
Many-body chemical reactions in a quantum degenerate gas

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Supplementary information for Many-body chemical reactions in a quantum degenerate gas

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I. MANY-BODY CHEMICAL REACTIONS IN QUANTUM DEGENERATE REGIME

Here we derive the effective potential V for three-body and two-body processes and calculate the minimum position of V and the oscillation frequency of the system near the minimum. We start from the many-body Hamiltonian for the three-body recombination process $A + A + A \longleftrightarrow A_2 + A$ near a Feshbach resonance,

$$\hat{H} = \varepsilon_m \hat{\psi}_m^\dagger \hat{\psi}_m + g_3 (\hat{\psi}_m^\dagger \hat{\psi}_a^\dagger \hat{\psi}_a^3 + \hat{\psi}_a^{\dagger 3} \hat{\psi}_a \hat{\psi}_m), \quad (\text{S1})$$

where we only consider the ground states for atoms and molecules since their associated coupling terms dominate over others that involve excited states, due to the macroscopic population in the ground state of atoms that we begin with.

To characterize the evolution of the system, we derive the equation of motion for the atomic population $\hat{N}_a = \hat{\psi}_a^\dagger \hat{\psi}_a$ and molecular population $\hat{N}_m = \hat{\psi}_m^\dagger \hat{\psi}_m$, which only depends on the number operators and conserved quantities of the system as [39, 40]

$$\begin{aligned} \frac{\hbar^2}{2} \dot{\hat{N}}_m^2 &= \frac{\hbar^2}{8} \dot{\hat{N}}_a^2 = -\frac{1}{2} [\hat{N}_m, \hat{H}]^2 \\ &= -\frac{1}{2} (\hat{H} - \varepsilon_m \hat{N}_m)^2 + g_3^2 \hat{N}_a [(\hat{N}_m + 1)(\hat{N}_a - 1)(\hat{N}_a - 2)^2 + \hat{N}_m \hat{N}_a (\hat{N}_a + 1)(\hat{N}_a + 2)], \end{aligned} \quad (\text{S2})$$

where $\hat{H}$ is the total energy. We introduce the many-body reaction potential $\hat{V}_3$ through $\hbar^2 \dot{\hat{N}}_m^2 / 2 + \hat{V}(\hat{N}_m) = \text{const.}$ as shown in Eq. (3) and obtain it under the boundary condition where the expectation value is $\langle \hat{V}_3 \rangle = 0$ for pure atoms $|N_a = N, N_m = 0\rangle$ as:

