Supplementary Information: Selective Elimination of the Homogeneous Broadening by Multidimensional Spectroscopy in EIT Regime

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S1. MODEL

Consider four-level scheme that represent molecular dimer system described by the Hamiltonian

$$\hat{H}_0 = \sum_j \hbar\omega_j |j\rangle\langle j| , j = b, a_1, a_2, c \tag{S1}$$

where the four level energies have been arranged such that $\omega_b < \omega_c < \omega_{a_2} < \omega_{a_1}$. Here b and c correspond to the two rovibrational states of the ground electronic state and a_1 and a_2 corresponds to the rovibrational states of the excited electronic state. The Hamiltonian $\hat{H}_{int}(t)$ for the system interacting with the strong control field is given by Eq.(3). Combining Eqs.(S1) and (3) one can express the total Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_{int}(t)$ in the matrix form:

$$\hat{H} = \begin{pmatrix} \hbar\omega_b & 0 & 0 & 0 \\ 0 & \hbar\omega_{a_1} & 0 & -\dfrac{\hbar}{2}\Omega_1 e^{-i\nu t} \\ 0 & 0 & \hbar\omega_{a_2} & -\dfrac{\hbar}{2}\Omega_2 e^{-i\nu t} \\ 0 & -\dfrac{\hbar}{2}\Omega_1 e^{i\nu t} & -\dfrac{\hbar}{2}\Omega_2 e^{i\nu t} & \hbar\omega_c \end{pmatrix} \tag{S2}$$

Hereafter we will explore the effects of control field via Ω_1 and Ω_2 separately, assuming that CW control field may interact resonantly only with one transition. For instance we set $\Omega_1 = \Omega$ and $\Omega_2 = 0$. The evolution of the system is governed by the Liouville-von Neumann equation Eq.(2). The total density matrix can be recast as

$$\hat{\rho} = \begin{pmatrix} \rho_{bb} & \rho_{ba_1} & \rho_{ba_2} & \rho_{bc} \\ \rho_{a_1 b} & \rho_{a_1 a_1} & \rho_{a_1 a_2} & \rho_{a_1 c} \\ \rho_{a_2 b} & \rho_{a_2 a_1} & \rho_{a_2 a_2} & \rho_{a_2 c} \\ \rho_{cb} & \rho_{ca_1} & \rho_{ca_2} & \rho_{cc} \end{pmatrix} \tag{S3}$$

While the control field is described to all orders, the probe field is treated perturbatively. The nonlinear polarization is given by

$$\mathbf{P}^{(n)}(r,t) = \int_0^\infty dt_n \int_0^\infty dt_{n-1} \cdots \int_0^\infty dt_1 S^{(n)}(t_n, t_{n-1}, \ldots, t_1) E(\mathbf{r}, t - t_n)$$

$$\times E(\mathbf{r}, t - t_n - t_{n-1}) \cdots E(\mathbf{r}, t - t_n - t_{n-1} \cdots - t_1), \tag{S4}$$

with

$$S^{(n)}(t_n, t_{n-1}, \ldots, t_1) \equiv \left(\frac{i}{\hbar}\right)^n \langle\langle V | \mathcal{G}(t_n) \mathcal{V} \mathcal{G}(t_{n-1}) \mathcal{V} \ldots \mathcal{G}(t_1) \mathcal{V} | \rho(-\infty)\rangle\rangle, \tag{S5}$$

where $\mathcal{G}$ and $\mathcal{V}$ denote the Green's function and dipole operator in Liouville space, respectively. The photon echo is a third order nonlinear process described by Eq.(1).

We next calculate the coherence Green's funcions. By using the unitary transformation method, we got all the 4 Green's functions in Eq. (1) like:

$$\mathcal{G}_{ba_1,ba_1}(\omega_1) = \frac{4(\omega_1 - i\gamma_3 - \omega_{a_1b})}{4(\omega_1 - i\gamma_1^{(1)} - \omega_{a_1b})(\omega_1 - i\gamma_3 - \omega_{a_1b}) - \Omega_1^2} \tag{S6}$$

$$\mathcal{G}_{a_1b,a_1b}(\omega_1) = \frac{4(\omega_1 + i\gamma_3 - \omega_{a_1b})}{4(\omega_1 + i\gamma_1^{(1)} - \omega_{a_1b})(\omega_1 + i\gamma_3 - \omega_{a_1b}) - \Omega_1^2} \tag{S7}$$

$$\mathcal{G}_{a_2b,a_2b}(\omega_3) = \frac{1}{\omega_3 + i\gamma_1^{(2)} - \omega_{a_2b}} \tag{S8}$$

$$\mathcal{G}_{ba_2,ba_2}(\omega_3) = \frac{1}{\omega_3 - i\gamma_1^{(2)} - \omega_{a_2b}} \tag{S9}$$

