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Pathway for two-color photoassociative ionization with ultrafast optical pulses in a Rb magneto-optical trap

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Ultrafast and narrow linewidth lasers are combined to study multiphoton photoassociative ionization (PAI) in a Rb magneto-optical trap. Through the use of time of flight spectroscopy and by varying the parameters of the ultrafast laser, the excitation pathway for PAI was determined. It was found that Rb_2^+ is formed, not by direct photoionization, but by sequential excitation of Rb_2 to an autoionizing state. Determining the excitation and ionization pathway was a necessary first step for future efforts in trying to establish coherent control techniques, first for the efficient production of translationally cold Rb_2, and then for transferring population to a desired vibrationally cold molecular state.

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In the past decade, the advent of cooling and trapping techniques have made it possible to study photon-assisted formation [1], evolution [2], and ionization [1,3] of cold molecules in greater detail than ever before. These studies were further made possible due to the availability of narrow linewidth cw lasers whose optical frequencies can be controlled to sub-MHz precision through, for example, Doppler-free spectroscopy [4] and optical combs [5]. These techniques have allowed researchers to measure molecular structure [6] with impressive precision.

In contrast, femtosecond lasers make excellent tools for probing the dynamics of molecular processes, including photoassociation (PA) and photoassociative ionization (PAI). For example, a number of extraordinary experiments have been devised in which cold, colliding atoms were excited to a bound molecular state with one femtosecond pulse, and the time evolution of the excited vibrational state was monitored using a second femtosecond pulse as a probe that tracked the dynamics of the molecule by ionizing it at a variable time delay from the excitation [2]. The same short pulse duration of the ultrafast laser that makes it a powerful tool in the study of evolutionary dynamics gives the femtosecond laser pulse a broad spectral content. The pulses can be manipulated in the frequency and phase domains, and the effects on a variety of physical processes studied. For example, Brown *et al.* reported [7] the results of an experiment in which a chirped femtosecond pulse was chirped in order to minimize the production of the Rb_2 molecules formed through photoassociation of cold, colliding atoms in a magneto-optical trap (MOT). In an experiment by Salzmann *et al.* [8] a genetic algorithm [9,10] was used to optimize excitation of the Rb_2 that was formed in a ^{85}Rb MOT by the trapping lasers. If one thinks of a femtosecond pulse as a collection of phase-locked optical waves spanning a range of frequencies, it seems feasible to explore the coherent processes involved in the formation of cold molecules, by properly shaping the femtosecond pulses.

Somewhat mitigating the benefits of using femtosecond pulses for molecular studies, is the disadvantage that with the broad bandwidth contained in the ultrashort pulses one loses selectivity of transitions through which the populations are moved, and at what internuclear separations transitions take place. This is unlike an earlier study [11] of photoassociation using narrow linewidth cw lasers with which molecular potential curves could be mapped out, and/or excitation pathways could be determined.

It is the goal of the experiments described in this paper to extend previous cw laser work [11] in which we determined the pathway for the production of Rb_2^+ via photoassociation followed by stepwise excitation and ionization, to a system in which one of the two cw lasers is replaced by a femtosecond laser. The motivation for this is that once the excitation or ionization pathway has been identified, we can start to investigate the enhancement of this process through the shaping of the femtosecond pulse. The system under study is a cloud of cooled and trapped atomic Rb. We apply a pulse of light from a narrow linewidth 1529 nm laser and an ultrashort pulse of light, centered at 790 nm. The goal is to determine the pathway(s) through which the resulting Rb_2^+ ions are formed.

For the sake of simplicity, molecular levels are labeled by their infinitely separated atomic designations. Thus, the molecular electronic ground state is referred to as $(5s_{1/2}+5s_{1/2})$; the lowest electronically excited state is $(5s_{1/2}+5p_{1/2})$, etc. This notation is justified by the extremely large internuclear separations (many hundreds of atomic units) at which the initial interaction, photoassociation, takes place.

A typical ^{87}Rb MOT was created inside a recoil ion momentum spectrometer [12]. Any ions produced as a result of the interaction of cold Rb atoms or molecules with the lasers were extracted by the weak (~10 V/cm) electric field of the momentum spectrometer and were detected by a position-sensitive detector (PSD). The ion's time-of-flight (TOF) and position on the PSD were recorded in event mode so that correlations with other experimental parameters could be readily measured.