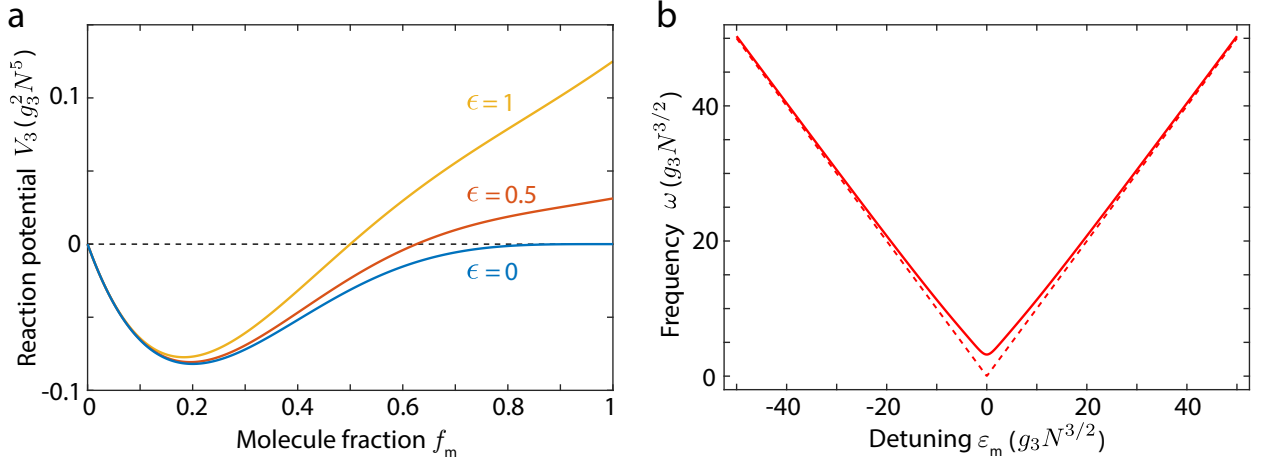


FIG. S1: **The reaction potential V_3 for the three-body process and the oscillation frequency ω near the minimum of V_3 at different detuning ϵ .** **a**, The reaction potential calculated based on Eq. (S5) at $\epsilon = 0$ (blue), $\epsilon = 0.5$ (orange) and $\epsilon = 1$ (yellow). The region below the dashed line at $V_3 = 0$ is where the system is allowed to reach based on the conservation law in Eq. (??). **b**, The oscillation frequency ω at different detunings ϵ_m (solid line). The dashed line represents the asymptote $|\epsilon_m|$ in the large detuning limit. On resonance $\epsilon = 0$, the frequency is $\omega = 16g_3N^{3/2}/5$.

$$\begin{aligned}\hat{V}_3 &= \frac{1}{2}[\hat{N}_m, \hat{H}]^2 + \text{const.} \\ &= -\epsilon_m \hat{N}_m (\hat{H} - \frac{\epsilon_m}{2} \hat{N}_m) - g_3^2 P_3(\hat{N} - 2\hat{N}_m, \hat{N}_m) + g_3^2 \hat{N}(\hat{N} - 1)(\hat{N} - 2)^2,\end{aligned}\quad (\text{S3})$$

where the three-body polynomial is $P_3(x, y) = x[(y + 1)(x - 1)(x - 2)^2 + yx(x + 1)(x + 2)]$ and $\hat{N} = \hat{N}_a + 2\hat{N}_m$ is the conserved total population that commutes with the Hamiltonian.

In our experiment, the atoms and molecules have macroscopic population in the reaction process $N_a, N_m \gg 1$. We may replace all the operators by their expectation values and express the reaction potential in terms of the total particle number N and the molecular fraction $f_m = 2N_m/N$ as

$$\begin{aligned}V_3 &= -g_3^2 N f_m \left\{ [(1 - f_m)^4 - \frac{\epsilon^2}{8} f_m] N^4 + (\frac{\epsilon \tilde{H}}{2} + 2f_m^3 - 7f_m^2 + 9f_m - 5) N^3 \right. \\ &\quad \left. + 5(2f_m^2 - 5f_m + 4) N^2 + 2(5f_m - 9) N + 4 \right\},\end{aligned}\quad (\text{S4})$$

where the dimensionless detuning and total energy are $\epsilon = \varepsilon_m/g_3N^{3/2}$ and $\tilde{H} = H/g_3N^{3/2}$, respectively. In the thermodynamic limit where the particle number $N \gg 1$, the potential is reduced to:

$$V_3 = -g_3^2N^5f_m[(1-f_m)^4 - \epsilon^2f_m/8]. \quad (\text{S5})$$

The potential curves at different detunings are shown in Fig. S1a. The potential minimum f_{m0} satisfies $\partial_{f_m}V_3|_{f_{m0}} = 0$. On resonance $\epsilon = 0$, the molecule fraction at the minimum is

$$f_{m0} = \frac{1}{5}, \quad (\text{S6})$$

and the oscillation frequency ω_0 of the system around the minimum determined by the curvature of the potential V_3 at f_{m0} is

$$\omega_0 = \frac{16}{5}g_3N^{3/2}. \quad (\text{S7})$$

At finite detuning, the minimum position f_{m0} and the oscillation frequency ω can be solved numerically from $(1-f_{m0})^3(1-5f_{m0}) - \epsilon^2f_{m0}/4 = 0$ and $\omega = g_3N^{3/2}\sqrt{16(1-f_{m0})^2(2-5f_{m0}) + \epsilon^2}$, see Fig S1b. In the large detuning limit $\epsilon \gg 1$, the frequency approaches the absolute value of the molecular energy $|\varepsilon_m|$.

For the nonuniform Thomas-Fermi density distribution of a BEC in a harmonic trap, the coupling strength g_3 depends on the particle number and is given by $g_3 = g'_3/\Omega^{3/2}$, where g'_3 is a coupling constant, the effective trap volume is $\Omega = (14\pi/15^{2/5})(Na\bar{a})^{3/5}$ and the oscillator length $\bar{a}$ is determined by the trap frequencies as $\bar{a} = \sqrt{\hbar/m(\omega_x\omega_y\omega_z)^{1/3}}$ [26]. Thus on resonance the frequency $\omega_0 \propto N^{3/5}$. Note that in our experiment, we measure the dependence of the oscillation frequency ω_0 on the initial total atom number N_0 and we assume that the atom number in the equilibration phase is proportional to N_0 . By fitting the data in Fig. 4b, we extract the three-body coupling constant $g'_3/h = 5.5(5) \times 10^{-18}\text{cm}^9/\text{s}$.