We next turn to population calculations. To compute populations analytically we assume Γ to be small compared to other parameters such as γ_2 and Ω and first recast Eq. (4) in a matrix form, setting $\Gamma = 0$

$$\hat{\mathcal{L}} = \begin{pmatrix} 0 & -\frac{i}{2}\Omega_1 & \frac{i}{2}\Omega_1 & 0 \\ -\frac{i}{2}\Omega_1 & -\gamma_2 & 0 & \frac{i}{2}\Omega_1 \\ \frac{i}{2}\Omega_1 & 0 & -\gamma_2 & -\frac{i}{2}\Omega_1 \\ 0 & \frac{i}{2}\Omega_1 & -\frac{i}{2}\Omega_1 & 0 \end{pmatrix} \tag{S10}$$

To zeroth order in Γ the solution for coherences ρ_{a_1c}, ρ_{ca_1} read:

$$\rho_{a_1c}(t) = -\frac{ie^{-\frac{\gamma_2 t}{2}}\Omega\sinh\left(\frac{t}{2}\sqrt{\gamma_2^2 - 4\Omega^2}\right)}{\sqrt{\gamma_2^2 - 4\Omega^2}} \tag{S11}$$

$$\rho_{ca_1}(t) = \frac{ie^{-\frac{\gamma_2 t}{2}}\Omega\sinh\left(\frac{t}{2}\sqrt{\gamma_2^2 - 4\Omega^2}\right)}{\sqrt{\gamma_2^2 - 4\Omega^2}} \tag{S12}$$

Then we substitue Eqs.(S11) - (S12) into Eq.(4) and transform it into first-order differential equation. We assume that only $|a_1\rangle$ was populated after the first period t_1, namely: $\rho_{a_1a_1} = 1$ and $\rho_{a_2a_2} = 0$, thus the initial condition in second period is like this, then the solution of $\rho_{a_1a_1}(t)$ in the second period is given by Eq. (7) of the main text. We then find the expression of $\rho_{a_2a_2}$ using the zero-order expression for $\rho_{a_1a_1}$ using the long term asymptotic decay:

$$\rho_{a1a1}^{(0)}(t) = -\Gamma\rho_{a_1a_1}^{(0)} \tag{S13}$$

S3

we obtain

$$\rho_{a1a1}^{(0)}(t) = e^{-\Gamma t}. \tag{S14}$$

We thus find the expression for $\rho_{a_2 a_2}$:

$$\rho_{a_2 a_2}(t) \simeq 1 - e^{-\Gamma t} \tag{S15}$$

Last, we utilize the population conservation condition and obtain for ρ_{cc}

$$\rho_{cc}(t) = 1 - \rho_{a_1 a_1}(t) - \rho_{a_2 a_2}(t) \tag{S16}$$

Similarly we obtain for the initial conditions $\rho_{a_1 a_1}(0) = 0$ and $\rho_{a_2 a_2}(0) = 1$:

$$\rho_{a_1 a_1}(t) = 0, \tag{S17}$$

$$\rho_{a_2 a_2}(t) = 1, \tag{S18}$$

$$\rho_{cc}(t) = 0. \tag{S19}$$

So far we considered the case when the control field is resonant with $a_1 - c$ transition by setting $\Omega_1 = \Omega$ and $\Omega_2 = 0$. We now turn to the case when the control field drives $a_2 - c$ transition by setting $\Omega_1 = 0$ and $\Omega_2 = \Omega$. Considering initial conditions $\rho_{a_1 a_1}(0) = 1$ and $\rho_{a_2 a_2}(0) = 0$, the populations can be similarly obtained:

$$\rho_{a_1 a_1}(t) \simeq e^{-\Gamma t}, \tag{S20}$$

$$\rho_{a_2 a_2} \simeq \rho_{cc}(t) \simeq \frac{1}{2}[1 - e^{-\Gamma t}]. \tag{S21}$$

Finally using initial conditions $\rho_{a_1 a_1}(0) = 0$ and $\rho_{a_2 a_2}(0) = 1$, we obtain the solution:

$$\rho_{a_1 a_1}(t) = 0, \tag{S22}$$

$$\rho_{a_2 a_2}(t) \simeq \frac{1}{2}\left[1 + e^{-\frac{\gamma_2 t}{2}}\left(\cosh(\tilde{\Omega}t) + \frac{\gamma_2 \sinh(\tilde{\Omega}t)}{2\tilde{\Omega}}\right)\right], \tag{S23}$$

$$\rho_{cc}(t) \simeq \frac{1}{2}\left[1 - e^{-\frac{\gamma_2 t}{2}}\left(\cosh(\tilde{\Omega}t) + \frac{\gamma_2 \sinh(\tilde{\Omega}t)}{2\tilde{\Omega}}\right)\right]. \tag{S24}$$

