

Ultracold ground-state molecule production in sodium

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We have observed the formation of ground-state Na₂ molecules via the spontaneous decay of excited molecules created by the photoassociation of ultracold atoms. We measure the binding energies of molecules created in three hyperfine components of the lowest singlet and triplet potentials of Na₂ by two different methods. Two of the features are purely triplet $a\ ^3\Sigma_u^+$ ($v=15$) (quasibound) states that have not been previously observed, while the third is a mixed $X\ ^1\Sigma_g^+ - a\ ^3\Sigma_u^+$ state. The molecules are detected with high-resolution cw laser ionization techniques and binding energies are measured to within 10 MHz.

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I. INTRODUCTION

A number of new techniques have provided sources of ultracold molecules for spectroscopic study. Recent progress has allowed the slowing and trapping of molecules with a permanent dipole moment [1] and species with magnetic moments have been trapped and sympathetically cooled with helium gas in a cryogenic magnetic trap [2]. In addition, the photoassociation of laser-cooled atoms has provided a source of ultracold diatomic molecules. Excited molecules created in this way can be vibrationally and rotationally selected, and are translationally as cold as the source of atoms that they are created from. While electronically excited molecules are now routinely created, it is only recently that the formation of radiatively stable, or metastable, “ground-state” molecules (in the lowest singlet or triplet potentials) has been detected in Cs [3–5], Rb [6], and K [7,8] photoassociation experiments. The present work reports observations of Na₂ molecule formation in the lowest triplet and mixed singlet/triplet potentials, via ultracold photoassociation. In addition, we have used cw laser ionization techniques to directly detect the product molecules in individual hyperfine-rovibrational states in these potentials with 10 MHz resolution.

The idea of molecule formation in the lowest singlet and triplet potentials via spontaneous emission following photoassociation was originally discussed by Thorsheim *et al.* [9]. (While spectroscopic convention restricts the designation of the electronic ground state solely to the $X\ ^1\Sigma_g^+$ potential, this state, in the region of interest here, mixes heavily with the $a\ ^3\Sigma_u^+$, the lowest triplet potential of Na₂. Because of this ambiguity, and also because both of these potentials dissociate to two $3S_{1/2}$ ground-state sodium atoms, we will refer to both the $X\ ^1\Sigma_g^+$ and the $a\ ^3\Sigma_u^+$ potentials as “ground states.”) Band and Julienne [10] later proposed a method for improving the production rate of ground-state molecules by following the photoassociation of cold atoms by an excita-

tion of the molecule to a Rydberg state. Such a state has a much better Franck-Condon factor for decay to stable ground-state molecules than most of the long-range states that are accessible directly in photoassociation. Nikolov *et al.* [8] used this technique to observe a variety of singlet ground states in K₂. Côté and Dalgarno have also discussed the feasibility of spontaneous-emission pumping schemes for molecule formation in the electronic ground state in Li photoassociation [11,12].

Fioretti *et al.* [3] first observed the formation of Cs₂ molecules in the lowest triplet state via the spontaneous decay of atoms photoassociated to the 0_g^- ($6S+6P_{3/2}$) “purely long-range” state in Cs₂ in a magneto-optical trap (MOT). The photoassociation in Cs could be induced either with an additional tunable laser, or directly by the trapping lasers themselves. This 0_g^- state has an unusual double-well structure wherein the inner turning point of the long-range well is at $\approx 15a_0$ (where $1a_0 \approx 0.0529$ nm), nearly matching the outer turning point of the upper bound states in the triplet ground-state potential. This provides unusually favorable Franck-Condon factors for spontaneous emission to these bound states. Cs₂ molecules in the lowest triplet state, formed in a MOT, have also been trapped in an off-resonant laser trap [4]. Gabbanini *et al.* [6] were able to observe Rb₂ in the lowest triplet potential formed in a MOT and to compare molecule formation in the different isotopes, ⁸⁵Rb and ⁸⁷Rb. Singlet ground-state K₂ molecules formed by photoassociation were observed by Nikolov *et al.* [7]. In each case the molecules were detected by a pulsed, resonant two-photon ionization technique. While providing a selective identification of the molecules in the presence of a large number of atoms, nanosecond pulsed lasers result in limited resolution, on the order of 1 GHz, and are not able to selectively address individual hyperfine states.