Similarly, for the Hamiltonian in Eq. (1) for the two-body process $A + A \longleftrightarrow A_2$, the exact effective potential $\hat{V}_2$ under the boundary condition where the expectation value is $\langle \hat{V}_2 \rangle = 0$ for pure atoms $|N_a = N, N_m = 0\rangle$ is derived to be

$$\hat{V}_2 = \varepsilon_m \hat{N}_m \left(\frac{1}{2} \varepsilon_m \hat{N}_m - \hat{H} \right) - 2g_2^2 \hat{N}_m [(\hat{N} - 2\hat{N}_m)^2 - \hat{N} + 2]. \quad (\text{S8})$$

After replacing the operators by their expectation values we obtain

$$V_2 = -g_2^2 N f_m \left\{ [(1 - f_m)^2 - \epsilon'^2 f_m / 8] N^2 + (\epsilon' \tilde{H}' / 2 - 1) N + 2 \right\}, \quad (\text{S9})$$

where the dimensionless detuning and total energy are $\epsilon' = \varepsilon_m / g_2 \sqrt{N}$ and $\tilde{H}' = H / g_2 \sqrt{N}$ for the two-body process. In the thermodynamic limit $N \gg 1$, the potential is reduced to:

$$V_2 = -g_2^2 N^3 f_m [(1 - f_m)^2 - \epsilon'^2 f_m / 8], \quad (\text{S10})$$

based on which we derive the analytical expressions for the minimum position and the oscillation frequency near the minimum as:

$$\begin{aligned} f_{m0} &= \frac{16 + \epsilon'^2 - \sqrt{\epsilon'^4 + 32\epsilon'^2 + 64}}{24}, \\ \omega &= g_2 \sqrt{N} (\epsilon'^4 + 32\epsilon'^2 + 64)^{1/4}. \end{aligned} \quad (\text{S11})$$

On resonance $\epsilon' = 0$, we have

$$\begin{aligned} f_{m0} &= \frac{1}{3}, \\ \omega_0 &= 2\sqrt{2} g_2 \sqrt{N}. \end{aligned} \quad (\text{S12})$$

For the nonuniform density distribution, the frequency is $\omega_0 \propto \sqrt{N/\Omega} = N^{1/5}$.

In general, for reactions of order α where α is the maximum number of field operators in the terms of the reaction Hamiltonian, the reaction potential is $V \propto N^\alpha$ in the thermodynamic limit for a uniform system where each mode is macroscopically occupied. Then the oscillation frequency of the system around the potential minimum f_{m0} is determined by the curvature of the potential as $\omega_0 \propto \sqrt{\partial^2 V / \partial N^2 |_{f_{m0}}} \propto N^{\alpha/2-1}$.

II. EVALUATION AND THEORY OF THE MOLECULE FORMATION RATE COEFFICIENT

The molecule formation rate coefficient β presented in Fig. 2b is evaluated based on $\beta = \dot{N}_m/N_0 n_0$. Apart from the growth rate of the molecule fraction $f_m = 2N_m/N_0$ shown in Fig. 2a, we also need to evaluate the initial mean atomic density n_0 to calculate β . We model the atomic density distribution for the general case where both normal and BEC components exist as [41]

$$n(\mathbf{r}, t) = n_n(\mathbf{r}, t) + n_B(\mathbf{r}, t) = n_{np} g_{3/2}(\prod_{i=1}^3 e^{-r_i^2/\sigma_i^2}) + n_{Bp}(1 - \sum_{i=1}^3 \frac{r_i^2}{R_i^2})\theta(1 - \sum_{i=1}^3 \frac{r_i^2}{R_i^2}), \quad (\text{S13})$$

where $(r_1, r_2, r_3) = (x, y, z)$ are spatial coordinates, σ_i and R_i are the widths of the normal and BEC components, $g_{3/2}(x) = \sum_{k=1}^{\infty} x^k/k^{3/2}$ is the polylogarithm function and $\theta(x)$ is the Heaviside step function. Our vertical absorption imaging integrates over the z axis and we obtain the 2D column density as

