

# Coherent optical association of a single molecule

Yichao Yu,<sup>\*</sup> Kenneth Wang, J. D. Hood, Lewis Picard, Jessie T. Zhang,  
William Cairncross, Jeremy Hutson, Till Rosenband, and Kang-Kuen Ni<sup>†</sup>

*Department of Chemistry and Chemical Biology,*

*Harvard University, Cambridge, Massachusetts, 02138, USA*

*Department of Physics, Harvard University, Cambridge, Massachusetts, 02138, USA and*

*Harvard-MIT Center for Ultracold Atoms, Cambridge, Massachusetts, 02138, USA*

(Dated: September 19, 2020)

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.

Diverse species of fully quantum controlled ultracold molecules are desired for a wide variety of applications including precision measurements [1], quantum simulations [2], quantum information processing [3, 4], and the studies of ultracold chemistry. While many innovative approaches demonstrated in the last few years have directly cooled different species of diatomic or polyatomic molecules below 1 mK [5], the coldest and the highest phase-space-density gas to date in an ensemble [6] or as individuals [7] have been achieved through the associations of ultracold atoms.

Such ultracold molecular associating takes advantage of the much developed cooling and trapping techniques for atoms as a starting point. To overcome the challenges of small wavefunction overlap and the large release of binding energy of converting atoms to deeply-bound molecules, an established two-step approach have been taken to first associate atom pairs into weakly-bound molecules, then transfer the molecules from one internal state to a desired rovibrational and electronic state [8–16]. So far, all of such association process utilize a magnetic Feshbach scattering resonance. The only exception is  $\text{Sr}_2$  [17, 18] where narrow excited states are available and optical association can be driven. The requirement of a Feshbach resonance to enhance atom-to-molecule wavefunction overlap (and the narrow excited state) limits the generality of the association technique to more diverse species of molecules which are needed (or picked) for a desired application.

Here, we demonstrate coherent association of an atom pair to a weakly bound molecules using an optical Raman transfer via an electronic excited state, without the use of a Feshbach resonance nor a narrow excited state. Our scheme is based on theoretically determined most suitable vibrational state of the electronic excited state  $c^3\Sigma$  that balances coupling/transfer efficiency and photon scattering. Furthermore, to reduce technical requirements such as intensity stability, etc , we choose a initial

and final state ... This approach is general and can be use to associate other molecular species or large molecules atom-by-atom.

While optical Raman transfer of atoms to molecules utilizing an electronic excited state has been shown previously. Those demonstrations were incoherent where the signal comes from loss of population (and therefore more like spectroscopy and the transferred molecules cannot be further utilized). The challenge lies at achieve high enough Raman Rabi frequency to drive this transition due to the wavefunction size mismatch with the excited molecular state. 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  $\delta_{thresh}$  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.

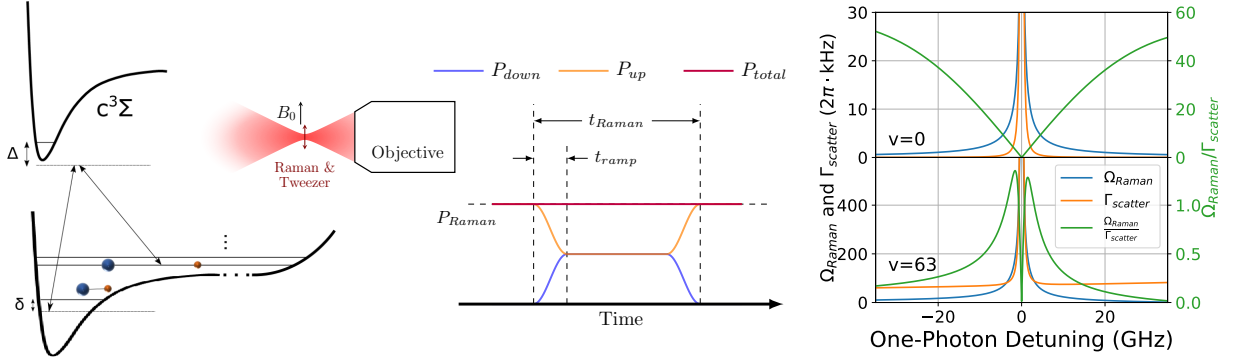


FIG. 1. Optical creation of single molecule from single atoms in tweezer. (A) Schematics of the Raman transition. (B) Geometry and polarization of trap and Raman beam relative to the bias magnetic field. (C) Molecule formation pulse sequence. The tweezer initially consists of only up leg power. This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

