

Coherent optical association of single molecules

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We report on coherent association of a single weakly-bound NaCs molecule in an optical tweezer through an optical Raman transition without the use of a Feshbach resonance. Our scheme borrows transition dipole moment while reducing photon scattering by selecting a deeply bound electronic excited intermediate state. Starting from two atoms in their relative motional ground state, we achieve optical transfer efficiency of 50% . The molecule has a (change to 8.8G) zero-field binding energy of 770MHz and lifetime up to 1ms . (center of mass motional state population.) This technique is general (does not rely on narrow excited state linewidth) and could allow a wider range of molecular species to be assembled atom-by-atom.

Trapped neutral molecules, assembled in an array of optical tweezers, are a promising platform to study quantum information and quantum simulation. (more detail to add here about applications?).

Production of ultracold molecules in optical tweezers is challenging due to their internal degrees of freedom including rotation and vibration. In certain molecular species with relatively closed cycling transitions, direct laser cooling remains a viable option. However, for many species, including NaCs, the vibrational branching ratios are unfavorable, making direct laser cooling challenging. In these systems, a bottom-up approach of assembling the molecule from its constituent atoms has been demonstrated both in bulk gas and in optical tweezers. The challenge in a bottom-up approach is the vastly different length scales between the free atoms and a ground state molecule, leading to small coupling between them. For atoms in the motional ground state in the tweezer, the average distance between the two atoms is about $1000a_0$. However, for the ground rovibrational molecule, the bond length is only around $4a_0$. Because of this, it is necessary to use an intermediate state with a size in between the initial and final states, and accomplish the transfer in two steps in order to increase the coupling.

The traditional choice for such an intermediate state is a weakly-bound Feshbach molecule, which can be coherently produced by ramping a magnetic field across the Feshbach resonance . However, this requires a suitable Feshbach resonance, which limits the generality of this technique. An alternative approach uses a weakly bound ground electronic molecular state as the intermediate state (I'm wondering how we can distinguish this weakly bound molecular state from the weakly-bound Feshbach molecule state, we can maybe specify typical binding energies? "most weakly bound state of the low field ground state electronic potential" maybe?), populated by an optical Raman transition, schematically shown in figure . In this scheme, a pair of Raman beams is used to drive

the unbound, but confined, atoms to a bound molecular state via an excited molecular state. This approach minimizes the reliance on system specific properties and can therefore be more generally applied to creating other molecules. Such a transfer using an optical transition has been observed in previous experiments . However, they either require the use of a narrow optical transition which limits the generality or were driving the transition incoherently due to scattering.

In this Letter, we theoretically determine the best initial hyperfine combination of the atoms to use and best single photon frequency that balances coupling/transfer efficiency and photon scattering. Using these parameters, we demonstrate coherent association of a electronic ground-state molecule from two atoms via an optical Raman transition in an optical tweezer.

Even for this first step transfer to a weakly bound molecular state, it is still a challenge to achieve high Raman Rabi frequency to drive this transition due to the wavefunction size mismatch with the excited molecular state. Due to the small size of the molecular wavefunction, the coupling between the ground atomic state and the excited molecular state is approximately proportional to the value of the relative atomic wavefunction at short distance within the molecular potential. In addition to the confinement, this value is related to the interaction between the two atoms. For states with a large scattering length (positive or negative), the phase shift in the relative wavefunction between the atoms can significantly increase the short range wavefunction (add figure?). The increase in the coupling is proportional to (quote/cite Olive's equation?). For our system, among the stable spin combinations, 4422 and 3311 has a small scattering length of $|a| = \dots$ respectively and 3322 has a large and negative scattering length. (interaction shift \approx binding?) Thus, we use the 3322 spin combination as our initial state and drive to the first bound state for the 3322 spin combination.

