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Photoassociation in Cold Atoms via Ladder Excitation

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We explore 2-color photoassociative ionization in cold Rb vapor and present experimental evidence that the molecular ions are produced from the stepwise excitation of a ladder of molecular states. We also explore a new process, dubbed photoassociative-dissociative ionization, by which atomic ions are created by excitation through a ladder of molecular states, finally autoionizing to a *dissociative* potential curve of Rb_2^+. We submit that these experiments could be the starting point for the same sort of high resolution spectroscopy that has already been done for lower electronic states of cold Rb_2 at large internuclear separation.

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Introduction.—Almost from the first days since magneto-optical traps (MOT) have been developed, trap loss in the form of molecular ions has been observed [1–3]. The molecular ions were initially thought to be due to associative ionization, in which two atoms excited by the trapping lasers collided and autoionized. It was later realized [4] that this process was not possible because in the low temperature environment of a MOT, the time required for the excited atoms to approach close enough to autoionize is far longer than their radiative lifetimes. A new mechanism was therefore proposed [4] in which quasimolecules, formed when two ground state atoms approached close enough, were stepwise excited to an autoionizing molecular state. This new process was referred to as photoassociative ionization or PAI. In sodium, this process can occur through the absorption of two photons from the trapping laser, which is detuned to the red of the atomic resonance and is therefore resonant with the sodium molecular transition, albeit at very large internuclear separation. Expressed in terms of the infinitely separated atom configuration, the reaction is

$$\begin{aligned} &Na_2(3s_{1/2},3s_{1/2})+\hbar\omega\rightarrow Na_2(3s_{1/2},3p_{3/2})\\ &Na_2(3s_{1/2},3p_{3/2})+\hbar\omega\rightarrow Na_2(3p_{3/2},3p_{3/2})\rightarrow Na_2^+ + e^-, \end{aligned} \tag{1}$$

where ω is the radial frequency of the trapping laser, and the product molecular ion is in the ground electronic state. The final step, autoionization, can only take place if the doubly excited molecule can survive radiative decay long enough for the nuclei to approach a curve crossing with the molecular ion.

In the case of sodium, two photons from the trapping laser are sufficient to cause PAI; in rubidium, they are not. However, two color PAI in rubidium has been observed [5,6]. In that experiment, described by the reaction

$$\begin{aligned} &Rb_2(5s_{1/2},5s_{1/2})+\hbar\omega_1\rightarrow Rb_2(5s_{1/2},5p_{3/2})\\ &Rb_2(5s_{1/2},5p_{3/2})+\hbar\omega_2\rightarrow Rb_2^+ + e^-, \end{aligned} \tag{2}$$

$\hbar\omega_1$ comes from the trapping laser, while $\hbar\omega_2$ comes from a second, much higher frequency laser and directly photoionizes the molecule. This is unlike the case in sodium, in which a doubly excited molecule is created, which then autoionizes by means of a curve crossing with Na_2^+.

In the Letter presented here, PAI from a multiply excited quasimolecule formed in a MOT is measured. We speculate on the excitation pathway to the molecular ion and show the results of experiments that support this hypothesis. We also show that the molecular ion is formed not by direct photoionization, but rather by stepwise excitation to an autoionizing state in molecular rubidium. In the same series of experiments, we also measure the production of atomic rubidium ions. We speculate that these are produced through stepwise excitation to a neutral molecular curve which subsequently autoionizes upon approaching a dissociative curve of a molecular ion and shows experimental support for this process. This new process is referred to as photoassociative-dissociative ionization, or PADI.

The earlier work already described has become the basis for an entirely new system of ultrahigh resolution spectroscopy [7], for example [5,8], on the levels associated with the lowest electronically excited states of the intermediate molecule, $Rb_2(5s_{1/2},5p_{3/2})$, at large internuclear separation. The work presented here sets the stage for similar measurements on the hithertofore unmeasured—and only recently calculated [9]—multiply excited states associated with $Rb_2(5s_{1/2},4d_{5/2})$, $Rb_2(5p_{3/2},4d_{5/2})$, and $Rb_2(4d_{5/2},4d_{5/2})$.

