Rotational excitations in two-color photoassociation

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We show that it is possible to excite higher rotational states $J > 2$ in ultracold photoassociation by two laser fields. Usually higher J states are suppressed in photoassociation at ultracold temperatures in the regime of Wigner threshold laws. We propose a scheme in which one strong laser field drives photoassociation transition close to either $J = 1$ or $J = 2$ rotational state of a particular vibrational level of an electronically excited molecule. The other laser field is tuned near photoassociation resonance with $J > 2$ rotational levels of the same vibrational state. The strong laser field induces a strong continuum-bound dipole coupling. The resulting dipole force between two colliding atoms modifies the continuum states forming continuum-bound dressed states with a significant component of higher partial waves in the continuum configuration. When the second laser is scanned near the resonance of the higher J states, these states become populated due to photoassociative transitions from the modified continuum.

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I. INTRODUCTION

Photoassociation (PA) spectroscopy [1,2] of ultracold atoms by which two colliding atoms absorb a photon to form an excited molecular state is an important tool for studying ultracold collisional properties at the interface of atomic and molecular states. PA is particularly useful for producing translationally cold molecules [3–9] and generating optical Feshbach resonance [10–14]. More than a decade ago, theoretical models [15,16] were developed to explain PA line shape in the weak-coupling regime. The effects of laser intensity on PA spectra [17–22] have been an important current issue. Over the years, two-color Raman-type PA has emerged as an important method for creating translationally cold molecules in the ground electronic configuration. Recently, using this method, cold polar molecules [7] in rovibrational ground state have been produced. Molecules created by one- or two- color PA of ultracold atoms generally possess low-lying rotational levels $J \leqslant 3$. Motivated by recent experimental observation of excitation of higher rotational states in ultracold PA with an intense laser field [23], we here explore theoretically the possibility of rotational excitations in two-color PA. This may be important for producing translationally cold molecules in selective higher rotational states. Previously, two-color PA has been investigated in different other contexts [24–31], such as photoionization of excited molecules [24–27], shielding of atomic collision [28–30], measurement of s wave scattering length [31], and so on.

In this article we propose a method of two-color photoassociation of two homonuclear atoms for exciting higher rotational levels. Our proposed method is schematically shown in Fig. 1. Laser L_A is a strong field and the laser L_B is a weak one. L_A is tuned near either the $J_A = 1$ or $J_A = 2$ rotational state of a particular vibrational level v of the excited state. This rotational state is predominantly accessed by PA transition from s-wave scattering state. A photon from L_A causes PA excitation from the continuum (s wave) to the bound level J_A. A second photon from the same laser can cause a stimulated de-excitation back to the continuum state.

This is a stimulated Raman-type process which can lead to significant excitation of higher partial waves in the two-atom continuum. Now, if a weak laser L_B is tuned near $J_B > 2$ states, these higher rotational states get excited due to PA from the modified continuum. In this scheme of two-color PA, three photons are involved. This does not fit into a standard Λ or V-type process. Here bound-bound transition is absent. All the transitions are of continuum-bound type. This scheme may be viewed as a combination of Λ and V-type process with continuum acting as an intermediate state for V-type transitions. In the previous Raman-type PA experiments, the excited molecular state is used as an intermediate state. Furthermore, usually two-color PA is carried out in the weak coupling regime. In contrast, our proposed scheme involves necessarily one strong laser field for inducing strong PA coupling. We demonstrate excitation of higher rotational levels in two-color ultracold PA by resorting to a simplified model. We first evaluate higher partial-wave scattering states modified due to strong photoassociative coupling [14] induced by the strong laser L_A. We employ these modified wave functions to calculate two-color stimulated line widths which are significantly enhanced compared to those in the case of one-color.

The article is organized as follows. In the following section we describe the formulation of the problem and its solution. The numerical results and discussion has been given in Sec. III. Finally the article is concluded in Sec. IV.

