Pair Correlations and Photoassociation Dynamics of Two Atoms in an Optical Tweezer

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We investigate the photoassociation dynamics of exactly two laser-cooled 85Rb atoms in an optical tweezer and reveal fundamentally different behavior to photoassociation in many-atom ensembles. We observe non-exponential decay in our two-atom experiment that cannot be described by a single rate coefficient and find its origin in our system’s pair correlation. This is in stark contrast to many-atom photoassociation dynamics, which are governed by exponential decay with a single rate coefficient. We also investigate photoassociation in a three-atom system, thereby probing the transition from two-atom dynamics to many-atom dynamics. Our experiments reveal additional reaction dynamics that are only accessible through the control of single atoms and suggest photoassociation could measure pair correlations in few-atom systems. It further showcases our complete control over the quantum state of individual atoms and molecules, which provides information unobtainable from many-atom experiments.

Chemical processes govern the natural world and are used to create desired molecular structures. Such reactions usually occur in macroscopic samples of atoms and molecules that interact in many different ways. However, the tantalizing prospect of assembling individual molecules atom-by-atom via optical tweezers is emerging.15,28,21,22 We observe non-exponential decay in our two-atom experiment that cannot be described by a single rate coefficient and find its origin in our system’s pair correlation. This is in stark contrast to many-atom photoassociation dynamics, which are governed by exponential decay with a single rate coefficient. We also investigate photoassociation in a three-atom system, thereby probing the transition from two-atom dynamics to many-atom dynamics. Our experiments reveal additional reaction dynamics that are only accessible through the control of single atoms and suggest photoassociation could measure pair correlations in few-atom systems. It further showcases our complete control over the quantum state of individual atoms and molecules, which provides information unobtainable from many-atom experiments.

An ideal process for controlled molecular formation is photoassociation, where light converts two colliding atoms into a molecule. All prior studies into photoassociation dynamics were conducted in many-atom ensembles of laser-cooled or Bose-condensed atoms.9,13 In these systems, the molecule formation dynamics is characterized by a single rate coefficient $K_2$.[14,15]

In this work, we observe the dynamics of exactly two atoms undergoing photoassociation in an optical tweezer for the first time. The dynamics significantly differ from those in many-atom ensembles and the molecule formation cannot be described by a single rate coefficient. This is due to conserved pair correlation in the two-atom system; two atoms in the center-of-mass and relative-position degrees of freedom are separable in an optical tweezer. Consequently, thermally-populated relative-position states either possess strong pair correlations (i.e. a high chance of finding both atoms in the same position) or are anti-correlated (i.e. a low chance of finding the pair in the same position). We show that relative-position states where the atoms are anti-correlated are unaffected by photoassociation on short timescales, whereas states where the atom pair is correlated lead to fast molecule formation. We confirm that this is the underlying cause by investigating the photoassociation dynamics of three atoms, which approach the well-known dynamics of many-atom experiments.

Experiment.— Our single-atom preparation scheme allows us to prepare a single atom in an optical tweezer with an efficiency of around 80% and to detect it.16 We prepare exactly two atoms in a single tweezer by adiabatically merging two spatially-separated tweezers that each contain a single atom.17 The central components of the setup are shown in Fig. 1(a). We use a high-numerical aperture lens (NA = 0.55) to create the tightly focused light of the optical tweezers (red beams), as well as to collect a large proportion of the scattered imaging light (green beam), which is sent to a camera to confirm atom capture in both tweezers.

After the tweezers are merged to transfer both atoms to the same tweezer, the atoms are exposed to photoassociation light at a frequency near 377.001 14 THz. Using a stable cavity we can reproduce this frequency with a precision of 2 MHz. A Ti:Sapph laser delivers this light using multiple short pulses, during which the optical tweezer is turned off to eliminate any light shift due to the tweezer light. Photoassociation dynamics occur on timescales from several µs to several ms. We form molecules in a high vibrational level of a 0+ + state, as illustrated in Fig. 1(b), with the target state determined by the polarization and frequency of the light that drives the transition.[18,19,21]

We detect a photoassociation event by imaging the tweezer after a given time of exposure to photoassociation light. Formed molecules either quickly decay to the ground state, which does not scatter imaging light,
Ground state $0^+$ with identical bosonic freedom are separable. Our experiments are performed on two-atom centre-of-mass and relative motional degrees of freedom. The tweezer is well-approximated as a harmonic potential, the eigenstates of a 1D harmonic oscillator with frequency $\omega_i$ and mass $\mu = m_{Rb}/2$ with $m_{Rb}$ being the mass of a rubidium atom (Fig. 1(b) inset). To ensure that $\phi_n(r)$ is symmetric under particle exchange, $(-1)^{n_x+n_y+n_z} = 1$. At zero separation between the atoms, these eigenstates either have a peak $(n_x, n_y, n_z$ all even) or a node (two of $n_x, n_y, n_z$ odd, one even). Atom pairs thermally populate these relative-position eigenstates, and since they do not interact with any other particles, they remain in them. Note that the anti-correlated nodal states remain eigenstates if a zero range atom-atom interaction is included in Eq. (2), so the classification of states into correlated and anti-correlated remains valid for two atoms even in the presence of short-range interactions.