Experimental setup.—For this work, a rubidium MOT was created inside a well-characterized momentum spectrometer.[10] The weak electric field (~10 V/cm) in the spectrometer extracts any ions produced; a subsequent drift region allows a flight time separation between the atomic and molecular products. The two external cavity diode lasers used to excite the cold target are referred to as $L1$ and $L2$, and have wavelengths of about 780 nm and 1529 nm, respectively. $L1$ was detuned 53 MHz to the red of the $5s_{1/2}$, $(F = 2) \rightarrow 5p_{3/2}(F' = 3)$ atomic transition while $L2$ was locked 53 MHz to the blue of the $5p_{3/2}(F = 3) \rightarrow 4d_{5/2}$ atomic transition, with unresolved hyperfine structure in the $4d$ state. Using acousto-optic modulators (AOMs), 50 ns pulses are extracted from both $L1$ and $L2$ and are superimposed both spatially and temporally on a cloud of cold ($\sim$150 μK) ^{87}Rb atoms in a MOT. Peak intensities are on the order of 100 mW/cm^2.

Figure 1 shows a typical time-of-flight (TOF) spectrum for this system. Although the spectrometer resolution is approximately 2 ns, the resolution of the TOF spectrum is limited by the width of the laser pulses to be about 50 ns. Several features in this spectrum are immediately obvious. First of all, the dominant structure, corresponding to Rb_2^+, is more than 2 orders of magnitude greater than the peak corresponding to Rb^+. Second, the Rb_2^+ peak shows a fast rise time followed by an exponential decay, whereas the Rb^+ peak is much broader, much more symmetric, and totally lacking in either an exponential decay or in any structure that would indicate direct photoionization [11].

The major question is, by what mechanism(s) are these ions produced? We propose the excitation or ionization paths shown schematically in Fig. 2. We believe that Rb_2^+ is produced by PAI; a photon from $L1$ first excites a state in the $\mathrm{Rb}_2(5s_{1/2}, 5p_{3/2})$ manifold of molecular states, the same starting point seen in other PAI experiments [5]. A photon is then absorbed from $L2$, exciting the molecule to a level in the $\mathrm{Rb}_2(5s_{1/2}, 4d_{5/2})$ manifold. A second photon from $L1$ is then absorbed, bringing the system to a level in the $\mathrm{Rb}_2(5p_{3/2}, 4d_{5/2})$ molecular manifold. The atoms move together along this bound potential curve until autoionization can occur at a curve crossing with a Rb_2^+ potential curve, leading to the final product. The proposed process can be expressed as

$$\begin{aligned}
&\mathrm{Rb}_2(5s_{1/2}, 5s_{1/2}) + \hbar\omega_1 \rightarrow \mathrm{Rb}_2(5s_{1/2}, 5p_{3/2}) \\
&\mathrm{Rb}_2(5s_{1/2}, 5p_{3/2}) + \hbar\omega_2 \rightarrow \mathrm{Rb}_2(5s_{1/2}, 4d_{5/2}) \\
&\mathrm{Rb}_2(5s_{1/2}, 4d_{5/2}) + \hbar\omega_1 \rightarrow \mathrm{Rb}_2(5p_{3/2}, 4d_{5/2}) \rightarrow \mathrm{Rb}_2^+ + e^-.
\end{aligned} \tag{3}$$

Here, $\hbar\omega_1$ and $\hbar\omega_2$ refer to photons from $L1$ and $L2$, respectively. From published molecular curve data [12], an $L1$ detuning of 53 MHz implies excitation of $\mathrm{Rb}_2(5s_{1/2}, 5p_{3/2})$ at an internuclear separation of about 1000 atomic units. Note the order of photon absorption is $L1$-$L2$-$L1$, rather than $L1$-$L1$-$L2$. We know that the latter route is not followed because after a resonant (due to the $1/R^3$ curvature of the $5s$-$5p$ levels) absorption of $L1$, another $L1$ would be $\sim$106 MHz red of resonance with the $5p$-$5p$ manifold, while an $L2$ would be on resonance with the $5s$-$4d$ manifold. Experimentally, we have seen that with the $L2$ pulse delayed with respect to the $L1$ pulse, the ionization rate is significantly reduced. If, however, $L1$ and $L2$ are pulsed simultaneously and some time later, $L1$ is pulsed again, we see significant ionization from the second $L1$ pulse. In the inset in Fig. 1, the first peak comes from the simultaneous $L1$ and $L2$ pulses while the second peak comes from the second $L1$ pulse, indicating that some fraction of the population is being stored in a $\mathrm{Rb}_2(5s_{1/2}, 4d_{5/2})$ state. However, we cannot completely rule out some small contribution from the $L1$-$L1$-$L2$ process.

