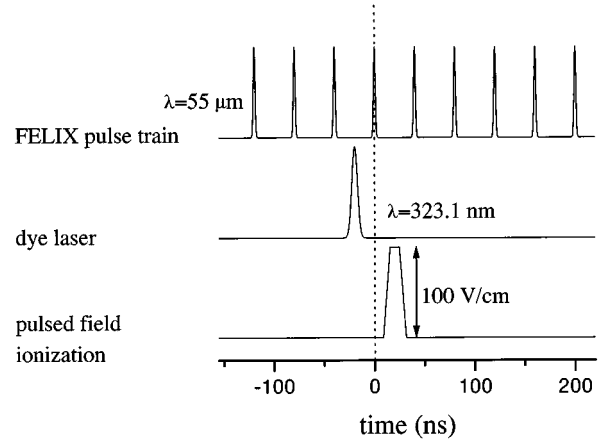


FIG. 3. The timing of laser and field pulses. The far-infrared radiation is emitted in picosecond micropulses separated by 40 ns. The dye laser is timed such that it excites the atoms between two of these pulses. If bound states are to be detected, a pulsed field can be applied after the far-infrared pulse to field ionize the atoms. This pulse has a full width at half maximum of approximately 10 ns, so that the atoms are ionized before the next far-infrared pulse arrives. The sequence is repeated at 5 Hz, the repetition rate of the macropulses that envelop the micropulses of FELIX.

response to the first micropulse that arrives after the dye laser. If the final state is an ionized atom this can be achieved by detecting photoelectrons time dependently. The multi-channel-plate signal is directly fed into a digital oscilloscope so that the ionization events from subsequent micropulses can be isolated. If the final state is a bound state, a more complicated detection scheme needs to be used. Population bound in Rydberg states can be detected with pulsed electric-field ionization. The timing sequence of the laser and field pulses is depicted in Fig. 3.

IV. EXPERIMENTAL RESULTS

A. Climbing a three-state Rydberg ladder with far-infrared radiation

The dye laser was tuned to excite the cesium atoms to the $18^2p_{3/2}$ state. This is the initial state of the ladder mentioned in Sec. II. After excitation of the $18p$ state, the atoms were irradiated with far-infrared pulses with a central wavelength of $54 \mu\text{m}$. The bandwidth of the pulses was 3% of the central frequency, sufficient to bridge the detunings of both steps of the ladder with respect to the central wavelength. At $54 \mu\text{m}$ this bandwidth corresponds to a bandwidth-limited pulse duration of 2.7 ps. The estimated focused peak intensity in the experiment, for pulses with no chirp, was 10^9 W/cm². In Fig. 4 the ionization signal that is obtained by detecting photoelectrons is shown as a function of time.

The train of pulses that is seen reflects the temporal structure of the macropulse. Ionization events are separated by the 40-ns spacing between the infrared micropulses. We can clearly separate the ionization events, which is crucial for the experiment since we are interested in the effect of a single pulse. The ionization with such a single pulse is thus given by the first peak, labeled 1 in Fig. 4. The rapid decay of the ionization signal, within approximately 10 to 15 micropulses, shows that the interaction between the atoms and the light is

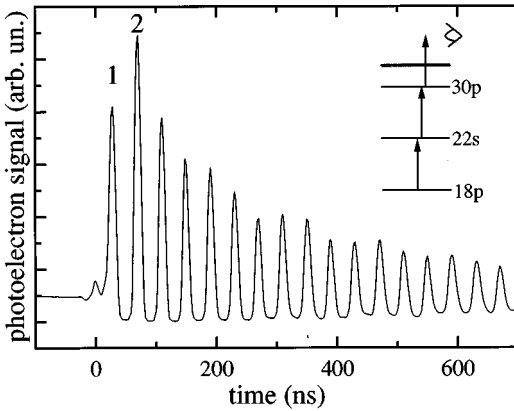


FIG. 4. Ionization signal obtained by detecting photoelectrons after illuminating the cesium $18p$ state with FELIX radiation at $54 \mu\text{m}$. The pulses had a bandwidth of 3% and an estimated peak intensity up to 10^9 W/cm^2 . The dye laser excitation takes place at $t=0$, at which time a small ionization signal is obtained from direct ionization of a fraction of the Rydberg population by the dye laser.