$$\begin{aligned} n(x, y, t) &= \int_{-\infty}^{\infty} n(\mathbf{r}, t) dz \\ &= \sqrt{\pi} n_{np} \sigma_z g_2(\prod_{i=1}^2 e^{-r_i^2/\sigma_i^2}) + \frac{4}{3} n_{Bp} R_z (1 - \frac{x^2}{R_x^2} - \frac{y^2}{R_y^2})^{3/2} \theta(1 - \frac{x^2}{R_x^2} - \frac{y^2}{R_y^2}). \end{aligned} \quad (\text{S14})$$

We use Eq. (S14) to fit 2D column density distributions from our experiments and extract the widths σ_x , σ_y , R_x and R_y and total particle number N_n and N_B in the normal and BEC components. We use the scaling to calculate the cloud widths in the z direction as $\sigma_z = (\omega_y/\omega_z)\sigma_y$ and $R_z = (\omega_y/\omega_z)R_y$ based on our independent measurements of trap frequencies ω_y and ω_z . Then the 3D peak densities are evaluated as

$$n_{np} = \frac{N_n}{g_3(1)\pi^{3/2}\bar{\sigma}^3}, \quad n_{Bp} = \frac{15N_B}{8\pi\bar{R}^3}, \quad (\text{S15})$$

where $\bar{\sigma} = (\sigma_x\sigma_y\sigma_z)^{1/3}$ and $\bar{R} = (R_xR_yR_z)^{1/3}$. Eventually, with all the parameters in Eq. (S13) determined, we evaluate the initial mean 3D density as

$$n_0 = \frac{\int n^2(\mathbf{r}, 0) d^3\mathbf{r}}{\int n(\mathbf{r}, 0) d^3\mathbf{r}}, \quad (\text{S16})$$

as shown in Fig. S2a.

To capture the sharp transition of the rate coefficient around the critical temperature T_c as shown in Fig. 2b, we develop the following two-component model incorporating both the thermal and condensed atoms. There are three possible collision processes leading to molecule formation, which are represented by the following rate equations involving molecular density $m(\mathbf{r}, t)$ and atomic density $n(\mathbf{r}, t)$ with the subscripts n and B indicating normal and BEC components, respectively. Experimentally, both two- and three-body processes contribute to the atom-molecule dynamics, confirmed by measurements shown in Figs. 3 and 4. To describe the transition of the molecular formation rate coefficient in Fig. 2, we develop a theoretical model based on two-body scattering in the unitarity limit:

1. Molecule formation from collisions between condensed atoms:

$$\dot{m}_B(\mathbf{r}, t) = \beta_B n_B^2(\mathbf{r}, t) \quad (\text{S17})$$

with the rate coefficient given by $\beta_B = b_Q \Gamma_Q$, where the collision rate is $\Gamma_Q = \frac{4\sqrt{3}}{(6\pi^5)^{1/3}} \frac{h}{m} \frac{\langle n^{2/3} \rangle}{\langle n \rangle}$, $\langle n \rangle = \int n^2(\mathbf{r}, t) d^3\mathbf{r} / \int n(\mathbf{r}, t) d^3\mathbf{r}$ and $\langle n^{2/3} \rangle = \int n^{5/3}(\mathbf{r}, t) d^3\mathbf{r} / \int n(\mathbf{r}, t) d^3\mathbf{r}$.

2. Molecule formation from collisions between thermal atoms:

$$\dot{m}_n(\mathbf{r}, t) = \beta_n n_n^2(\mathbf{r}, t), \quad (\text{S18})$$

with the rate coefficient given by $\beta_n = b_{Cl} \Gamma_{Cl}$, where the collision rate is $\Gamma_{Cl} = 8h^2(\pi^3 m^3 k_B T)^{-1/2}$.

3. Molecule formation from collisions between one BEC atom and one thermal atom:

$$\dot{m}_{nB}(\mathbf{r}, t) = 2\beta_{nB} n_B(\mathbf{r}, t) n_n(\mathbf{r}, t) = 2\beta_n n_B(\mathbf{r}, t) n_n(\mathbf{r}, t), \quad (\text{S19})$$

where we assume $\beta_{nB} = \beta_n = b_{Cl} \Gamma_{Cl}$.