In the following we demonstrate that ground-state molecules can be formed via spontaneous emission into the highest-lying states at the ground-state asymptote of Na₂, in much the same way as has been demonstrated in the heavier alkali metals. Using cw lasers we are able to resonantly ionize the product molecules with MHz resolution, sufficient to select and identify individual rovibrational-hyperfine states. Our resolution is limited by the radiative lifetime of the ex-

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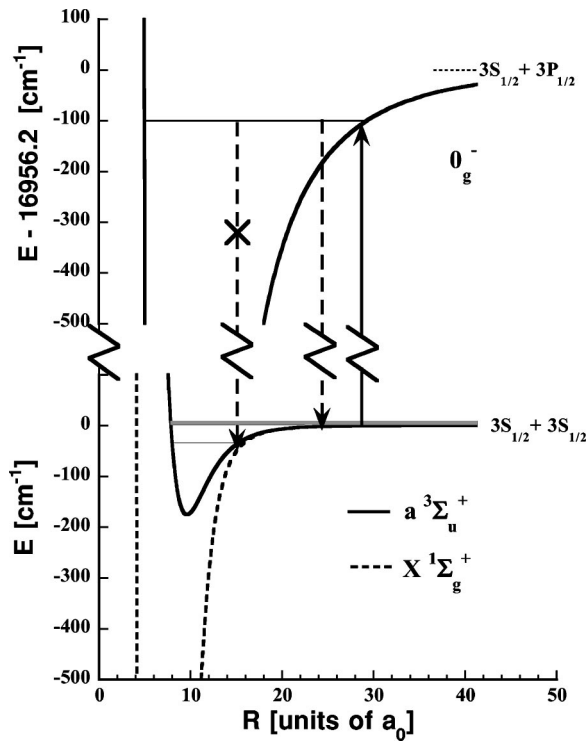


FIG. 1. Formation of triplet ground state molecules via spontaneous emission from the Na_2 0_g^- ($S+P_{1/2}$) state. The Rydberg-Klein-Rees potentials for these states show how the outer turning points of the ground-state vibrational levels will match the excited state vibrational levels accessible via photoassociation only for the last few bound states near dissociation (dashed arrow). Deeper levels will tend not to have good overlaps (dashed arrow with “X”). The wave function overlaps determine the efficiency of molecule formation. Without matching the outer turning points only very few states will accidentally have good Franck-Condon factors. The $a^3\Sigma_u^+$, $v=15$ state has a binding energy of ≈ 0.01 cm^{-1} and an outer turning point of $67a_0$.

cited state that we ionize through. The ionization efficiency is not known, so we cannot measure the absolute rate of molecule formation. Whatever the efficiency, these demonstrated ionization rates of several kHz set a lower bound on the rate of molecule formation in two different hyperfine components of the $v=15$ state of the $a^3\Sigma_u^+$ potential and in a mixed singlet/triplet state.

II. THEORETICAL AND EXPERIMENTAL CONSIDERATIONS

The alkali metals heavier than Na have been shown to produce ground-state molecules by spontaneous emission. Unlike Cs_2 , the 0_g^- ($3S+3P_{3/2}$) state in Na_2 does not have the fortuitous double-well structure described above. In general the lighter alkali metals also have the problem that the lower density of states due to the small mass makes the probability of decay to ground-state molecules much smaller. Without the favorable inner turning points of the purely long-range excited states to work with, the lighter alkali metals must rely simply on occasional favorable overlaps between the ground-state wave functions available and the typical

long-range excited states that are easily accessible by photoassociation, as is schematically shown in Fig. 1.