Optical pulses from an ultrafast laser, having a repetition rate of 1 kHz, pulse duration of ~50 fs and transform-limited bandwidth of ~20 nm were transported approximately 20 m in vacuum from the Kansas Light Source (KLS) to the momentum spectrometer. Before the KLS amplifica-

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tion stage, pulses from the laser oscillator were temporally stretched and passed through an acousto-optic programmable dispersive filter (AOPDF) [13]. Using the AOPDF we could effectively block portions of the KLS beam's spectral content. This enabled us to eliminate large numbers of pathways as potential contributors to Rb_2^+ production. After amplification the optical pulses were temporally compressed and directed to the MOT. Throughout the rest of the paper, this laser, as well as the light from this laser will be referred to as KLS.

Before entering the MOT chamber, light from a narrow linewidth (<1 MHz) quasi-cw laser having a wavelength of 1529 nm was merged with the KLS pulse using a band pass filter. This second laser, as well as the light from it will hereafter be referred to as L2. L2 was locked 53 MHz to the blue of the atomic $5p_{3/2}$, $F=3\rightarrow 4d_{5/2}$, $F=4$ transition. During the measurement, the trapping and repump lasers were turned off for 8 μs. Some time was allowed for the atoms in the MOT to radiatively decay to the upper hyperfine level of their electronic ground state $(5s_{1/2}, F=2)$ [14]. After that, the KLS and L2 pulses arrived and interacted with the atoms in the MOT. Ions produced in the interaction region were extracted through the time focusing drift tube and directed toward the PSD.

The KLS pulse provided the START signal, and the detection of a Rb^+ or Rb_2^+ ion generated the STOP signal for a time-to-digital-converter (TDC). The data acquisition computer, connected to the TDC, recorded the flight time of each detected ion in event mode. When only the KLS pulse is introduced into the MOT chamber, a high yield of atomic ions, produced by resonant three photon ionization, is observed; very few molecular ions are detected under these circumstances.

In order to determine the excitation pathway(s), four different experiments were performed. In the first, the AOPDF was used to verify that only a negligible fraction of Rb_2^+ was produced along paths that passed through molecular states involving either $5d_{3/2}$ or $5d_{5/2}$, for example, the $5s_{1/2}+5d_{5/2}$ manifold of states. In the second experiment, the polarization of KLS and L2 light was varied in order to determine whether or not Rb_2^+ was produced through direct photoionization. In the third experiment, the decay rate of the Rb_2^+ signal was used to support the hypothesis that the order in which the optical pulses are absorbed is KLS-KLS-L2, and not the energetically equivalent KLS-L2-KLS. In the fourth experiment, the relative timing between the KLS and L2 pulses was varied, lending additional support to the KLS-KLS-L2 excitation scheme.

In the first experiment, the AOPDF was used to create 3 nm wide (FWHM) "notches" in the spectral content of the KLS pulse. The notches were placed at 795, 761, and 776 nm, corresponding to the $5s_{1/2}\rightarrow 5p_{1/2}$, $5p_{1/2}\rightarrow 5d_{3/2}$, and $5p_{3/2}\rightarrow 5d_{5/2}$ transitions, respectively. Figure 1 schematically indicates that virtually all indicated transitions are allowed with no notches; but with one or more notches, successively more transitions are made impossible. In all combinations of these notches, the Rb_2^+ production rate remained a constant, although the Rb^+ production rate depended strongly on whether these notches were present. This indicates that the molecular states involving the $5d_{5/2}$ and