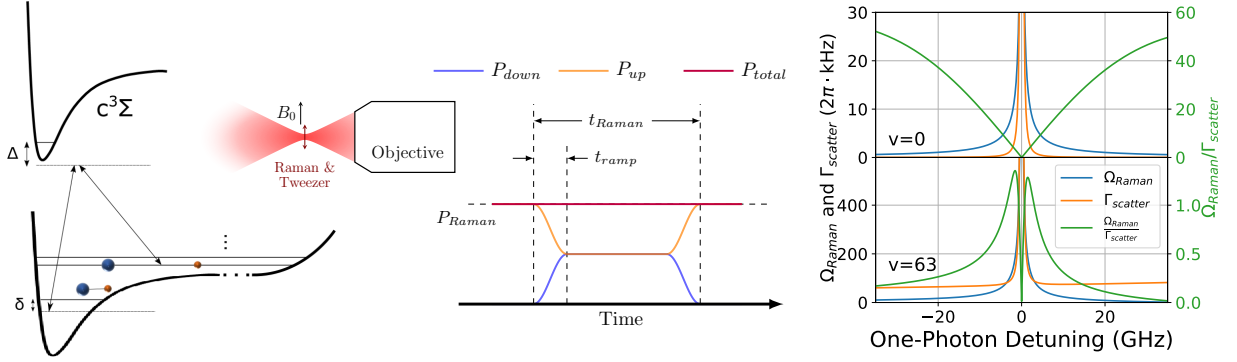


FIG. 1. Optical creation of single molecule from single atoms in tweezer. (A) Schematics of the Raman transition. (B) Geometry and polarization of trap and Raman beam relative to the bias magnetic field. (C) Molecule formation pulse sequence. The tweezer initially consists of only up leg power. This power is smoothly ramped down and the down leg power ramped up over $10\mu s$ while maintaining the total power of the tweezer.

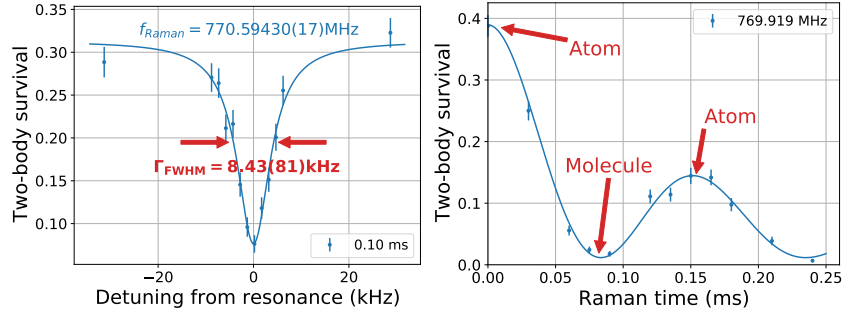


FIG. 2. (A) Raman resonance from atomic state to molecular state, showing Fourier limited linewidth. (B) Rabi oscillation on resonance

In addition to the choice of initial state, the choice of the intermediate state also plays a role. Previous experiments use weakly bound molecular excited states in the Raman transition to increase the Raman Rabi frequency. However, this choice of state also increases the scattering during the transfer process for two reasons. Firstly, since for a typical molecular potential the spacing between states decreases with increasing vibrational levels, a weakly bound excited molecular state limits maximum usable detuning and therefore the effectiveness of scattering reduction by increasing the detuning for the Raman transition. Secondly, due to size similarity, the weakly bound molecular ground state has a strong coupling with the atomic excited state which contributes significantly to the total scattering rate. The rate of such scattering process is proportional to $1/\delta_{thresh}^2$, where δ_{thresh} is the detuning from the dissociation threshold. (Should we also mention scattering of the atomic initial state too? This should affect the Raman process as well) Based on these considerations, we calculated both the Raman Rabi frequency and the scattering rate at different detunings. As seen in figure (1....), despite a higher Raman Rabi frequency at the same detuning, using a weakly bound

intermediate state results in a much higher scattering rate and ultimately a smaller Rabi frequency to scattering rate ratio as compared to deeply bound states. As a result, we use a deeply bound molecular excited state to drive the Raman transition.

(goes to SM?)

(mention scattering/lightshift depends on up/down matrix element ratio?)