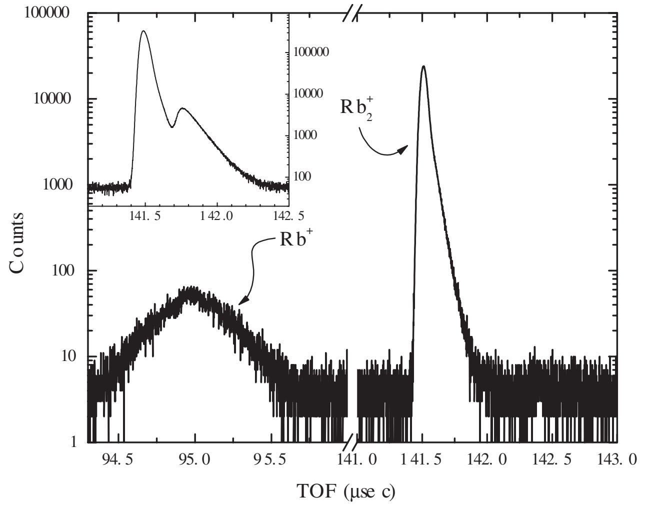

FIG. 1. Counts as a function of flight time. The peak on the left is due to Rb^+, and the peak on the right is due to Rb_2^+. The inset contains data from a different (longer) experiment that shows what the Rb_2^+ peak looks like when $L1$ and $L2$ are pulsed simultaneously and 300 ns later, $L1$ is turned on again, showing that the population moves through the relatively long-lived states near the $5s$-$4d$ asymptote. The longer lifetime on this second peak is because $L1$ is left on.

In the case of Rb^+, we propose the scheme also shown in Fig. 2 and by

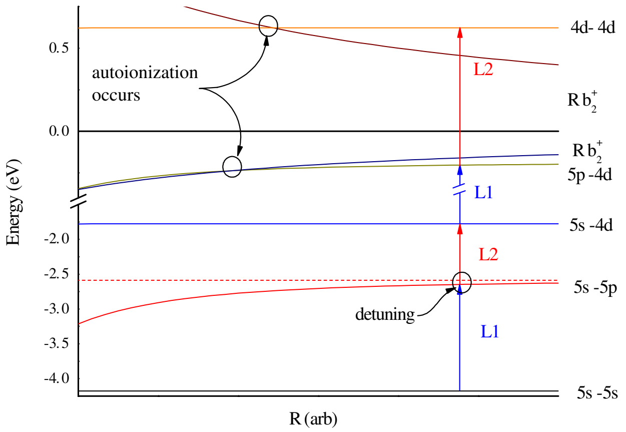

FIG. 2 (color online). Molecular energy levels showing the excitation paths for Rb^+ and Rb_2^+. The detunings and curvatures have been exaggerated for clarity. Note the change in scale above the axis break.

$$\begin{aligned} \mathrm{Rb}_2(5s_{1/2}, 5s_{1/2}) + \hbar\omega_1 &\rightarrow \mathrm{Rb}_2(5s_{1/2}, 5p_{3/2}) \\ \mathrm{Rb}_2(5s_{1/2}, 5p_{3/2}) + \hbar\omega_2 &\rightarrow \mathrm{Rb}_2(5s_{1/2}, 4d_{5/2}) \\ \mathrm{Rb}_2(5s_{1/2}, 4d_{5/2}) + \hbar\omega_1 &\rightarrow \mathrm{Rb}_2(5p_{3/2}, 4d_{5/2}) \\ \mathrm{Rb}_2(5p_{3/2}, 4d_{5/2}) + \hbar\omega_2 &\rightarrow \mathrm{Rb}_2(4d_{5/2}, 4d_{5/2}) \\ &\rightarrow \mathrm{Rb}(5s_{1/2}) + \mathrm{Rb}^+ + e^-, \end{aligned} \tag{4}$$

where the last step is due to autoionization outside a curve crossing with a dissociative state of Rb_2^+. We call this process photoassociative-dissociative ionization, or PADI.