In our experiments we have chosen to photoassociate to vibrational levels in the 0_g^- ($S+P_{1/2}$) potential. This 0_g^- state is purely triplet in character and thus permits access to the $a^3\Sigma_u^+$ ground state. We have identified doubly excited states near the ($P_{3/2}+P_{3/2}$) asymptote [13] which permit us to resonantly ionize vibrational levels from this 0_g^- potential. (Unlike some other states in Na_2 [14] the 0_g^- states in the spectral region of interest do not ionize with a second photon of the photoassociation laser frequency.) The resonant character of the ionization permits us to selectively ionize individual vibrational levels of the 0_g^- potential and thus individual ground states. The $A^1\Sigma_u^+$ state is also a possible target state for photoassociation in order to access the mixed singlet-triplet states near the ground-state asymptote; however, this would suppress transitions to purely triplet states.

The most weakly bound, $v=14$ and $v=15$, vibrational levels in the $a^3\Sigma_u^+$ state have outer turning points of $34a_0$ and $67a_0$, respectively. Calculations of the Franck-Condon factors for transitions between the 0_g^- and $a^3\Sigma_u^+$ potentials show that transitions between vibrational levels in these two potentials are dominated by the wave function overlap at the outer turning points. Thus, in order to have a favorable probability for producing molecules in the $a^3\Sigma_u^+$ state, we need to choose a 0_g^- vibrational level with an outer turning point comparable to that of the target $a^3\Sigma_u^+$ vibrational level. Most potentials that dissociate to the $3S+3P$ asymptote are dominated by R^{-3} behavior at long range; however, the 0_g^- potential behaves as R^{-6} , as do the ground-state potentials. These considerations dictate that to reach the $v=15$ level of the $a^3\Sigma_u^+$ state we want to use a 0_g^- level bound by about 10 cm^{-1} . In general, photoassociation becomes more difficult as one tries to reach more tightly bound levels. In the current work we have concentrated on producing molecules in the $v=15$ level which can be reached via the relatively high-lying levels in the 0_g^- potential.

The present experiments are performed in a dark-spot MOT, described elsewhere [15], and this places most of the atomic population in the $f=1$ atomic hyperfine ground state at a temperature of approximately 500 μK . The small population remaining in the $f=2$ state will also play a role in the experiments.

III. EXPERIMENT

A. Autler-Townes spectroscopy

A number of ultracold photoassociation experiments that do not rely on spontaneous emission have been performed to locate the uppermost bound states in the ground state potentials of alkali-metal dimers. In these experiments the presence of bound states is detected by inducing an Autler-Townes splitting with a laser driving a transition between the excited state that the photoassociation laser is tuned to, and the ground states that one desires to locate. One laser, L1, is tuned to a photoassociation resonance with an excited state, inducing trap loss. A second laser, L2, is then tuned to drive

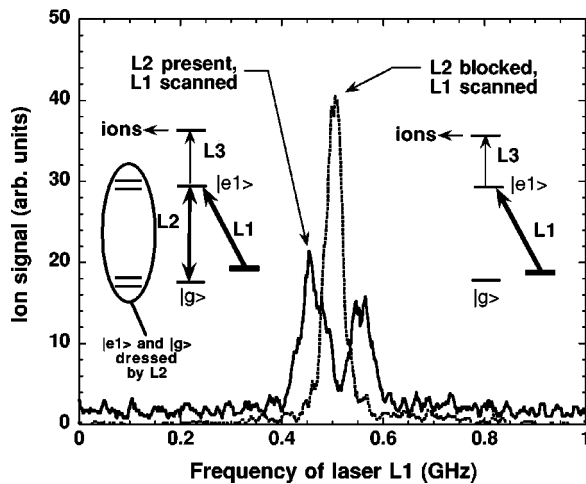


FIG. 2. Ion signal versus the detuning of laser L1. Laser L1 photoassociates atoms from the continuum to a molecular state $|e1\rangle$. Laser L3 is relatively weak and causes the resonant ionization of state $|e1\rangle$. A single peak, the unperturbed photoassociation line, is observed when laser L1 is scanned. When an additional laser L2 is tuned to a bound-bound resonance connecting the state $|e1\rangle$ to a ground molecular state, an Autler-Townes splitting of state $|e1\rangle$ is seen in the photoassociation line as laser L1 is scanned. This is indicated in the level scheme as the inset sketch in the oval showing the dressed-state picture of the apparent splitting of $|e1\rangle$ and the ground state to which it is coupled, dressed by photons of laser L2. The state $|e1\rangle$ in this case is the $0_g^-(S+P_{1/2})$, $v=105$, $J=1$ state at $16\,908.20\text{ cm}^{-1}$.

a bound-bound molecular transition between the excited state and a bound ground state. Driving this bound-bound transition causes an Autler-Townes splitting of the excited state and results in a reduction in the photoassociation rate, and thus a reduction in the trap loss.