S2.   DETAILS OF THE SIMULATIONS FOR Cs_2 DIMER

We now simulate results for cesium dimer using realistic parameters. The spectra is given by:

$$G(\nu) = E_\nu/hc = \omega_e(\nu + 1/2) - \omega_e \chi_e (\nu + 1/2)^2 \tag{S25}$$

where the coefficients for the ground electronic state $X^1\Sigma_g^-$: ω_e is 41.990 cm^{-1} and $\omega_e\chi_e$ is 0.08005 cm^{-1}; and for the excited electronic state $B^1\Pi_u$: ω_e is 34.230 cm^{-1} and 0.07799 cm^{-1}. Although it has both linear and nonlinear terms but the coefficient of the nonlinear term $\omega_e\chi_e$ is much smaller than that of the linear term (approximately 4 orders of magnitude smaller). The maximum of the vibrational quantum number ν is 12. We then obtain for the ground state $X^1\Sigma_g^-$: $E_{\nu=0} = 21.02$ cm^{-1}, $E_{\nu=1} = 62.51$ cm^{-1}, $E_{\nu=2} = 104.85$ cm^{-1}, $E_{\nu=3} = 145.18$ cm^{-1}, $E_{\nu=5} = 228.97$ cm^{-1}, $E_{\nu=6} = 270.08$ cm^{-1}. We similarly obtain for the excited state $B^1\Pi_u$: $E_{\nu=0} = 17.10$ cm^{-1}, $E_{\nu=1} = 51.62$ cm^{-1}, $E_{\nu=2} = 85.49$ cm^{-1}, $E_{\nu=3} = 118.56$ cm^{-1}, $E_{\nu=5} = 186.27$ cm^{-1}, $E_{\nu=6} = 219.63$ cm^{-1}. By comparison we conclude that the energy gap of the excited state is narrower than that in ground state. Furthermore the rotational spectra values $F(J) = E_J/hc$ is:

$$F(J) = B_e J(J+1) - D_e J^2 (J+1)^2 \tag{S26}$$

where $B_e = \dfrac{h}{8\pi^2 I_e} = 0.036 cm^{-1}$, where $I_e = \mu r_e^2$, is the moment of inertia; the constant $D_e = \dfrac{4B_e^3}{\omega_e^2} = 1.058\times10^{-7}$ for $X^1\Sigma_g^- cm^{-1}$ and $1.59\times10^{-7} cm^{-1}$ for $B^1\Pi_u$. Since the coefficient of the nonlinear term $\omega_e\chi_e$ is much smaller than that of linear term (about 5 orders of magnitude smaller), difference in the values between the ground and optically excited is negligible. The maximum of the rotational quantum number J defined by constraint in pertubative expansion is 583. Thus, we get for $X^1\Sigma_g^-$ state: $E_{J=10} = 3.96406$ cm^{-1}, $E_{J=11} = 4.75657$ cm^{-1}, $E_{J=12} = 5.62098$ cm^{-1}, for $B^1\Pi_u$ state: $E_{J=10} = 3.96342$ cm^{-1}, $E_{J=11} = 4.75564$ cm^{-1}, $E_{J=12} = 5.61972$ cm^{-1}.

The total energy is $E_{0,10} = E_{\nu''=0} + E_{J''=10} = 21.02 + 3.96406 = 24.9841$ cm^{-1}, similarly we get $E_{1,10} = E_{\nu''=1} + E_{J''=10} = 62.51 + 3.96406 = 66.4741$ cm^{-1}, $E_{1,11} = E_{\nu''=1} + E_{J''=11} = 62.51 + 4.75657 = 67.2666$ cm^{-1}, $E_{1,12} = E_{\nu''=1} + E_{J''=12} = 62.51 + 5.62098 = 68.131$ cm^{-1}, $E_{2,11} = E_{\nu''=2} + E_{J''=11} = 104.85 + 4.75657 = 109.607$ cm^{-1}, $E_{2,12} = E_{\nu''=2} + E_{J''=12} = 104.85 + 5.62098 = 110.471$ cm^{-1}, $E_{3,10} = E_{\nu''=3} + E_{J''=10} = 145.18 + 3.96406 = 149.144$ cm^{-1}, $E_{3,12} = E_{\nu''=3} + E_{J''=12} = 145.18 + 5.62098 = 150.801$ cm^{-1}.