In order to test the hypothesis that the excitation or ionization schemes follow those indicated in Eqs. (3) and (4), we measure the production rates of Rb^+ and Rb_2^+ as functions of $L1$ and $L2$ intensities. PAI should be quadratic in $L1$ and linear in $L2$ intensities, while PADI should be quadratic in both $L1$ and $L2$ intensities.

To control the intensities of $L1(L2)$ a voltage staircase signal was sent to an rf mixer and used to modulate the rf power driving the acousto-optical modulator (AOM) through which light from $L1(L2)$ was directed. The staircase consists of 16 steps each having a constant dwell time of about 10 seconds. When an ion, molecular or atomic, was observed, the voltage of the corresponding step was also recorded, allowing us to plot relative count rates for either Rb^+ or Rb_2^+ versus relative $L1(L2)$ intensity. Low laser intensities were used throughout so as to reduce the effects of saturation and nonresonant processes.

The lasers were pulsed in the following cycle which had a period of 7.2 μs: The trap laser was first turned off. After waiting 200 ns in order to allow the population to be completely optically pumped to the $F = 2$ ground state, $L1$ and $L2$ were pulsed on for 50 ns. After the atoms have relaxed to the ground state, the trap laser was turned on again. In total, the trap laser was left off for 500 ns out of each 7.2 μs cycle. In this way, the MOT's time-averaged population was undiminished as indicated by inspection of its average level of fluorescence. The length of the pulses allowed easy spatial and temporal overlap throughout the MOT. The staircase generators were run asynchronously from the laser cycles, ensuring that any systematic variations in the system were averaged out. It should be noted that turning the repump laser off at the same time as the trap laser did not noticeably alter the result.

Plots of the counts versus $L1$ and $L2$ power, with each beam having constant spot size of ~1 mm, are shown in Fig. 3. The statistical uncertainty in counts and relative laser powers are about the size of the data points. Simple models were constructed to compare with the measurements. The curves in Fig. 3 are fits to the data from the steady state solution of incoherent rate equations including spontaneous emission with the Einstein A and B coefficients as the fitted parameters. The dashed curves are fits for a simple two level system. The solid curves are fits of a system of four levels with 3 photons. The first and third transitions used are resonant with the same color light, the intensity of which is the independent variable. Both models include saturation effects; in the absence of saturation, the single photon model would yield a purely linear dependence of population on laser intensity, while the two-photon model would show a quadratic dependence on laser intensity. Clearly, as $L1$'s intensity is varied, both Rb^+ (PADI) and Rb_2^+ (PAI) production show a good agreement with the two-photon model. However, as $L2$'s intensity is varied, the single photon model gives a better fit with Rb_2^+ production while the two-photon model gives a better fit to Rb^+ production. This result is completely consistent with the production mechanism shown in Fig. 2 and Eqs. (3) and (4).

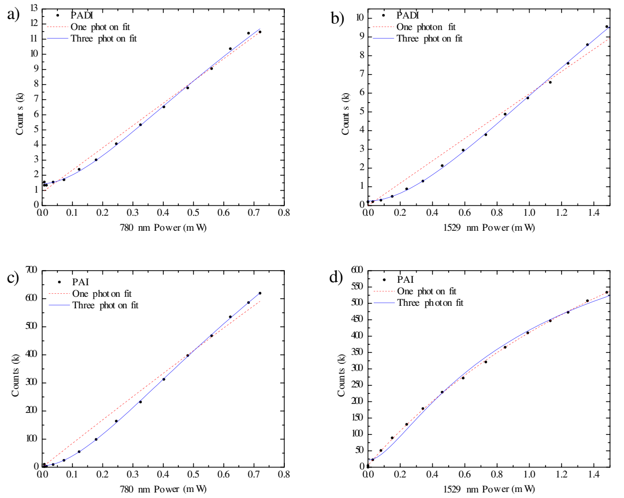

FIG. 3 (color online). Count rate as a function of $L1$ and $L2$ powers. (a) PADI vs $L1$, (b) PADI vs $L2$, (c) PAI vs $L1$, (d) PAI vs $L2$. The dashed lines are fits to one photon rate equations. The solid lines are fits to three photon rate equations with the first and third photons being the same color (the two-photon model).