Taking advantage of this effect the location of the ground-state resonances can be accurately determined by fixing L1 on the photoassociation transition and scanning the frequency of L2 and observing the trap loss. Abraham *et al.* were the first to use this technique to locate the last bound state in the lowest triplet potential of Li_2 [16]. The technique has also been applied in Rb [17], K [18], and Cs [19]. While the ground states are located, the formation rate of stable molecules in these ground states is not necessarily made large by driving the bound-bound transition in this way.

An alternative to the trap-loss technique just discussed is to detect via a modulated ionization signal. L1 is again tuned onto the photoassociation resonance. An additional laser L3 is then introduced to resonantly ionize the photoassociated, excited molecules from this state. The ionization gives a signal, which is then reduced when laser L2 is tuned through the bound-bound resonances [20]. As shown in Fig. 2, the Autler-Townes splitting can be easily observed by doing the opposite, fixing L2 on the bound-bound resonance and scanning L1 across the photoassociation resonance. The spectroscopy of some of the uppermost states (binding energy $<5\text{ GHz}$) of K_2 was also obtained by observing a modulated ion signal [18]. We have recently used this technique to locate a number of $a^3\Sigma_u^+$ states within 30 cm^{-1} of disso-

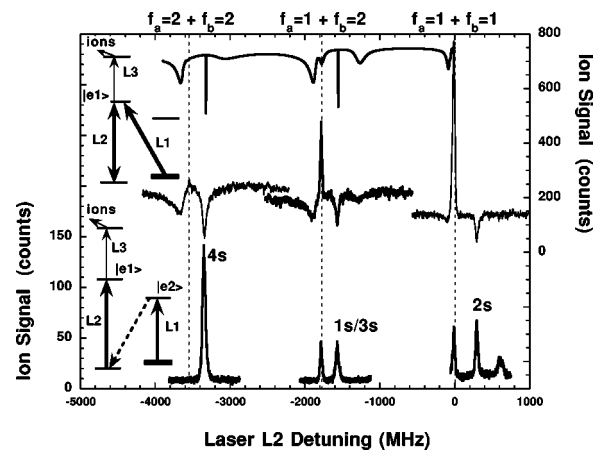


FIG. 3. Ionization signal versus the detuning of laser L2. The hyperfine asymptotes are indicated as vertical dashed lines and labeled across the top of the plot. The level diagrams next to the experimental traces indicate the corresponding photoassociation and detection procedures. Top trace: theoretical curve (offset for clarity) which reproduces the bound states as well as the d -wave shape resonances for negative detunings (see text). Middle trace: probe ionization versus detuning of laser L2 showing, as dips, the locations of the ground-state resonances. These dips are a consequence of the Autler-Townes effect, shown as a function of the detuning of laser L1 in Fig. 2. Additional photoassociation resonances appear as peaks. Lower trace: experimental scan showing the ionization of the ground-state molecules formed by spontaneous emission along with two additional photoassociation resonances (peaks at 0 MHz and -1770 MHz). The five resonances seen in the lower trace are identified in Fig. 4. The zero of the frequency scale indicates that L2 is tuned to drive two atoms from the lower, $f=1$, hyperfine state, and with zero collision velocity, to state $|e1\rangle$.

ciation [21] in Na_2 . A spectrum taken in this way, spanning 6 GHz near the ground-state dissociation limit, is shown in the central trace in Fig. 3. The identification of the spectral features is discussed below.