relatively strong. On the other hand, the transitions are not completely saturated because it takes several pulses before the signal decays and the atoms are completely ionized. One can then conclude that this particular intensity is a reasonable intensity to use for the ladder climbing experiment. Control of the atom-light interaction has been verified by checking that the ionization train gets longer if the intensity is lowered, and if the intensity is increased the train gets shorter. As can be seen from Fig. 4, at least part of the ionization is a sequential process: the ionization peak from the second micropulse, labeled 2, is higher than the first one, suggesting that population excited to one of the upper states in the first pulse is ionized with the second. This suggests that a ladder is really climbed before ionization occurs and that not only direct multiphoton ionization from the initial state takes place. The effect of chirp on the efficiency with which the ladder is climbed can now be investigated by recording the yield in the peak arising from the first micropulse that hits the atoms after excitation of the initial Rydberg state by the dye laser. This yield is recorded versus the chirp of the FELIX pulse. The result is shown in Fig. 5. The data are plotted versus the stretch factor of the pulse that is caused by the chirp. Negative pulse stretch factors indicate negative chirp. Because the first step, $18p \rightarrow 22s$ at $53.9 \mu\text{m}$, is bluer than the second step, $22s \rightarrow 30p$ at $54.4 \mu\text{m}$, we expect the population of the upper state to proceed more efficiently for pulses with a negative (blue to red) chirp. Therefore the ionization signal should be larger for negative chirp (pulse stretch factors) than for positive chirp.

To our surprise, we found no dependence of the yield in the ionization first peak on chirp. No such dependence was found in the later peaks either. The experiment was repeated for several peak intensities, ranging from 10^8 to 10^9 W/cm^2 . The enhancement for negative chirp should be present for all intensities, even if the intensity is not high enough to drive the individual steps in the ladder with 100% efficiency. Also for small transfer efficiencies per step, the order in which the proper frequencies are available should strongly affect the efficiency of climbing the ladder as a whole. No chirp dependence was found for any intensity.

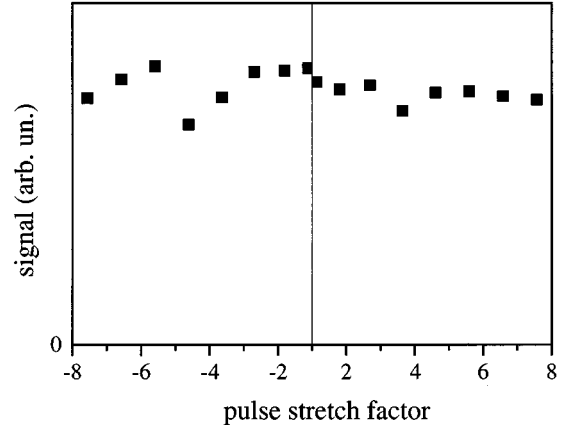


FIG. 5. Integrated yield in photoionization signal from the first micropulse that ionizes the Rydberg atoms as a function of chirp. The chirp is quantified with the pulse stretch factor. Negative pulse stretch factors indicate negative chirp. The initial state was the $18p$ state. The far-infrared pulses had a central wavelength of $54 \mu\text{m}$. The pulses had a bandwidth of 3% and an estimated peak intensity up to 10^9 W/cm^2 . For zero chirp the pulses had a duration of 2.5 ps.

One complication of the investigated ladder may be that the last step, ionization, proceeds much slower than all the other steps that are bound-bound transitions. In that case, ionization out of the upper bound state, which is independent of the sign of the chirp, is the bottleneck, and the transition probability to reach the upper bound state may already be saturated. If this is the case, it would be hard to isolate chirp dependence in the bound part of the ladder in the present system.

To isolate the bound part of the ladder we performed a completely different experiment. In that experiment, described in the next section, the last step in the ladder is a bound state, chosen such that it can be analyzed using field ionization.