II. THE MODEL AND ITS SOLUTION

To start with, let us consider that PA laser couples continuum (scattering) states of collision energy $E = \hbar^2 k^2/(2\mu)$ (where μ is the reduced mass) of two alkali-metal-type homonuclear ground-state S atoms to an excited diatomic (molecular) bound state which asymptotically corresponds to one ground S and another excited P atom. Under electric dipole approximation, the interaction Hamiltonian can be
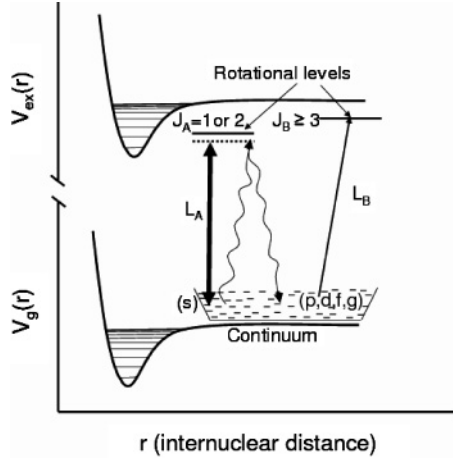
FIG. 1. A schematic diagram showing the strong (double-arrow thick line) and weak (single-arrow thin line) field couplings between the excited rotational levels J_α ($\alpha = A, B$) and the continuum state. Strong laser L_A modifies the continuum state by a two-photon process (curly lines) as described in the text. The laser L_B is tuned near resonance with the rotational levels $J_B \geqslant 3$ which are then populated due to PA transition from the modified continuum. Molecular rotational levels $J = 1$ and $J = 2$ are accessible from s-wave ($\ell = 0$) scattering state, but $J \geqslant 3$ can only be accessed from higher partial-wave ($\ell > 0$) scattering states.

expressed as

$$H_{\text{int}} = \sum_{i=1,2} E_L \hat{\pi} \cdot \hat{d}_i, \qquad (1)$$

where $\hat{d}_i = -e\mathbf{r}_i$ is the dipole moment of i-th atom whose valence electron's position is given by $\mathbf{r}_i$ with respect to the center of mass of this atom. Here e represents an electron's charge, E_L is the laser field amplitude, and $\hat{\pi}$ is the polarization vector of the laser. The total Hamiltonian in the center-of-mass frame of the two atoms can be written as

$$H = H_{\text{elec}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_a, \mathbf{r}_b) - \frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{\hbar^2}{2M}\nabla_R^2 + H_{hf} + H_{\text{int}}, \qquad (2)$$

where H_{elec} is the electronic part of the Hamiltonian which includes terms corresponding to kinetic energy of the two valence electrons, mutual Coulomb interactions between nuclei and the electrons, exchange, and electronic spin-orbit interaction. Here $\mathbf{r}_a$ and $\mathbf{r}_b$ represent the position vectors of the nuclei of atoms a and b, respectively; ∇_r and ∇_R denote the Laplacian operators corresponding to the relative coordinate $\mathbf{r} = \mathbf{r}_a - \mathbf{r}_b$ and the center-of-mass coordinate $\mathbf{R} = (\mathbf{r}_a + \mathbf{r}_b)/2$ and H_{hf} stands for the hyperfine interaction of two atoms. Under the Born-Oppenheimer approximation, while solving the electronic part of the Hamiltonian, the nuclear coordinates appear merely as parameters. PA laser couples only two electronic molecular states which are the initial ground and the final excited diatomic states represented by $\langle \mathbf{r}_1, \mathbf{r}_2; r \mid g \rangle = \phi_g(\mathbf{r}_1, \mathbf{r}_2; r)$ and $\langle \mathbf{r}_1, \mathbf{r}_2; r \mid e \rangle = \phi_e(\mathbf{r}_1, \mathbf{r}_2; r)$, respectively. These internal electronic states have parametrical dependence on the internuclear coordinate r. They satisfy the eigenvalue equations

$$H_{\text{elec}}\phi_\alpha(\mathbf{r}_1, \mathbf{r}_2; r) = V_\alpha(r)\phi_\alpha(\mathbf{r}_1, \mathbf{r}_2; r); \alpha = g, e. \qquad (3)$$

We assume that the matrix element $\langle e \mid H_{int} \mid g \rangle \simeq \Omega_{eg}(r)$ depends only on separation r. Then the center-of-mass motion gets decoupled from relative motion. Henceforth we consider only the relative motion. By specifying the electronic parts of both the bound and the continuum states, one can calculate the matrix element of H_{int} over the electronic parts of the two molecular levels involved in free-bound transition and thus obtain molecular coupling strength $\Lambda(r)$.