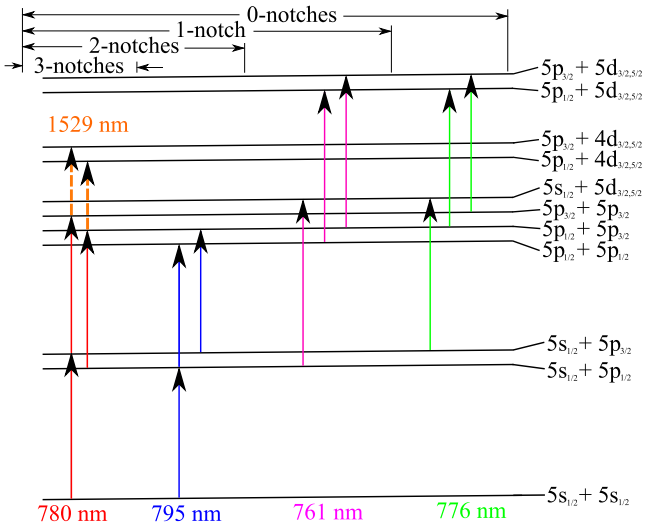

FIG. 1. (Color online) Schematic (not to scale) of the molecular energy levels relevant to the excitation pathways discussed in the text. The "notches" labels indicate which wavelengths are available under the different "notch" conditions discussed in the text. The cw laser's 1529 nm radiation, indicated by dashes, was available during all notch configurations.

$5p_{1/2}$ atomic states are negligibly involved in excitation pathway(s) leading to Rb_2^+, even though Rb^+ production definitely relies on excitation paths through these states.

In the time of flight (TOF) spectra of Fig. 2, Rb^+ peaks are shown for the cases in which the polarization of the KLS pulse is perpendicular [Fig. 2(a)] or has a component parallel [Fig. 2(b)] to the momentum spectrometer's extraction electric field. In the latter situation the Rb^+ peak is split because photoionization gives the ions an initial velocity along the optical field axis, which is sometimes parallel and sometimes antiparallel to the extraction field. This results in the two different flight times seen in Fig. 2(b). By contrast, if the polarization of the optical field is perpendicular to the extraction field, then photoions released along either direction along the polarization axis will have equal flight times to the

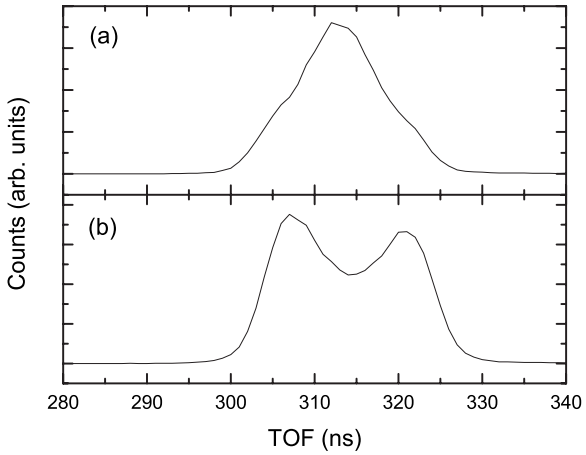

FIG. 2. TOF spectra for Rb^+. In (a) the polarization of KLS is perpendicular to the spectrometer extraction field. In (b) the polarization of KLS is parallel to the extraction field.

PSD. Thus, in agreement with earlier work [15,16], carried out with picosecond laser pulses, we see that Rb^+ production is due to the KLS pulse directly ionizing atomic Rb. This is due to resonant three photon ionization via $5s \rightarrow 5p \rightarrow 5d \rightarrow \epsilon l$, consistent with the results of the first experiment. In contrast, the shape of the Rb_2^+ TOF peak shows no dependence on the polarization of either the KLS or the L2 pulse. This implies that the last step in the production of Rb_2^+ is not due to direct photoionization, but rather due to autoionization near a curve crossing between the Rb_2^+ and $(5p_{3/2}+4d_{5/2})$ potentials, since otherwise the effect of the polarized optical field on the molecular ion would manifest itself in a split peak, as in the case of Rb^+.

The challenge now is to determine through which excitation series Rb_2 is formed and ionized. There are two possible excitation pathways for the formation and the ionization of Rb_2:

$$(5s_{1/2}+5s_{1/2}) \xrightarrow{\text{KLS}} (5s_{1/2}+5p_{3/2}) \xrightarrow{\text{L2}} (5s_{1/2}+4d_{5/2}) \xrightarrow{\text{KLS}} (5p_{3/2}+4d_{5/2}), \quad (1)$$

$$(5s_{1/2}+5s_{1/2}) \xrightarrow{\text{KLS}} (5s_{1/2}+5p_{3/2}) \xrightarrow{\text{KLS}} (5p_{3/2}+5p_{3/2}) \xrightarrow{\text{L2}} (5p_{3/2}+4d_{5/2}), \quad (2)$$

followed by autoionization near a curve crossing with Rb_2^+. For shorthand, the first path is termed KLS→L2→KLS and the second path is termed KLS→KLS→L2.