B. Chirp dependence of two-photon excitation of Rydberg states

The investigated ladder, consisting of all bound states, is shown in Fig. 6. High-lying resonances are excited through an intermediate state. The initial state in this system is the $20p$ state. Using a central wavelength of $56 \mu\text{m}$, this state is coupled to the $26s$ state. Further excitation to the high-lying Rydberg states with principal quantum number around $n=50$ can then take place. With the bandwidth of the pulses that were used, 4% of the central frequency, states from $49p$ to $53p$ are accessible with the second absorbed photon. If the FELIX pulse is chirped, which states are populated after excitation of the $26s$ state depends on the sign of the chirp. If the pulse has a positive (negative) chirp, states with higher (lower) energy than the $50p$ state are preferentially populated. This preferential population of states, depending on the sign of the chirp, is similar to the experiments in sodium using optical radiation by Melinger *et al.* [2]. To determine the state-specific population of these high-lying states, state-selective field ionization is used. Field ionization was done with a very fast pulse generator, providing pulses with variable peak voltages up to 100 V with a rise time of

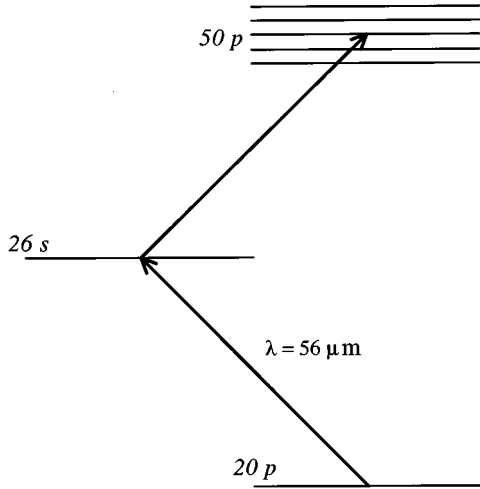


FIG. 6. Two-photon excitation of high-lying Rydberg states through an intermediate resonance. The initial state is the $20p$ state. FELIX is tuned to the intermediate resonance to the $26s$ state, after which population of the high-lying Rydberg states around $n=50$ takes place.

10 ns. By recording the ionization yield as a function of the peak electric field, the distribution over the various high-lying states can be determined. We calibrated this field ionization technique by directly exciting the relevant np states with the dye laser. The calibration field ionization signal is shown in Fig. 7 for various states around $n=50$. As can be seen from the difference in ionization thresholds, it is relatively easy to determine which state, or combination of states, are excited by the (chirped) FELIX pulse. The calibration results show that the threshold for 50% ionization is reached for an electric field strength $F = \frac{1}{13}n^{-4}$. This indicates that field ionization, even with these short pulses, is still in the adiabatic regime for cesium p states around $n=50$. In Fig. 8 the results are displayed that are obtained after exciting the $20p$ state with the dye laser and irradiating the atoms with chirped FELIX pulses. The bandwidth-limited pulse duration of the pulses is 2 ps. The peak intensity was the same as in the first experiment, up to

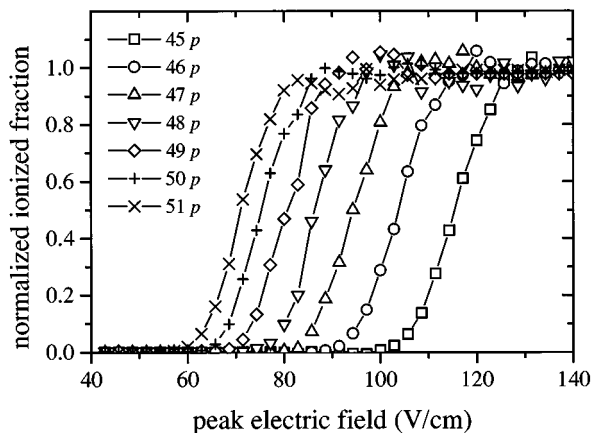


FIG. 7. Field ionization signal as a function of peak electric field of the field ionizing pulse. The results are shown for various states, ranging from the $45p$ to the $51p$ state.