The shape of the Rb_2^+ peak is suggestive of a 50 ns excitation pulse followed by exponential decay having a time constant of 42 ns. According to our model, this is due to radiative decay from $\mathrm{Rb}_2(5p\text{-}4d)$ as that molecular state approaches a crossing with a Rb_2^+ potential curve. However, it is not clear to us at this time why the lifetime is ~42 ns since at such large internuclear separations, one might expect a lifetime closer to that of atomic Rb($5p$). Perhaps the $5p$-$4d$ molecule has a somewhat unfavorable Franck-Condon overlap with the $5s$-$4d$ state.

Because the recoil spectrometer has been carefully characterized [10], the shape of the PADI peak in flight time can be converted into a kinetic energy distribution, as shown in Fig. 4. It should be noted that the width of this distribution is 3 orders of magnitude larger than one would expect for direct atomic photoionization and more than an order of magnitude smaller than expected from photodissociation. It is related to the distribution of internuclear separations at which autoionization of the Rb($4d$-$4d$) molecules takes place. That is, autoionization that takes

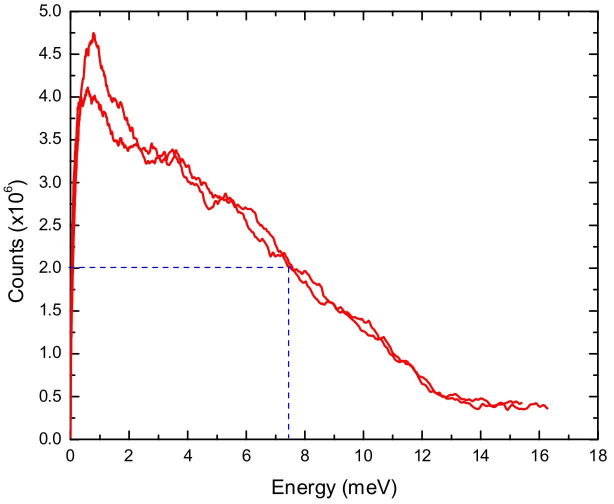

FIG. 4 (color online). The distribution of the kinetic energy of the Rb^+ ion is about 7 meV wide. What looks like two traces is a result of the conversion from time-of-flight to energy giving distributions from both rising and falling edges of the time-of-flight peak.

place at a particular internuclear separation R will give rise to $Rb^+ + Rb(5s)$ fragments having a shared energy of $P(R) - P(\infty)$, where P represents the relevant dissociative potential curve of Rb_2^+. Unlike the case discussed above for PAI, it is energetically possible for $Rb(4d\text{-}4d)$ to autoionize at any value of R greater than that for which there is a curve crossing with Rb_2^+. Since there are no calculated bound-free transitions that would result in the appropriate amount of kinetic energy anywhere near resonance with $L2$, it is unlikely that there is direct photodissociation of the Rb_2^+ molecule.

Summary.—In this Letter, we describe the measurement of atomic and molecular ions produced in a MOT interacting with laser light at 1529 and 780 nm. We propose a model in which the molecular ions are produced through photoassociation followed by stepwise excitation through a series of neutral molecular states and, finally, autoionization. This is essentially a generalization of PAI. We also propose a new mechanism for producing cold atomic ions; we call this process photoassociative-dissociative ionization, or PADI. We suggest that PADI is similar to PAI, but results in autoionization to a dissociative potential curve in the ionic molecule. We described experiments, the results of which support these models.

The identification of these cold collision processes leads to other questions. First of all, what determines the observed lifetime of the molecular level in the $5p$-$4d$ manifold? Second, precisely which molecular curves are involved in the sequential excitation process? That is, while we have identified the curves in the separated-atom limit, it is not yet known which of the many true molecular curves are involved. Finally, the shapes of highly excited molecular curves have not yet been determined. At the extremely large internuclear separations that these experiments suggest, it is likely that hyperfine structure dominates over spin-orbit. At least rudimentary determination of the structure of these molecular curves should be done in the future. Perhaps detailed spectroscopy on the excited molecular states from the $5s$-$5p$, $5p$-$5p$ and $5p$-$4d$ manifolds can be done in the same manner as has already been done on the $5s$-$5p$ manifold at smaller internuclear separations, using photoionization spectroscopy. Because excitation to Rb_2^+ can be done at much larger internuclear separations than is done with conventional PAI, the regime where the hyperfine interaction is comparable to or larger than the electrostatic interaction can now be explored. This will be the object of further inquiry. Similar work could also be done with ^{85}Rb and with the various j levels in the $5p$ and $4d$ manifolds.

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