The first argument against KLS→L2→KLS is as follows: the first and third transitions would be due to the same pulse from KLS. The intermediate transition is due to L2. However, because L2 is relatively weak, 150 mW/cm^2, only a negligible fraction of molecules will have made the transition from $(5s_{1/2}+5p_{3/2}) \rightarrow (5s_{1/2}+4d_{3/2,5/2})$ during the available 50 fs. In other words, the Rabi period of L2 is much longer than the temporal width of KLS, which means that almost no population would exist in the $(5s_{1/2}+4d_{3/2,5/2})$ molecular state by the time the KLS pulse would have ended. Thus, there would be no mechanism for transferring population from the $(5s_{1/2}+4d_{3/2,5/2})$ states to the $(5p_{3/2}+4d_{3/2,5/2})$ autoionizing levels. While this is a reasonable argument, it is still desirable to obtain experimental support, especially since the sequence of levels in Eq. (1) is known to be the pathway to Rb_2^+ in the case of narrow linewidth excitation or ionization of Rb_2 [11].

One piece of indirect evidence for the KLS→KLS→L2 path is given by the lifetime of the Rb_2^+ TOF peak. An experiment was therefore done in which L2 was turned on as soon as the MOT trapping lasers were turned off, and turned off just before the trapping lasers were turned back on 7.5 μs later. The reason for using an effectively cw and not pulsed L2 was to see the effects of the excited Rb_2 lifetime on the TOF spectrum, which otherwise would be convoluted with the temporal profile of the L2 pulse. As shown in Fig. 3, the molecular ion peak shows an exponential decay with a lifetime of 19 ns. If we approximate the radiative lifetime of the $(5p_{3/2}+5p_{3/2})$ molecule as being that of a system of two independent $Rb(5p_{3/2})$ atoms, then the lifetime of this molecular state would be one half of the lifetime of a single atom, or ~13.5 ns. However, if L2 has sufficient intensity to saturate the transition between $(5p_{3/2}-5p_{3/2})$ and $(5p_{3/2}+4d_{3/2,5/2})$, then the populations of these coupled levels would decay together. Thus, the lifetime of the combined two-level system $(5p_{3/2}+5p_{3/2})$ and $(5p_{3/2}+4d_{3/2,5/2})$, becomes twice the lifetime of the $(5p_{3/2}+5p_{3/2})$ level alone, because part of the $(5p_{3/2}+5p_{3/2})$ population is shelved in the $(5p_{3/2}+4d_{3/2,5/2})$ manifold [17]. If the L2 laser is not intense enough to saturate the transition, then the populations of these two states will not be equal and the lifetime of the combined two-level system will be closer to the lifetime of an uncoupled $(5p_{3/2}+5p_{3/2})$ state. Therefore, the observed decay rate of the Rb_2^+ is completely consistent with the KLS→KLS→L2 model.

The lifetime evidence supports the KLS→KLS→L2 path argument, but is hardly conclusive. An additional set of measurements was therefore made, in which L2 was pulsed with a FWHM of 30 ns and its delay with respect to KLS was varied from negative to positive values in steps of 5 ns by using a variable delay circuit [18]. When an ionization event was detected by the PSD, the state of the delay generator was also recorded. In this way it was possible to sort the TOF data according to the delays between KLS and L2 pulses. The result of this experiment was a set of sixteen time-of-