The total molecular formation rate is given by the summation of Eqs. (S17)-(S19):

$$\dot{m}(\mathbf{r}, t) = \beta_B n_B^2(\mathbf{r}, t) + \beta_n [n_n(\mathbf{r}, t) + 2n_B(\mathbf{r}, t)] n_n(\mathbf{r}, t) = \beta n(\mathbf{r}, t). \quad (\text{S20})$$

After the spatial integration, we obtain the molecular formation rate coefficient in the mixture

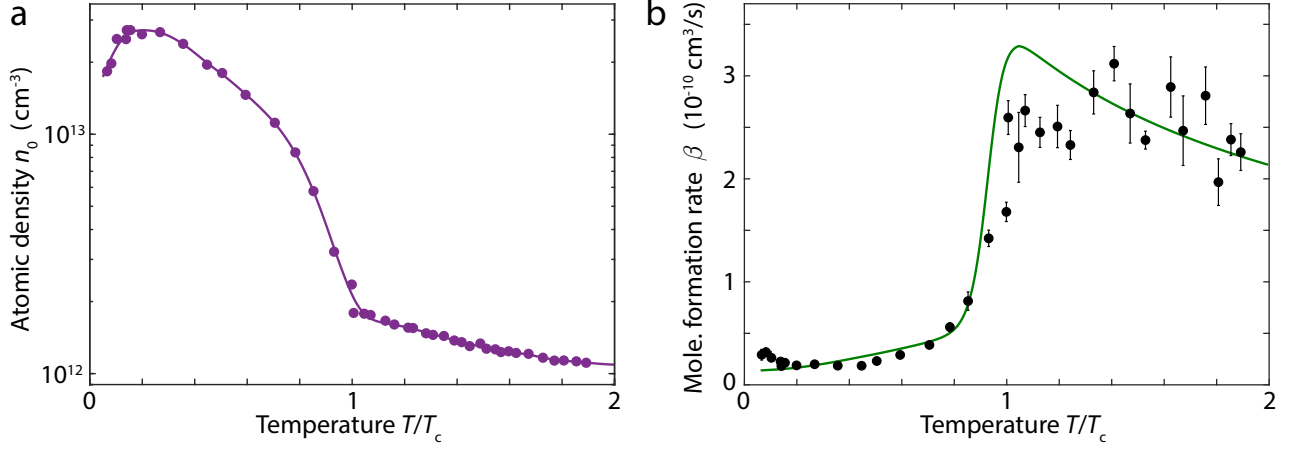


FIG. S2: **Measurement of the mean atomic density n_0 and fitting the molecule formation rate coefficient by the two-component model.** **a**, Initial 3D mean atomic density as a function of temperature, evaluated based on Eq. (S16). The solid line is a guide to the eye. **b**, Molecule formation rate coefficient fit by Eq. (S21) with the branching ratio b_Q as a fitting parameter (green solid line).

$$\beta = w_B \beta_B + (1 - w_B) \beta_n, \quad (\text{S21})$$

where the weight of the BEC component is

$$w_B = \frac{\int n_B^2(\mathbf{r}, t) d^3\mathbf{r}}{\int n^2(\mathbf{r}, t) d^3\mathbf{r}}. \quad (\text{S22})$$

For a uniform system, the weight is reduced to $w_B = f_{\text{BEC}}^2$ where $f_{\text{BEC}} = N_B/N$ is the BEC fraction. Since we perform the rate coefficient measurements in a harmonic trap, the density distributions are nonuniform and the weight is enhanced to be $w_B > f_{\text{BEC}}^2$. Our two-component model captures the transition of the measured rate coefficients around T_c very well, see Fig. S2b.

III. AMPLIFICATION OF THE MOLECULE OSCILLATION THROUGH MAGNETIC FIELD MODULATION

To amplify the molecule number oscillation, we apply additional external driving to atomic BECs near the Feshbach resonance. The coupled atomic and molecular BECs in