One obvious idea is that it might be possible to strongly drive transitions from free atoms to bound molecules as stimulated Raman transitions. Unfortunately, the same Autler-Townes splitting that makes detection of the transitions possible in the experiments discussed above will limit the molecule production rates obtainable with this technique. The Raman transition rate peaks and then begins to fall as the laser intensity on the bound-bound transition is increased. In addition, the lasers driving Raman photoassociation transitions to the bound ground state will also induce photodissociation transitions back to free atom states. Driven Raman photoassociation transitions to form ground-state molecules in Bose-Einstein condensates have been reported [22,23]. These experiments demonstrated extremely narrow trap-loss features to bound molecular states, but did not detect the product molecules. Molecule formation rates in such experiments are limited to being less than the rate at which ground-state molecules leave the interaction region.

B. Molecule formation by spontaneous emission

In lieu of working with driven Raman transitions, we have been able to detect the formation of ground-state molecules

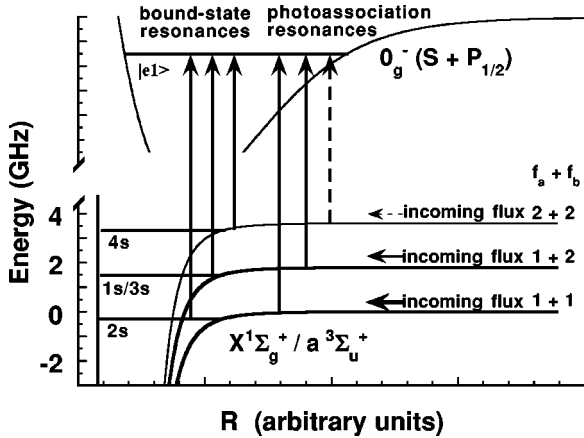


FIG. 4. Schematic plot of the adiabatic potential energy surfaces of Na_2 near the ground-state dissociation limit. The potentials in this region are highly mixed singlet-triplet potentials. The three transitions that produce ionization of bound ground-state molecules as well as the two photoassociation transitions apparent in Fig. 3 are indicated by the vertical arrows. Photoassociation from the 2+2 asymptote (dashed arrow) is possible, in principle, but the population of the $f=2$ atomic state is so small in the dark-spot MOT that this transition is suppressed. The levels are labeled by F_{tot} and ℓ . The upper two levels are $v=15$ $a^3\Sigma_u^+$ levels, while the state labeled $2s$ is a mixture of the $X^1\Sigma_g^+$ and $a^3\Sigma_u^+$ states.

following spontaneous emission, as in the heavier alkali metals. By tuning the photoassociation laser to an excited molecular state independent of the state that is resonantly ionized, we can look for ground-state molecules formed by spontaneous emission. The lower trace in Fig. 3 shows the result of such an experiment. In it many of the spectral features observed in the middle trace are again seen. The three peaks labeled “2s,” “1s/3s,” and “4s” are due to ionization of cold ground-state molecules, as discussed below. The dashed lines show the three dissociation limits of the $a^3\Sigma_u^+$ state. These correspond to atomic collisions with $f_a+f_b=1+1$, $1+2$, and $2+2$, where f_i indicates the total angular momentum of the hyperfine state of atom i . (See Fig. 4.) Each bound (or, for the upper two, quasibound) level lies about 200–300 MHz below a dissociation limit. In addition, there are two photoassociation resonances at the 1+1 and 1+2 asymptotes due to the photoassociation of two colliding $f=1$ atoms to the state $|e1\rangle$, and of one $f=1$ with one $f=2$ atom to the state $|e1\rangle$, respectively. (An additional photoassociation resonance would appear at the 2+2 asymptote but is suppressed by the relative lack of $f=2$ atoms in the MOT.) The origins of these features are indicated in Fig. 4.

The middle trace in Fig. 3, where both lasers L1 and L2 can connect the ground state to the same excited state $|e1\rangle$, has a baseline ionization signal due to the presence of laser L1. Peaks in the ion signal occur when laser L2 is scanned through a resonance where it can act as an additional photoassociation laser to this state. On the other hand, when laser L2 is tuned to a frequency where it connects $|e1\rangle$ to a bound ground state, the Autler-Townes splitting produces a “dip” in the ionization signal. When laser L1 photoassociates to a different excited state $|e2\rangle$, however, as in the bottom trace

in Fig. 3, the signal looks somewhat different. First, there is no baseline ionization signal since L1 no longer populates the state $|e1\rangle$, which is resonantly ionized. As L2 is scanned it will again produce peaks when it acts as a photoassociation laser to $|e1\rangle$, and the lower trace reproduces these peaks from the upper trace. Now, however, ground states that are populated by spontaneous emission from $|e2\rangle$ also produce peaks in the spectrum, with the peak heights approximately proportional to the population in each state.