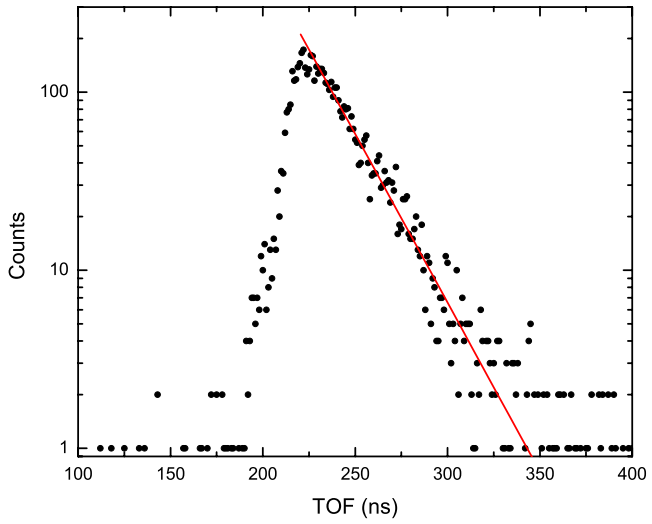

FIG. 3. (Color online) TOF spectrum for Rb_2^+. The solid line is a fit to an exponential decay and shows a lifetime of 19 ns.

flight (TOF) spectra for the atomic and molecular Rb ions, each having a different delay of L2 with respect to the KLS pulse. If the KLS→L2→KLS scheme is responsible for the formation and the ionization of the Rb_2, one would expect the Rb_2^+ TOF peak to be symmetric about the delay for which the L2 pulse is temporally centered on KLS pulse. On the other hand, if the KLS→KLS→L2 scheme is responsible for the formation and the ionization of the Rb_2, the peak position of the Rb_2^+ would step nearly in time with the L2 pulse. [We say "nearly" because the $(5p_{3/2}+5p_{3/2})$ begins to decay as soon as the KLS pulse has ended.] Thus, production of Rb_2^+ should be asymmetric with respect to the relative timing of the L2 and KLS pulses. Figure 4(a) is a density plot of TOF for various values of delay between L2 and KLS. Here, a negative delay means that the L2 pulse precedes the KLS pulse. A close examination of Fig. 4(a) shows that when L2 precedes KLS, the TOF spectra always peak at the same flight time, but when L2 follows KLS, the position of the Rb_2^+ TOF peak shifts with the L2 pulse. The solid line in the figure connects the peak values in the 16 TOF spectra and emphasizes the asymmetry of Rb_2^+ production about 0 delay. That is, only that portion of L2 that follows KLS contributes to Rb_2^+ production. This is consistent with the notion that the association, excitation, or ionization process follows a path in which L2 comes last.

In summary, light from an ultrashort, broadband laser was combined with light from a narrow bandwidth laser in order to study multiphoton photoassociative ionization in a Rb MOT. From the momentum distribution of the resulting Rb_2^+ ions, photoassociation followed by excitation and autoionization is proposed as the mechanism for Rb_2^+ formation. Further, based on the dependence of the molecular ion yield on the delay between laser pulses, the excitation path given by Eq. (2) was proposed as the dominant mechanism for this process. Future plans include manipulation of this excitation path by controlling not only the spectral amplitude of the KLS pulse, but its spectral phase as well, in order to enhance Rb_2^+ production.

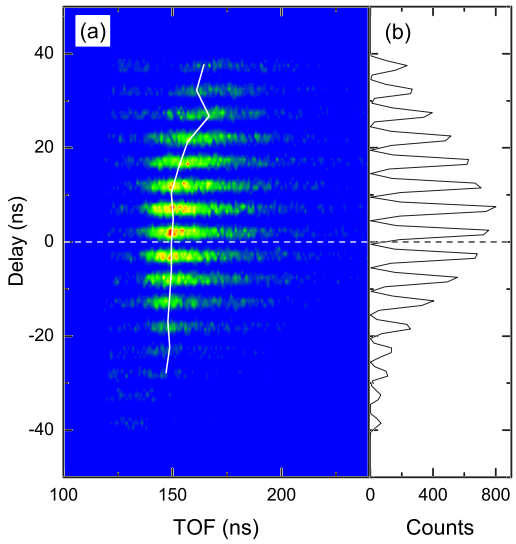

FIG. 4. (Color online) (a) Density plot of Rb_2^+ TOF spectra as a function of the delay between the KLS and L2 pulses. Negative delay means L2 preceded KLS. (b) Horizontal projection of (a).

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