Our experiment begins by loading a single ^{23}Na atom and a single ^{133}Cs atom into an optical tweezer from a dual-species MOT into separate optical tweezers. The atoms are imaged to distinguish between loading of two atoms, one atom (Na or Cs), or no atom during post selection. We then perform simultaneous Raman sideband cooling (RSC) to cool both atoms into the 3-dimensional motional ground state of their optical tweezers. After RSC, the Na tweezer is moved by sweeping the frequency on an acoustical optical beam deflector (AOBD) to overlap with the Cs tweezer before smoothly ramping off rso that the Na and Cs atoms are merged into the same tweezer. The spin states for the Na and Cs atoms after RSC and during the merge process are $|F=2, m_F=2\rangle$ and $|F=4, m_F=4\rangle$ respectively. This states combina-

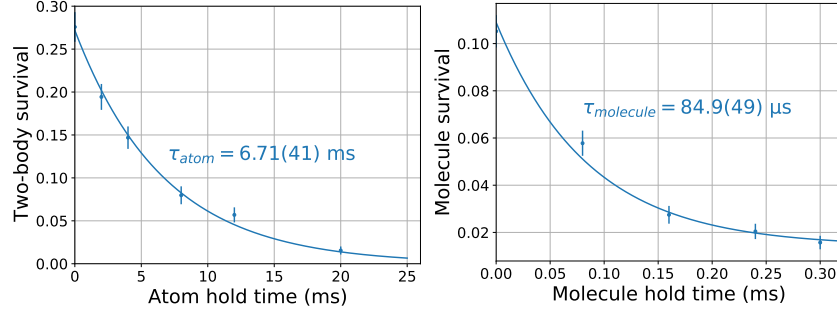


FIG. 3. (A) Two-body atom lifetime in 15 mW of trap depth (B) Molecule lifetime in 15 mW of trap depth

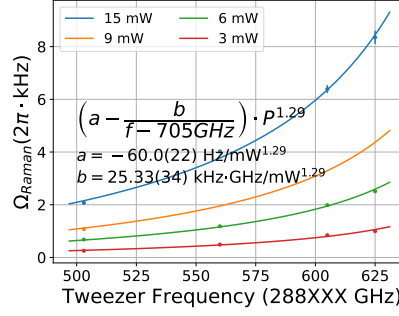


FIG. 4. Raman Rabi frequency vs detuning

tion has a low scattering length of $\dots a_0$ which allows the two atoms to be merged into the same tweezer with minimum perturbation on each other and thus they remain in the motional ground state after the merge.

After preparing the Na and Cs atoms in the same tweezer in a single quantum state, we need to drive the atoms into the large scattering length 3322 hyperfine combination. To do this, we perform interaction shift spectroscopy using a Cs Raman transition to drive the Cs into the $|F = 3, m_F = 3\rangle$ state (Is this really "performing spectroscopy"? Or should we just say we drive a Raman transfer to flip the spin). The new spin state combination has a larger scattering length of $\dots a_0$ which generates a interaction shift of $\dots \text{kHz}$ in the tweezer. This interaction shift is larger than the differential axial trapping frequency between Na and Cs atoms, which decouples the relative and center of mass motional state and improves the robustness of our preparation of relative motional ground state.

After the atoms are prepared in the 3322 hyperfine combination, we then perform the Raman transfer. The pulse sequence for this step is shown in figure (). Instead of adding another beam to drive the Raman transition on the atoms in the tweezer, we use the tweezer itself to achieve this goal. The dual use of the tweezer beam ensures that there is not any undesired laser frequency that can interfere with the Raman transition, and also allows us to maximize the Raman Rabi frequency and minimize

the transfer time (also minimize source of scattering). After the total tweezer power is set to the desired value, we smoothly ramp down the power of one frequency in the tweezer while simultaneously ramping up the power of a different frequency so that the total tweezer power remains unchanged. Both frequencies are kept on for a variable length of time before the process is reversed and we return to having a single frequency in the tweezer.

We locate the Raman resonance for the atom to molecule transition at $770 \dots \text{MHz}$ (figure) with a 15 mW tweezer at $288 \dots \text{GHz}$ which corresponds to a $\dots \text{GHz}$ single photon detuning. (We can maybe add information about the prediction here?) The background level of $\dots \%$ corresponds to the probability of preparing the two atoms in the relative motional ground state using interaction shift spectroscopy (can this be considered "interaction shift spectroscopy"?). When the atoms are transferred into the molecule state by the Raman transition, there is a decrease in the two body survival since the resulting molecule is not directly detected by our imaging step. We observed the narrowest linewidth of $\dots \text{kHz}$ for the Raman resonance at a pulse time of $\dots \text{ms}$, which corresponds to a linewidth-pulsetime product of \dots . This is consistent with the expected value of \dots for an ideal π pulse which is an evidence that the transfer is coherent. In order to verify the coherence of the transfer directly, we fixed the Raman frequency on the resonance and scanned the pulse time. figure ... shows the observed

Rabi oscillation between the atomic and molecular states. Fitting the data with a decaying Rabi oscillation suggests that ..% of initial ground state atoms are transferred into the molecular state.