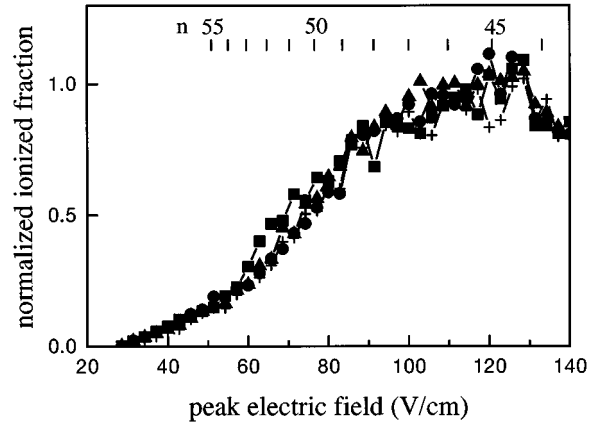


FIG. 8. Field ionization signal as a function of peak electric field of the field ionizing pulse. The field ionization signal was obtained after illuminating cesium atoms in the $20p$ state with chirped FELIX pulses at a wavelength of $56 \mu\text{m}$ with a bandwidth of 5%. The different curves show the result for various values of the chirp. The amount of chirp is indicated in terms of pulse lengthening s , where negative s means that the chirp is negative (blue to red): square, $s = -20$; circle, $s = 10$; triangle, $s = -10$; cross, $s = 1$.

10^9 W/cm^2 for unchirped pulses. If the pulse is chirped the peak intensity is inversely proportional to the pulse lengthening. The field ionization signal as a function of the strength of the field ionization pulse is shown in Fig. 8 for several values of the chirp of the FELIX pulses. Clearly many states around $n=50$ are populated by FELIX. The wide threshold indicates population of a large number of states. Surprisingly, however, the influence of chirp is again absent. In this experiment, as was the case in the ladder climbing experiment, the influence of chirp should be present regardless of the intensity used. Whether the level crossing between the dressed $20p$ and $26s$ state is traversed completely adiabatically (100% transfer efficiency) or almost diabatically (0% transfer efficiency), the fact remains that the sign of the chirp determines what frequencies are available for absorption by the atom after excitation of the $26s$ state, and thus which high-lying Rydberg states can be excited. If we use the onset at 33 V/cm and the saturation at 120 V/cm to estimate the highest and lowest states that are excited by the far-infrared laser pulse, we find that population is spread from $nl=46p$ to $nl=58p$. To reach these states from the $nl=26s$ state, wavelengths from 60 to $52.5 \mu\text{m}$ are required. These wavelengths suggest an effective bandwidth of $(60-52.5)/56.2 = 13.3\%$. Apparently, the effective bandwidth in the experiment is much larger than the 4% bandwidth of the laser pulses.

The results of both experiments show that the cesium Rydberg system is not behaving as intuitively expected under the influence of chirped far-infrared radiation. Possibly the evolution of the eigenenergies of the dressed states, when irradiated with the chirped pulses, is different from what we have assumed it is. In our discussion of the ladder in Sec. II we have not included the fact that the laser has a finite intensity. This simple discussion excludes coupling of the states forming the ladder with states *outside* the ladder. These couplings may lead to energy shifts that could, for example, change the order in which the crossings are tra-

versed. These shifts could also account for the fact that in the second experiment many more states around $nl=50p$ are excited than expected on basis of the bandwidth of the laser pulse. Generally, the eigenenergies of the states of the ladder system may evolve in such a complicated way as to make the transfer of population effectively independent of the chirp. However, it is still remarkable that the population of high Rydberg states also seems to be very insensitive of the peak intensity of the presently used pulses, which decreases as the chirp and therefore the pulselength increases proportional to the chirp of the pulse. In the next section we will explore the effect of coupling with states outside the ladder more carefully and give a qualitative theoretical analysis.

V. FLOQUET EIGENENERGIES OF CESIUM RYDBERG STATES DURING A FAR-INFRARED CHIRPED PICOSECOND LASER PULSE

A possible explanation for the observed lack of influence of chirp could be that the order in which the levels under consideration are traversed is heavily distorted by light-induced shifts when the pulse reaches some specific intensity in the experiment. In the analysis of an experiment in which lithium Rydberg states were ionized with far-infrared pulses around $54 \mu\text{m}$, such shifts turned out to be important in understanding the population of certain high-lying Rydberg states [15]. Consider the three-level quantum ladder described in Sec. II. The initial state in that ladder is the $18p$ state. To examine the influence of states outside the ladder, which couple to states in the ladder, we diagonalized the Hamiltonian of the system including the interaction between the Rydberg atom and the light. We have determined a subset of relevant states in the following way. Only the s , p , and d states are taken into account. States with higher angular momenta are effectively decoupled from the system under study. A Cooper minimum in the d - f matrix elements causes the coupling to these states to be very small [16]. All states belonging to the s , p , and d series of which the principal quantum number lies between 6 and 35, are subjected to the following test: If the energy of state nl lies between $E_{18p} - (\nu + \frac{1}{2})\omega$ and $E_{18p} - (\nu - \frac{1}{2})\omega$, with ν a positive (negative) integer number of photons, then the change in angular momentum Δl with respect to $l=1$ from the initial $18p$ has to satisfy