Similarly for $B^1\Pi_u$, $E_{0,10} = E_{\nu'=0} + E_{J'=10} = 17.10 + 3.96342 = 21.0634$ cm^{-1}, $E_{1,10} = E_{\nu'=1} + E_{J'=10} = 51.62 + 3.96342 = 55.5834$ cm^{-1}, $E_{1,11} = E_{\nu'=1} + E_{J'=11} = 51.62 + 4.75564 = 56.3756$ cm^{-1}, $E_{1,12} = E_{\nu'=1} + E_{J'=12} = 51.62 + 5.61972 = 57.2397$ cm^{-1}, $E_{2,11} = E_{\nu'=2} + E_{J'=11} = 85.49 + 4.75564 = 90.2456$ cm^{-1}, $E_{2,12} = E_{\nu'=2} + E_{J'=12} = 85.49 + 5.61972 = 91.1097$

cm^{-1},

We can then choose the parameters of the probe pulses such that it can excite both states a_1 and a_2 simultaneously and observe the population dynamics. We can thus set the control and probe pulse bandwidth $62.51cm^{-1}$ and $104.81cm^{-1}$, respectively. The pure lifetime broadening is given by:

$$\Gamma \sim \tilde{\Gamma}_{e'e} = \frac{\omega_{a_1a_2}k_BT}{\hbar\Lambda_a} \qquad \gamma_3 \sim \tilde{\Gamma}_{g'g} = \frac{\omega_{bc}k_BT}{\hbar\Lambda_b} \tag{S27}$$

Assuming collisional broadening with $\gamma_{col} \simeq 50cm^{-1}$, the dephasing rates are given by: $\gamma_1 \simeq 50cm^{-1}$,$\gamma_2 \simeq 50cm^{-1}$,$\gamma_3 = 0.01cm^{-1}$, and for the population relaxation rate between virbrational states $\nu' = 1$ and $\nu' = 2$, $\Gamma = 0.03cm^{-1}$.

To finalize the states for simulations we select for $X^1\Sigma_g^-$: $\nu'' = 1$ and $J'' = 10$ and $\nu'' = 3$ and $J'' = 12$. For $B^1\Pi_u$, we select $\nu' = 1$ and $J' = 10$ and $\nu' = 2$ and $J' = 11$. Thus $\nu'' = 1$, $J'' = 10$ corresponding to $|b\rangle$, which is the lowest energy level; and $\nu'' = 3$, $J'' = 12$ corresponding to the energy level $|c\rangle$, $\nu' = 1$, $J' = 10$ corresponding to $|a_2\rangle$ and $\nu' = 2$, $J' = 11$ correspond to $|a_1\rangle$.

S3. SIMULATIONS FOR THE $a_2 - c$ DRIVEN BY CONTROL FIELD.

It has been mentioned that the optimum control field strength determined by the overlap between the position of the $\omega_{a_1b}^-$ peak and the ω_{a_2b} obtained at $\Omega = 2(\omega_{a_1b} - \omega_{a_2b})$. Fig. S1 depicts the imaginary part of Eq. (5) and Eq. (6) to illustrate this point.