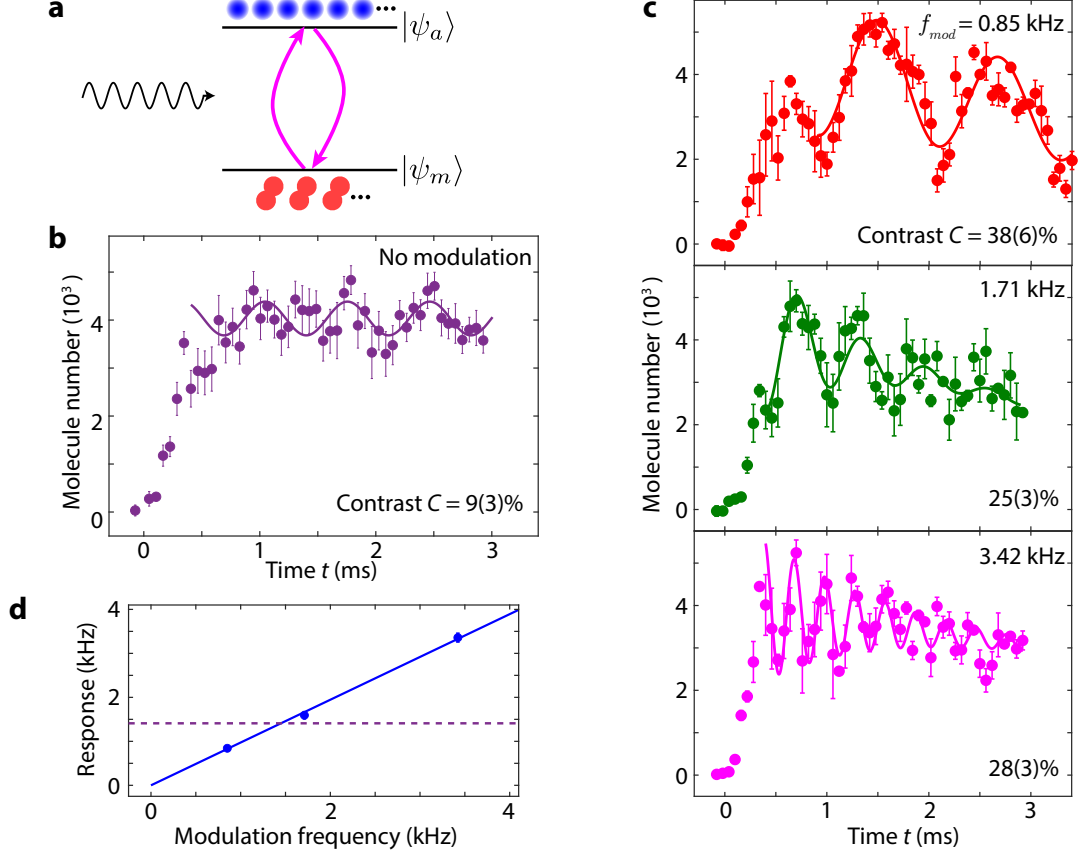


FIG. S3: **Amplification of coherent molecule oscillations through magnetic field modulation.** **a**, Schematic diagram of molecule formation near the Feshbach resonance with additional sinusoidal magnetic field modulation, where the black wavy arrow represents the RF photon from the modulation. **b**, Evolution of the molecular population after quench to a static magnetic field 2(1) mG below the resonance, where the contrast C of the molecule oscillation is 9(3)%. **c**, Time traces of molecule number with magnetic field modulation at 0.85 (red), 1.71 (green) and 3.42 kHz (magenta) with modulation amplitude $B_{ac} \approx 4$ mG around the same field as in panel **b**. The solid lines are fits based on Eq. (??). The contrast is defined as $C = N_m(0)/\Delta N_m$, see text. **d**, Frequency of the molecule oscillations extracted from the fits in panel **c**. Blue solid line is a linear fit without an offset, which gives a slope 0.97(3). The purple dashed line represents the molecule oscillation frequency in panel **b**.

our system effectively form a bosonic Josephson junction [42], in close analogy to Cooper-pair Josephson junctions in superconducting devices [43]. Inspired by the Shapiro resonance effect where adding a small resonant ac component to an applied voltage enhances dc tun-

neling current in the superconducting Josephson junction, we modulate the magnetic field at a frequency close to the free molecule oscillation frequency at a static field, with the hope to facilitate the reaction. At 2 mG below the resonance, the molecule number oscillates around 4,000 at 1.4 kHz, with a contrast of $\sim 9\%$ (see Fig. S3b). After adding a magnetic field modulation with an amplitude of 4 mG around the same field, we find the oscillation contrast increases by a factor of 3 to 4, see Fig. S3c. We also see clear damping in the oscillations with the driving field, likely due to additional heating introduced by the driving.

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