The zero of detuning in Fig. 3 implies that laser L2 is tuned to drive a transition from the excited level $|e1\rangle$ to a zero-energy collision of two $f=1$ atoms. Bound states appear at positive detunings while Feshbach and shape resonances above the $f_a=1+f_b=1$ collisional threshold appear at negative detunings. Laser L1 is tuned onto the peak of the photoassociation line shape, which in this case is -10 MHz from the location of the photoassociation resonance [24].

For the data in the middle trace of Fig. 3 state $|e1\rangle$ is the $0_g^-(S+P_{1/2})$, $v=119$ [25], $J=0$ feature at 16945.94 cm^{-1} . For the lower trace in Fig. 3 states $|e1\rangle$ and $|e2\rangle$ are the $0_g^-(S+P_{1/2})$, $J=0$ features for the $v=123$ and 119 vibrational levels at 16951.10 cm^{-1} and 16945.94 cm^{-1} , respectively. The laser intensities used to obtain the lower trace in Fig. 3 are $L1=340\text{ mW/cm}^2$, $L2=0.36\text{ mW/cm}^2$, and $L3=28\text{ mW/cm}^2$.

IV. ANALYSIS

The upper trace of Fig. 3 is a theoretical simulation of the experiment shown in the middle trace. The theoretical simulation depicts the transition strength between $|e1\rangle$ and two colliding Na atoms at a collision energy E/h (equal to minus the detuning of laser L2) above the $f_a=1+f_b=1$ collisional threshold. The theoretical trace is only calculated for negative detunings. The calculation of the transition amplitude is similar to that discussed in Ref. [26]. In Ref. [26], however, an $A^1\Sigma_u^+$ rovibrational level was used for $|e1\rangle$ and consequently pure triplet features were absent. Here, $|e1\rangle$ is a $0_g^-(S+P_{1/2})$, $v=119$, $J=0$ rovibrational level. From symmetry arguments it follows that this level can only contain $\ell=0$ and 2 partial waves, where ℓ is the nuclear mechanical angular momentum. Selection rules of the transition dipole moment then imply that only s - and d -wave collisions contribute to the line strength.

The agreement between theory and experiment is remarkable given the simplicity of the model. A complete calculation would require treatment of the multiphoton processes appearing in the experiment as well as the complicated spin structure in the molecule. Such modeling falls outside the scope of this paper. A low-intensity perturbative two-photon model ignoring the spin structure and in the spirit of Ref. [27], however, suggests that our experimental signal is, in fact, roughly proportional to the single-photon transition strength.

Three kinds of features can be observed in the theoretical simulation: Two extremely narrow dips detuned about 200 MHz to the blue of the $f_a=2+f_b=2$ and $f_a=1+f_b=2$ asymptotes, three asymmetric dips, each detuned about 100

MHz to the red of one of the three hyperfine asymptotes, and two weaker dips detuned about 500 MHz to the blue of the $f_a=2+f_b=2$ and $f_a=1+f_b=2$ limits. All states can be labeled by the good quantum numbers F_{tot} and the mechanical angular momentum ℓ . The total atomic angular momentum is defined as $\vec{F}_{tot}=\vec{f}_a+\vec{f}_b$.

In addition to the features appearing at negative detunings in the theoretical curve in Fig. 3, a truly bound state located at a detuning of +293(10) MHz has been observed in both experimental scans. It is a mixed singlet-triplet state with $\ell=0$, $I_{tot}=3$, and $F_{tot}=2$ symmetry and labeled $F_{tot}\ell=2s$. A bound state with $F_{tot}\ell=0s$ symmetry should lie nearby; however, its strength is five times smaller than that of the $2s$ state and it is likely to be unresolved.