$$(-1)^{\Delta l} = (-1)^\nu, \quad \Delta l \leq \nu, \quad (2)$$

as required by the selection rule $\Delta l = 1$ for dipole transitions. If l meets these criteria then all the fine-structure levels of the dressed or Floquet state (nl, ν) are included in the list of relevant states. This corresponds to taking into account the most relevant Floquet component of state nl . After determining all the relevant states, amounting to 62 s , p , and d states, the matrix \mathbf{H} is diagonalized, where the matrix elements \mathbf{H}_{ik} are determined by

$$\mathbf{H}_{ik} = \langle \psi_i | H | \psi_k \rangle. \quad (3)$$

The Hamiltonian H is given by $H = H^{\text{atomic}} + H^{\text{dipole}}$. The atomic part of the Hamiltonian is given by the dressed-field-free energies of the relevant states,

TABLE I. Relative coupling between relevant fine-structure components.

$(l_j)_i$	$(l_j)_k$	f_{ik}
$s_{1/2}$	$p_{1/2}$	0.408248
$s_{1/2}$	$p_{1/2}$	-0.57735
$p_{1/2}$	$d_{3/2}$	-0.645497
$p_{1/2}$	$d_{5/2}$	0
$p_{3/2}$	$d_{3/2}$	-0.0912871
$p_{3/2}$	$d_{5/2}$	0.67082

$$\mathbf{H}_{ik}^{\text{atomic}} = \delta_{ik} E_i \quad (4)$$

with

$$E_i = \frac{-1}{2(n_i - (\delta_{lj})_i)^2} + \nu\omega. \quad (5)$$

The interaction matrix, or dipole matrix elements, are approximated by a semiclassical approximation for the dipole coupling between Rydberg states in nonhydrogenic atoms. For an extensive discussion of the derivation of these matrix elements we refer to the work of Hoogenraad *et al.* [16]. Here we will just quote the final result for the approximation,

$$\begin{aligned} \mathbf{H}_{ik}^{\text{dipole}} &\approx \sqrt{I} C_{ik}^{lj} (n_i^*)^{-3/2} (n_j^*)^{-3/2} \Delta E^{-5/3} \\ &= \sqrt{I} C_{ik}^{lj} (-2E_i)^{3/4} (-2E_k)^{3/4} \Delta E^{-5/3} \end{aligned} \quad (6)$$

with I the intensity of the radiation field and ΔE the absolute energy difference between the states. C^{lj} is a prefactor depending on the orbital and total angular momentum,

$$C_{ik}^{lj} = f_{ik} 0.4744 \cos\left(\pi |(\delta_{lj})_i - (\delta_{lj})_k| \pm \frac{\pi}{6}\right), \quad (7)$$

with f_{ik} a factor that describes the relative coupling between the fine-structure components. Table I gives the values of f_{ik} for the states of interest. The sign in front of $\pi/6$ depends on the sign of the change of angular momentum and of the change of energy. If these signs are the same, then the sign in the formula is positive, otherwise it is negative. Although Eq. (6) is an approximation of the coupling matrix elements, it should suffice in providing a qualitative idea of how the eigenlevels behave in the field. Comparing the results from Eq. (6) to results from numerical integration of the overlap integrals between Rydberg wave functions in nonhydrogenic atoms [16], the matrix elements from Eq. (6) are found to have a relative accuracy of better than 10%. The purpose here is not to get accurate information on the spectroscopy of the levels in the field, but more to show the influence of the high density of states on the ladder under consideration. Since cesium is a heavy atom, the fine-structure levels are well separated in energy so that we choose to treat the fine-structure components explicitly. In Fig. 9 the eigenenergies of the dressed levels are displayed as a function of the wavelength of the far-infrared radiation that couples the states, for zero intensity. The ladder that has been discussed is identified in the figure with an arrow at each crossing. As is apparent in the figure, a blue-to-red or negative chirp is needed