The correlations of the two-atom wavefunction strongly determine the photoassociation dynamics [22]. The strength of the photoassociation process depends on the wavefunction at the Condon radius $r_c$ [13]. For laser-cooled atoms, the thermal de Broglie wavelength $\lambda_{dB}$ is large compared to the Condon radius (in our experiments $r_c = 4.3$ nm), so the wavefunction at the Condon radius is either close to zero for the anti-correlated nodal states or close to a maximum for correlated pairs (i.e. relative-position states with a peak at $r = 0$), as illustrated in the inset of Fig. 1(b). Consequently, atom pairs initially prepared with strong pair correlations exhibit a much faster photoassociation rate compared with atom pairs initially prepared in nodal states. Photoassociation for an atom pair therefore requires at least a two-timescale model that accounts for the formation of molecules at two different rates. Contrast this to the many-atom case, which is described by a one-timescale model [10].

**Two-timescale model of photoassociation.** — The upper panel of Fig. 2 shows a typical measurement of the probability to find zero or two atoms in the optical tweezer as a function of photoassociation time. Red crosses show the probability of having lost both atoms due to photoassociation, while blue circles show the probability of both atoms remaining in the tweezer. As shown from the one-timescale fit (dashed lines), the photoassociation dynamics cannot be reproduced using only one photoassociation rate. However, a good reproduction of the observed dynamics is obtained when using the two-timescale model (solid lines), which includes two independent two-atom populations with separate photoassociation rates.

Using a $\chi^2$ test [23] on all our rate measurements, we find that the one-timescale model is clearly rejected, while the two-timescale model fit is accepted in most cases [24]. Our statistical analysis clearly shows the importance of considering two-timescale dynamics.
FIG. 2. Evolution of the tweezer’s population as a function of photoassociation time for two atoms (upper panel) and three atoms (lower panel) at a temperature of 35 $\mu$K. In both panels, dashed and solid lines indicate the best one- and two-timescale fits to the experimental data, respectively.

The importance of atom-pair correlation on the photoassociation dynamics.

Further evidence for our two-timescale model is provided via ab initio numerical simulation of the relative co-ordinate wavefunction $\psi(r, t)$. We model photoassociation as an absorbing hard-sphere potential of strength $\hbar \gamma$ and radius $r_c$ [24]:

$$i\hbar \frac{\partial}{\partial t} \psi(r, t) = [H_{rel}(r) - iV_{PA}(r)] \psi(r, t), \quad \text{(3)}$$

where

$$V_{PA}(r) = \begin{cases} \hbar \gamma, & |r| \leq r_c, \\ 0, & \text{otherwise}. \end{cases} \quad \text{(4)}$$

The simulation was conducted by averaging over a thermal ensemble of initial states evolved under Eq. (3). The initial states were relative-position eigenstates $\phi_n(r)$ of the approximately harmonic trap.

Our simulations qualitatively capture the two-timescale behavior seen in the experiment. The fast timescale dynamics are almost entirely due to the decay of states with an initial peak at zero separation, whereas decay of states with an initial node at zero separation occurs on a slower timescale. The lower panel of Fig. 2 shows the density of the thermal ensemble after different durations of photoassociation. The peak at zero atom-atom separation in the $t = 0$ plot is due to the bosonic enhancement of correlations in a thermal cloud. We observe a fast depletion of density around zero atom-atom separation when evolving using Eq. (3) for some time, after which the remaining pairs are anti-correlated, as shown by a dip in the density at zero atom-atom separation.

FIG. 3. Numerical simulation of the atom-pair evolution in the tweezer under photoassociation. (Upper panel) The population over time for an ensemble at temperature 10.5 $\mu$K, with the separate contributions due to states where $n_x, n_y, n_z$ are all even (fast decay) and states where two of $n_x, n_y, n_z$ are odd (slow decay) also shown. (Lower panel) 1D slice of the thermal ensemble density along the weak-trapping axis of the tweezer at different times since illumination with photoassociation light started. Simulations used trapping frequencies of $\omega_x = 2\pi \times 20\,\text{kHz}$, $\omega_y = 2\pi \times 93\,\text{kHz}$, and $\omega_z = 1.01\omega_y$, consistent with our experimental setup, and $\gamma = 473\,\text{MHz}$.

Rate coefficients.— In many-atom ensembles, the single rate coefficient $K_2$ that governs photoassociation dynamics reaches its highest, unitarity-limited value when the photoassociation light is at the saturation intensity [8, 12, 25]. For photoassociation of two indistinguishable particles with a maximum photoassociation cross section of $\sigma = \lambda_A^2/(2\pi)$, the unitarity-limited rate coefficient is [26]:

$$K_2^{\text{unitarity}} = \sqrt{8\pi\hbar^4/(\mu^3 k_B T)}. \quad \text{(5)}$$

This highest achievable rate coefficient forms a fundamental limit that exists for every scattering process, however so far it has only been investigated in many-atom systems.

By adapting the rate equations for inelastic scattering in the many-atom case [27] to a two-atom system, we can determine $K_2$ from the experimentally-observed pair-loss
fast decay exceeds $K_t$ensity compared to the many-atom unitarity limit. The in our two-atom experiments around the saturation inefficients of the fast and the slow decaying populations value of our system's rate coefficient.

tation intensity in order to compare to the unitarity-limited toassociation dynamics are performed close to the saturationation in a three-atom system and determine how the ad-

dition of an extra atom influences the dynamics. In the three-atom system, the photoassociation dynam-

cics are well-described by a single rate coefficient, with a value consistent with the many-atom unitarity-limited rate coefficient. Our experimental results show that this state-dependent photoassociation rate could be used as a new tool for the production or detection of atom-pair correlations in future experiments.

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