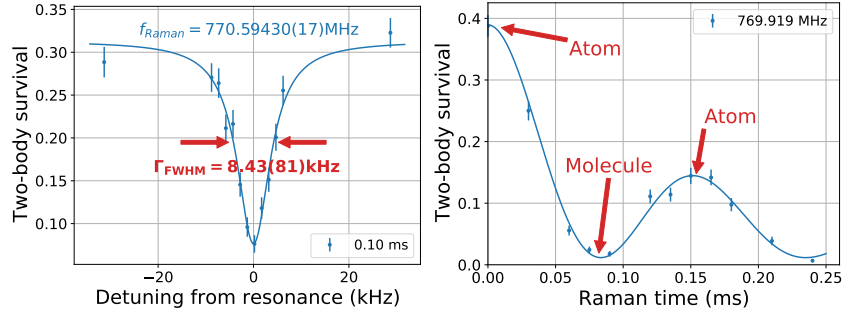


FIG. 2. (A) Raman resonance from atomic state to molecular state, showing Fourier limited linewidth. (B) Rabi oscillation on resonance

(goes to SM?)

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

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.

Our experiment begins by loading a single  $^{23}\text{Na}$  atom and a single  $^{133}\text{Cs}$  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 combination 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

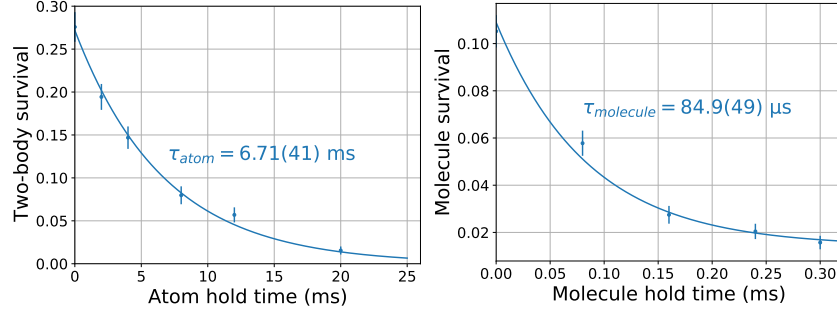


FIG. 3. (A) Two-body atom lifetime in 15 mW of trap depth (B) Molecule lifetime in 15 mW of trap depth

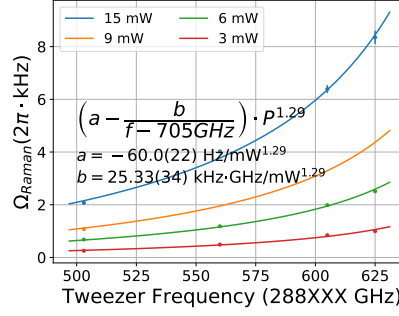


FIG. 4. Raman Rabi frequency vs detuning

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  $\dots kHz$  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...MHz (figure ) with a 15mW

tweezer at 288...GHz which corresponds to a ...GHz single photon detuning. (We can maybe add information about the prediction here?) The background level of ...% 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 ...kHz for the Raman resonance at a pulse time of ...ms, which corresponds to a linewidth-pulsetime product of .... This is consistent with the expected value of ... for an ideal  $\pi$  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  $\Omega$  vs  $\Omega'$  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?)

Next, we look at the atomic loss rate during the transfer process. The atomic loss rate scales as the tweezer intensity to the 2.58th power but shows little to no dependency on the tweezer frequency. The lack of frequency dependency suggests that most of the atomic loss are due to the coupling to states other than the  $v = 0$  one. After substrating 0.58 from the power scaling due to the change in the up leg matrix element, the loss rate is proportional to the tweezer power squared. This is an evidence that the loss is likely caused by a two photon scattering process rather than one photon scattering. The strong power scaling causes a faster than expected loss rate for the atom. However, the atomic scattering is contribution only a small fraction of the total scattering rate so this is not the limiting factor for the transfer.