Fig. S2 depicts the two dimensional(2D) spectra in the case when the control field is resonant with the $a2 - c$ transition using the population dynamics solution of Eqs. (S21) - (S25). In this case optimum case corresponds to matching $\omega_{a_1b} = \omega_{a_2b}^+$ obtained at $\Omega = 2(\omega_{a_1b} - \omega_{a_2b})$.
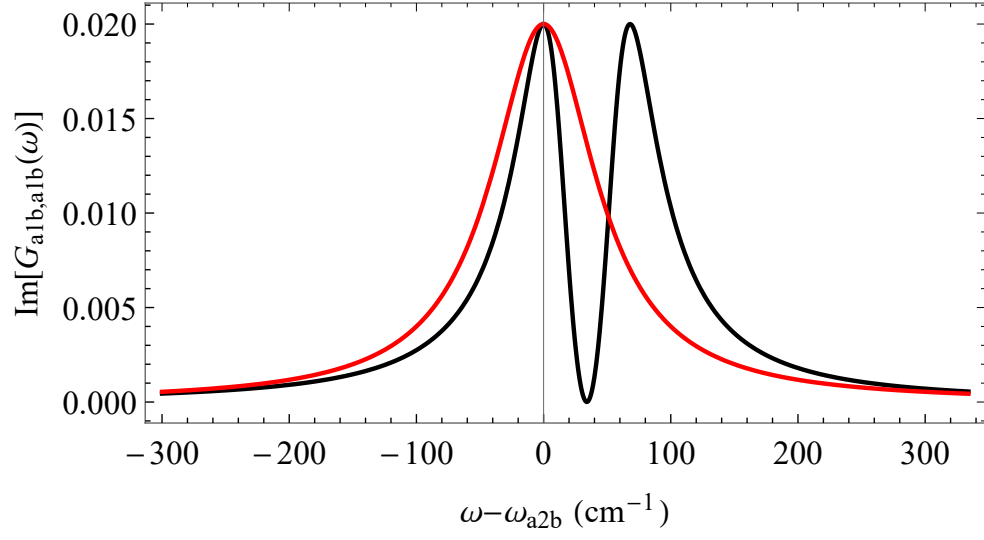
Figure S1. (color online): Imaginary part of the coherence Green's function in Eq. (5) - black and Eq. (6) - red.
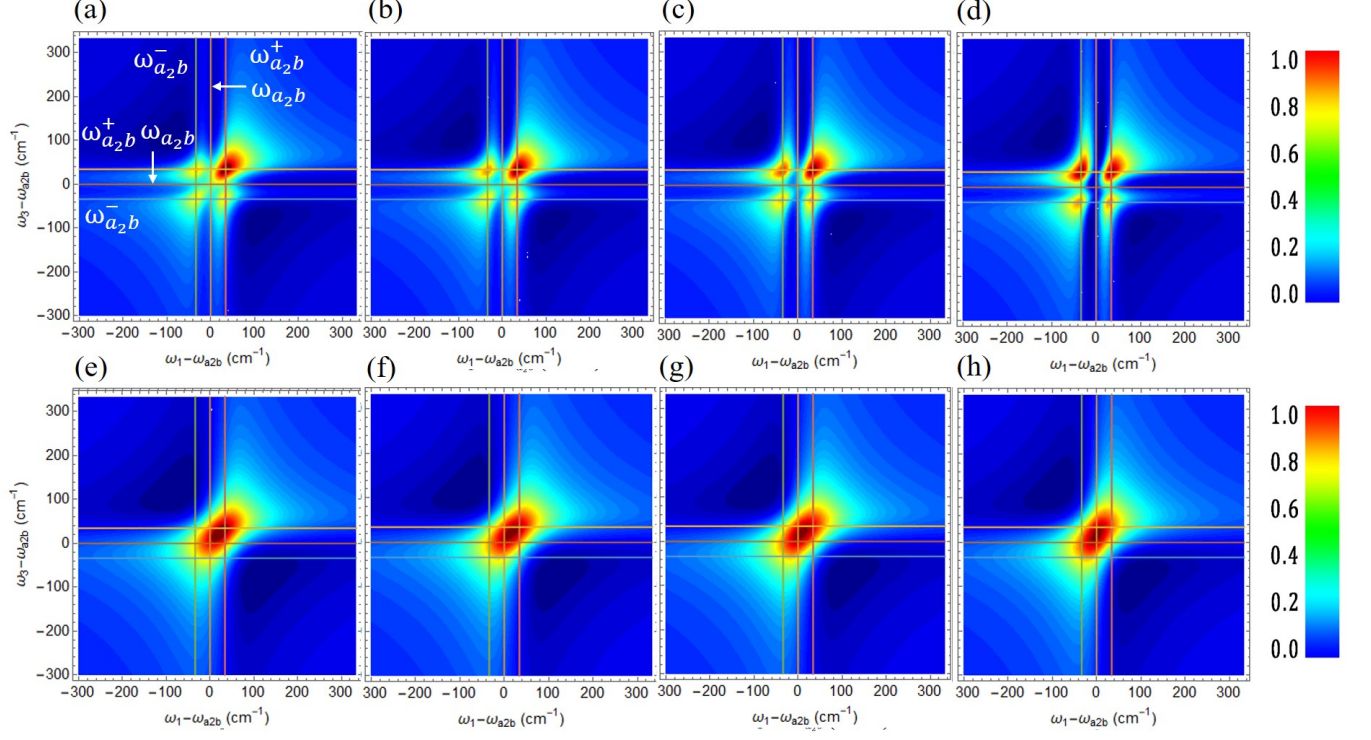
Figure S2. (color online): same as Fig. 3 in the main text, but assuming control field resonant with $a_2 - c$ transition. Three horizontal and vertical lines correspond to $\omega_{a_{1,2}b}$ as well as $\omega_{a_2b}^{\pm} \simeq \omega_{a_2b} \pm \Omega/2$. The control field strength is chosen such that $\omega_{a_2b}^{+} \equiv \omega_{a_1b}$.