The two narrow resonances in the theoretical curve are purely triplet states with $\ell=0$ and $F_{tot}=4$ for the state near $f_a=2+f_b=2$, and $F_{tot}=1$ and 3 for the state near $f_a=1+f_b=2$. The total nuclear spin I_{tot} of both states is 3. The states are quasibound and decay into the open $f_a=1+f_b=2$ and/or $f_a=1+f_b=1$ continua. Only a weak magnetic electron-spin–electron-spin interaction causes these two states to dissociate. Consequently, the features are very narrow in the theoretical simulation. In the middle trace the experimental linewidths are limited by the thermal broadening in the entrance channel as well as power broadening due to lasers L2 and L3. The experimentally observed widths in the lower trace are also due to coupling to the ionization channel. The measured locations of these features, obtained by a fit to the two-color line shapes of Ref. [27], are $-3343(10)$ MHz and $-1568(10)$ MHz. Uncertainties are one standard deviation, combined statistical and systematic uncertainties. Good agreement is found on comparing the above locations to those of the peaks in the lower trace, fitted to Lorentzian line shapes.

The three asymmetric dips to the red of each dissociation limit are overlapping $F_{tot}=0$ and 2, d -wave shape resonances. The width of the theoretical features is approximately 100 MHz, corresponding to a 1–2 ns decay time. The asymmetric dip near the $f_a=1+f_b=1$ limit in the middle experimental scan is obscured by the strong photassociation line. Finally, the weaker dips are $F_{tot}=2$, s -wave Feshbach resonances. Only the dip near -1300 MHz is observed in the experiment. The total nuclear spin is not a good quantum number for these five states. These features are not observed in ionization after spontaneous emission because the spontaneous emission into the collisional continuum is spread over many kelvin in range, and therefore the signals are too weak.

Thus far we have only observed production of molecules by spontaneous emission into the $a^3\Sigma_u^+$ $v=15$ and $v=14$ levels (or states that mix with these). These are the only states with appreciable Franck-Condon overlaps with the excited states used. We have calculated a Franck-Condon factor of 0.049 for the $0_g^-, v=119$ state decaying to $v=15$ of the $a^3\Sigma_u^+$ state, and 0.046 for $0_g^-, v=123$ to $a^3\Sigma_u^+, v=15$. The overlaps of these states with $v=14$ of the $a^3\Sigma_u^+$ state are 8.8×10^{-5} and 4.9×10^{-6} , respectively, so we do not

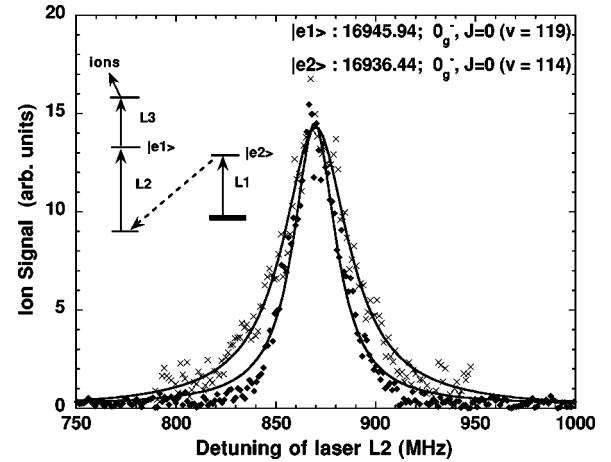


FIG. 5. Ion signal versus laser detuning for ionization of the last bound state 293(10) MHz below the $f=1+f=1$ atomic asymptote. The zero of the frequency scale is the $1+1$ photoassociation transition to the excited state. The smooth curves are Lorentzian line shapes that were fitted to the data. Linewidths of 40 MHz for L1, ≈ 360 mW/cm²; L2, ≈ 80 μ W/cm²; L3, ≈ 32 mW/cm², and 25.5 MHz with L1, ≈ 360 mW/cm²; L2, ≈ 0.2 μ W/cm²; L3, ≈ 1.6 mW/cm² were found. The linewidths are limited by the presence of lasers L2 and L3.

expect to find any significant population in $v=14$ when we excite through them, and we have not observed any. In such a case most of the excited molecular population is expected to spontaneously decay to free-atom states. Changing the excited state to a more deeply bound 0_g^- state with more favorable Franck-Condon factors allows us to populate the $v=14$ level and we have observed ionization from molecules in these levels as well, although we have not studied this in detail.