In order to understand the fidelity of molecule formation, we fit our measurements to a model that includes a Raman Rabi frequency and a finite lifetime for the final molecular state (figure 3...). The effect due to atomic state loss was taken into account by measuring the single and two body lifetime of the atoms directly (figure 3...). The fit shows that we have a Raman Rabi frequency of The molecule we form has a lifetime of ... which is the main limitation on the fidelity of the transfer. The molecule lifetime can be verified directly by adding a second Raman pulse to dissociate the molecule back to atoms after a variable wait time (figure 3...). The result shows a molecular lifetime consistent with our fitting of the Raman transition data.

The ratio of molecule scattering rate and the Rabi frequency is larger than the theory prediction. In order to understand the origin of this discrepancy, we measured the dependency of the Raman resonance as a function of the tweezer power and frequency. The important results from the fits are resonance frequency (light shift), Raman Rabi frequency, atomic lifetime and molecular lifetime, each provide us information about a different combination of physical processes.

First we look at the change in resonance frequency. As a function of the tweezer power, we observed a linear dependency on the resonance frequency caused by the differential light shift between the atomic and molecular state (figure ?). When we vary the tweezer frequency around the $v = 0$ excited state, we can further observe a $1/\delta$ component and a background component that is constant for different detunings. The background is caused by coupling to all the other excited states that are further away which is not very important in this case. The $1/\delta$ component, however, is due to the coupling to the $v = 0$ excited state and from equation (?) we know that this is mainly due to the coupling between the excited and ground molecular states. From this, we can calculate a down leg matrix element of which is similar to what we calculated from theory (ref/sm theory). (make sure theory part mentions $\Omega_{down} \gg \Omega_{up}$, also Ω vs Ω' for the single leg vs cross coupling number).

(talk about blue side?)

The Raman Rabi frequency shows a non-linear dependency on the tweezer power due to the change in the atomic wavefunction caused by the change in confinement. The up leg matrix element scales with the short length atomic wavefunction amplitude which is 0.375 for weakly interaction particles. However, due to the strong interaction between the two atoms, this approximation breaks down. Instead, theory calculation shows that the scaling is very well approximated by a power of 0.29 within the range of confinement in our experiment. Combined with the intensity factor of the Raman beams, the Raman Rabi frequency should scale with 1.29 power of the tweezer intensity, which agrees with our experimental result. Similar to the light shift, there is also a background component and a $v = 0$ component in the Raman Rabi frequency. The $v = 0$ component predicts a up leg Rabi frequency of ... which is consistent with theory. Unfortunately, the background Raman Rabi frequency cancels the Rabi frequency for red detuning Raman transition which is one of the factors that decreases our transfer efficiency. (need blue side?)

The molecule lifetime measured in the experiment is ... larger than the expected value of ... calculated from By measuring the lifetime for different tweezer powers, we observed a linear dependency of the lifetime (fig ...). This confirms that the short lifetime is mainly caused by scattering from the tweezer light rather than the intrinsic lifetime of the molecule itself. Additionally, we also measured the loss rate as a function of the tweezer frequency (fig ...) which shows only a very weak dependency for a ...x change in the detuning from the $v = 0$ excited state. This result is significantly different from the $1/\delta^2$ dependency expected from off-resonant scattering and suggests that the main source of the scattering is due to a broad-band process that is not directly related to the $v = 0$ excited state. (ASE filter?)

B field dependency $\dots kH_z/G$ which agrees with theory prediction of $\dots kH_z/G$. Dependency on tweezer power $\dots kH_z/mW$, extrapolated to obtain the bare resonance at 0 tweezer power to be at $\dots MHz$.

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