Finally, we fit the scaling for the molecular loss rate. We observed a dependency on the detuning that is consistent with  $1/\delta^2$  suggesting that the loss is indeed mostly coming from the  $v = 0$  excited state. (preliminary) We observed a power scaling power of  $\approx 1.2$  which is closed to the prediction for a single photon scattering process. The excited state line width calculated from the scattering rate is ...(1GHz?) which is much larger than the theory prediction of 10MHz as well as the 20MHz upper bound from our previous PA measurements (cite).

(ASE filter)

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

---

\* yichaoyu@g.harvard.edu

† ni@chemistry.harvard.edu

- [1] I. Kozyryev and N. R. Hutzler, *Physical Review Letters* **119**, 133002 (2017), publisher: American Physical Society.
- [2] N. Y. Yao, M. P. Zaletel, D. M. Stamper-Kurn, and A. Vishwanath, *Nature Physics* **14**, 405 (2018).
- [3] D. DeMille, *Phys. Rev. Lett.* **88**, 067901 (2002).
- [4] K.-K. Ni, T. Rosenband, and D. D. Grimes, *Chem. Sci.* **9**, 6830 (2018).
- [5] E. B. Norrgard, D. J. McCarron, M. H. Steinecker, M. R. Tarbutt, and D. DeMille, *Phys. Rev. Lett.* **116**, 063004 (2016).
- [6] L. De Marco, G. Valtolina, K. Matsuda, W. G. Tobias, J. P. Covey, and J. Ye, arXiv preprint arXiv:1808.00028 (2018).
- [7] J. T. Zhang, Y. Yu, W. B. Cairncross, K. Wang, L. R. B. Picard, J. D. Hood, Y.-W. Lin, J. M. Hutson, and K.-K. Ni, *Phys. Rev. Lett.* **124**, 253401 (2020).
- [8] J. G. Danzl, E. Haller, M. Gustavsson, M. J. Mark, R. Hart, N. Bouloufa, O. Dulieu, H. Ritsch, and H.-C. Nägerl, *Science* **321**, 1062 (2008).
- [9] K.-K. Ni, S. Ospelkaus, M. H. G. de Miranda, A. Pe'er, B. Neyenhuis, J. J. Zirbel, S. Kotochigova, P. S. Julienne,

- D. S. Jin, and J. Ye, *Science* **322**, 231 (2008).
- [10] F. Lang, K. Winkler, C. Strauss, R. Grimm, and J. Hecker Denschlag, *Phys. Rev. Lett.* **101**, 133005 (2008).
- [11] T. Takekoshi, L. Reichsöllner, A. Schindewolf, J. M. Hutson, C. R. Le Sueur, O. Dulieu, F. Ferlaino, R. Grimm, and H.-C. Nägerl, *Phys. Rev. Lett.* **113**, 205301 (2014).
- [12] P. K. Molony, P. D. Gregory, Z. Ji, B. Lu, M. P. Köppinger, C. R. Le Sueur, C. L. Blackley, J. M. Hutson, and S. L. Cornish, *Phys. Rev. Lett.* **113**, 255301 (2014).
- [13] J. W. Park, S. A. Will, and M. W. Zwierlein, *Phys. Rev. Lett.* **114**, 205302 (2015).
- [14] M. Guo, B. Zhu, B. Lu, X. Ye, F. Wang, R. Vexiau, N. Bouloufa-Maafa, G. Quémener, O. Dulieu, and D. Wang, *Phys. Rev. Lett.* **116**, 205303 (2016).
- [15] S. S. Kondov, C.-H. Lee, K. H. Leung, C. Liedl, I. Majewska, R. Moszynski, and T. Zelevinsky, *Nature Physics* **15**, 1118–1122 (2019).
- [16] K. K. Voges, P. Gersema, M. Meyer zum Alten Borgloh, T. A. Schulze, T. Hartmann, A. Zenesini, and S. Ospelkaus, *Phys. Rev. Lett.* **125**, 083401 (2020).
- [17] G. Reinaudi, C. B. Osborn, M. McDonald, S. Kotochigova, and T. Zelevinsky, *Phys. Rev. Lett.* **109**, 115303 (2012).
- [18] S. Stellmer, B. Pasquiou, R. Grimm, and F. Schreck, *Phys. Rev. Lett.* **109**, 115302 (2012).