The mixed singlet-triplet character of the $F_{tot}\ell=2s$ state has recently allowed it to be observed using a very similar technique in Na molecular beam experiments [26,28]. In these experiments singlet ground-state molecules are optically pumped into high-lying states and laser-induced fluorescence is observed by driving population to a vibrational level of the $A^1\Sigma_u^+$ state. A second laser drives a Raman transition to the ground states, Autler-Townes-splitting the transition and reducing the fluorescence. These experiments, because they use the “A” state as the intermediate, are primarily able to observe ground states of singlet character and so do not couple to the purely triplet states near the higher asymptotes. In the present experiments we have measured the location of three bound or quasibound states near the dissociation limits and have reduced the uncertainty in the location of the last $F_{tot}\ell=2s$ bound state from 30 MHz [26,28] to 10 MHz. This should enable an even more accurate determination of the triplet scattering length for Na, if desired.

An example of high-resolution scans over the uppermost truly bound state, the $F_{tot}\ell=2s$ state located 293(10) MHz below the $1+1$ asymptote, is shown in Fig. 5. The scans are taken at two different sets of laser powers. The linewidths obtained are 40 MHz with the intensities of the lasers as follows: L1, ≈ 360 mW/cm²; L2, ≈ 80 μ W/cm²; L3,

≈ 32 mW/cm², and 25.5 MHz with intensities of L1, ≈ 360 mW/cm²; L2, ≈ 0.2 μ W/cm²; L3, ≈ 1.6 mW/cm². The linewidths obtained are limited by the presence of the lasers L2 and L3. Both of these lasers affect the width of the resonance, as they couple in the widths of the singly and doubly excited states on the ionization path and potentially destroy the molecules by other photodissociation paths as well. The resonance continues to narrow as each of the two lasers is reduced in intensity until the signal-to-noise ratio is too small to work with. Presumably the presence of laser L1 affects the linewidth as well. While the $F_{\text{tot}}\ell = 3s$ and $4s$ resonances are, in fact, only quasibound, their observed linewidths are also dominated by the same induced ionization decay in these experiments. In particular, we have not observed any evidence of additional broadening due to tunneling to the open channels.

When the photoassociation laser is removed the ground state molecule signal decays on a time scale of several microseconds. The lifetimes of the ground molecular states are expected to be much longer than this—decaying primarily by collisional vibrational relaxation on millisecond time scales. Molecules would also fall out of the trap in several milliseconds, limiting the linewidth in this way as well. The bound state below the $1+1$ asymptote would presumably have a linewidth on the order of 1 kHz without the ionization lasers present, as was found for the Rb₂ states in [22]. The ionizing laser L3 was not turned off during these measurements and we have evidence that its presence also contributes to the relatively rapid decay of this state. The microsecond lifetimes do, however, rule out any possibility that an excited-

state molecular population is somehow confusing our measurements.

V. SUMMARY

Absolute production rates for ground-state molecules in our experiment are difficult to establish, as the efficiencies of both the ionization steps and the autoionization probability from the doubly excited state are difficult to determine. Ionization rates of several kHz have been obtained, however, and this sets a lower limit on the production rate of molecules in the individual hyperfine levels.

We have demonstrated that Na₂ molecules can be formed in the lowest triplet or mixed singlet-triplet ground-state potentials via the spontaneous decay of molecules formed by photoassociation. There are, however, only a few states that extend to large enough internuclear distances to have been populated appreciably in this way in these experiments. Nonetheless, product molecules were detected in individual hyperfine states with cw laser ionization techniques. We have located three of these states to within 10 MHz, an accuracy which may be used to improve the triplet ground-state scattering lengths. One option for producing molecules in more deeply bound levels is to start with the spontaneous emission process observed here and then use established bound-bound or STIRAP (stimulated Raman adiabatic passage) techniques [29] to transfer the population to the desired level.

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