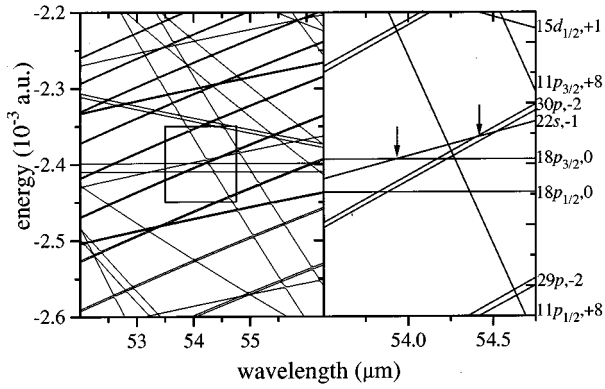


FIG. 9. Dressed eigenenergies of the Rydberg states in cesium relevant to the chosen ladder system as a function of the laser wavelength. The intensity of the light is zero, so that no coupling exists between the levels. The area containing the actual ladder is magnified and displayed in the right frame. In that frame the labels nl, ν refer to the Rydberg state nl of which the energy is raised with $\nu\omega$. The two crossings belonging to the ladder system $18p_{3/2} \rightarrow 22s_{-1}$ and $22s_{-1} \rightarrow 30p_{-2}$ are indicated with arrows.

to traverse the transitions in the right order. To simulate the experimental situation, both the frequency and the intensity should be varied over the pulse. As in the experiment, we chose a Gaussian power spectrum with a width of 3% around a central wavelength of $54 \mu\text{m}$. This also gives a Gaussian pulse in time, with a temporal width determined by the chirp. The horizontal axis therefore is also a time axis, but the conversion from frequency to time depends on the chirp. In Fig. 10 the dressed eigenenergies are shown for a pulse with a peak intensity of only $3.51 \times 10^6 \text{ W/cm}^2$. As can be seen in the figure, the coupling induced by the light creates avoided crossings between levels that cross at zero intensity. This is necessary for the transitions to become sufficiently adiabatic.

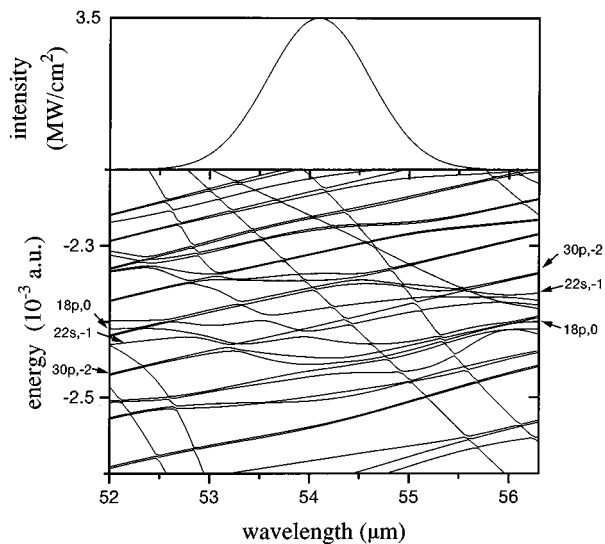


FIG. 10. Dressed eigenenergies of the Rydberg states in cesium relevant to the chosen ladder system as a function of the laser wavelength. The intensity of the light is given by a Gaussian power spectrum with a width of 3% around a central wavelength of $54 \mu\text{m}$. The intensity profile is plotted in the top frame. The peak intensity is $3.51 \times 10^6 \text{ W/cm}^2$.

What is also apparent from Fig. 10 is that the ladder, as originally intended, is no longer present. Already at this low intensity, the coupling among all the states included in the calculation has heavily distorted the ladder. This distortion is due to the fact that dressed Rydberg states with lower principal quantum number n shift through the relevant energy region. As the lower-lying states become almost resonant with the states of interest, the coupling with these states causes the ladder states to be shifted in energy. Why are the shifts of those lower-lying states so big? It turns out that, at the photon frequency chosen for the experiment, states with principal quantum number $n \approx 12$ are coupled with only one photon to neighboring states. The $11p$ state and the $12s$ state are coupled resonantly by light with a wavelength of $40.5 \mu\text{m}$. The dipole matrix elements from a Rydberg state to a neighboring Rydberg state are generally very large compared to matrix elements to other states. This is caused by the fact that the wave functions look so much alike: overlap between the two states extends over almost the whole wave function. The dipole coupling to those neighboring states dominates the shift of these lower-lying states. The off-resonant radiation ($55 \mu\text{m}$) with an intensity of $3.51 \times 10^6 \text{ W/cm}^2$ already shifts the $11p$ state 3×10^{-4} a.u. with respect to the $12s$. This is a large shift on the scale of Fig. 10. Unfortunately this distorts the ladder dramatically, already at intensities well below the intensities used in the experiment. However, these experimental intensities are needed to achieve significant ionization of the atoms. In the experiment the intensities were varied, both by varying the total energy of the pulse, and also implicitly by chirping the pulses. The range of intensities spanned by these variations, however, was not large enough to bridge the enormous gap between the experimental values of approximately 10^9 W/cm^2 and the value used in Fig. 10 of $3.51 \times 10^6 \text{ W/cm}^2$. Consequently, all the intensities used in the experiment resulted in heavy distortion of the original ladder system. We assume that these distortions are the cause of an influence of chirp on the transfer efficiency as observed in the experiment: at the experimental intensities the ladder loses its meaning because the ladder states are shifted around in energy.

VI. CONCLUSIONS

We have demonstrated the generation of far-infrared pulses with a controllable frequency chirp. The chirp can be manipulated using an all-reflective pulse shaper. We have used these chirped far-infrared pulses to excite quantum ladder systems in cesium Rydberg atoms.

Summarizing the observed behavior, we see that a three-step ladder from the $18p$ state in cesium to the ionization continuum is driven with reasonable efficiency with a laser pulse at $54 \mu\text{m}$ with a bandwidth of 3% of the central frequency and an intensity of 10^9 W/cm^2 . However, chirping the pulses does not influence the ionization efficiency. Simplifying the ladder to an all-bound system, of which the upper state can be analyzed state-selectively, yielded similar results. Chirping the pulse did not enhance the population of particular upper bound states, which is to be expected if the ladder is climbed in the intuitive way. Furthermore, the amount of upper bound states that was populated corresponded to an energy range much larger than the bandwidth

of the incident radiation, presumably also due to shifts induced by the intense radiation.

Calculations of the energy of the dressed eigenstates of the system show that the ladder is heavily distorted at the light intensities used in the experiment. Dressed Rydberg states of lower principal quantum number n , coupled to neighboring states with only one photon, are shifted through the ladder and induce the distortion. The intensities used in the experiment are needed to achieve significant transfer, but the induced distortions are already large enough to cause the ladder to lose its meaning. The order in which the frequency components of the pulse arrive at the atom has therefore become irrelevant, and the influence of chirp is absent. In conclusion it is impossible to controllably climb the current quantum ladder at intensities at which significant transfer occurs.

For a nondiabatic transition in an isolated two-level system, increasing the intensity of the interaction is never a problem. Above the intensity where a transition becomes nondiabatic, the transition remains nondiabatic for increasing intensity. This is in fact one of the features that makes the use of rapid adiabatic transfer so robust: no accurate control is needed over the intensity once the adiabatic regime is reached.

The current experiments show that this robustness is limited for more complicated systems. Interactions between states that are not an essential part of the ladder system may distort that system if the intensity becomes too high. A window in allowed intensities is therefore set. The adiabaticity criterion sets a lower limit on the intensity. The maximum

intensity that does not create significant distortions sets the higher limit. Future experiments should be designed such that the magnitude of the interactions stays within this window, if such a window exists.

In a molecular system, in which the vibrational ladder is climbed, the observed distortions could lead to similar problems in controllably climbing the ladder. Although for different parts of the vibrational ladder the windows of allowed intensity may be experimentally accessible, the different windows do not necessarily overlap. Due to variations in transition dipole matrix elements, different windows may exist for different parts of the ladder. If such a case arises, then the pulses that are used to climb the vibrational ladder must not only be chirped, but must also have a time-dependent intensity that matches the changing requirements on intensity as the ladder is climbed.

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