The continuum-bound dressed state can be written as $\Psi_E(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}) = \sum_{\alpha=g,e} \Phi_\alpha(\mathbf{r}) \mid \alpha \rangle$ which is assumed to be energy normalized with E being the energy eigenvalue. In the absence of atom-field interaction H_{int}, the problem is to find out the multichannel scattering wave function in the ground electronic configuration. The scattering channels correspond to two separated atoms a and b in hyperfine spin f_a and f_b, respectively. The molecular hyperfine state is characterized by the spin $\overrightarrow{F} = \overrightarrow{f}_a + \overrightarrow{f}_b$. A channel is defined by the angular state $\mid \mathcal{F}; f_a, f_b, \ell \rangle$, where $\overrightarrow{\mathcal{F}} = \overrightarrow{F} + \overrightarrow{\ell} = \overrightarrow{f}_a + \overrightarrow{f}_b + \overrightarrow{\ell}$, where ℓ is the mechanical angular momentum of the relative motion of the two atoms. This asymptotic basis $\mid \mathcal{F}; f_a, f_b, \ell \rangle$ can be expressed in terms of the adiabatic molecular basis $\mid \mathcal{F}; S, I, \ell \rangle$ [32], where S and I are the total electronic and nuclear spin angular momentum of two atoms. In the case of excited molecular state, S should be replaced by electronic angular momentum $J_e = S + L$. Alternatively, the adiabatic basis $\mid \mathcal{F}; J_e, I, \ell \rangle$ can also be expressed in terms of $\mid \mathcal{F}; J(J_e, \ell)I \rangle$. Thus the rotational state of a diatom can be expressed in terms of the matrix element $\mid J\Omega M \rangle = i^J \sqrt{\frac{2J+1}{8\pi^2}} \mathcal{D}_{M\Omega}^{(J)}(\hat{r})$ where M and Ω are the z component of J in the space-fixed and body-fixed coordinate frame and $\hat{r}$ represents the Euler angles for transformation from body-fixed to space-fixed frame. $\mathcal{D}_{M\Omega}^{(J)}(\hat{r})$ is the rotational matrix element. For the ground electronic configuration, we have $J = \ell$, $M = m_\ell$, and $\Omega = 0$; thereby, $\mathcal{D}_{M\Omega}^{(J)}(\hat{r})$ reduces to spherical harmonics $Y_{\ell m_\ell}$. We thus express the ground state $\Phi_g(\mathbf{r})$ in the following form

$$\Phi_g(\mathbf{r}) \propto r^{-1} \sum_{\ell, m_\ell} \left[\int_{E'} \beta_{E'} \psi_{E'\ell m_\ell}(r) dE' | \ell m_\ell 0 \rangle \right], \qquad (4)$$

where $\psi_{E'\ell m_\ell}(r)$ is the energy-normalized scattering state with collision energy E' and β'_E is the density of states of unperturbed continuum. Similarly, for a particular value of Ω, we can expand the excited state $\Phi_e(\mathbf{r})$ in the following form

$$\Phi_e(\mathbf{r}) \propto r^{-1} \sum_M [\phi_{vJ}(r) | J\Omega M \rangle]. \qquad (5)$$

Substitution of Eqs. (4) and (5) into time-independent Schrödinger equation leads to coupled differential equations. These equations are solved by the use of real space Green's function. The detailed method of solution for a model problem is given in Appendix A. In our model calculations, we consider only a single ground hyperfine channel. The solution $\phi_{vJ}(r)$ can be expressed as

$$\phi_{vJ}(r) = \int_{E'} \beta_{E'} \sum_{\ell m_\ell M} A_{JM;\ell m_\ell} \phi_{vJ}^0(r) dE', \qquad (6)$$

where $\phi_{vJ}^0(r)$ is the excited molecular state (unit-normalized) in the absence of laser field and

$$A_{J,M;\ell,m_\ell} = \left[f_{J,M;\ell m_\ell} + E_{J\ell}^{\text{shift}} \tilde{A}_J \right] \frac{1}{\hbar\delta + E - E_{vJ} + i\hbar\gamma/2} \tag{7}$$

is the probability amplitude of excitation of J from a particular partial wave ℓ. Here

$$f_{JM;\ell m_\ell} = \int \phi_{vJ}^0(r') \Lambda_{JM;\ell m_\ell}(r') \psi_{E\ell}^{0,reg}(r') dr' \tag{8}$$

is the continuum-bound dipole matrix element and $\Lambda_{JM;\ell m_\ell} = \langle JM\Omega|\Omega_{eg}|\ell m_\ell 0\rangle$. $\psi_{E\ell}^{0,reg}(r')$ represents the ℓ-th partial-wave regular scattering solution in the absence of laser field and

$$E_{J\ell}^{\text{shift}} = \pi \iint dr'dr \phi_{vJ}^0(r') \Lambda_{JM;\ell m_\ell}(r')$$
$$\times [\mathcal{K}_\ell(r', r)] \Lambda_{\ell m_\ell;JM}(r) \phi_{vJ}^0(r) \tag{9}$$

is the partial light shift of the excited state. Here $\mathcal{K}_\ell(r, r')$ is the propagator as defined in the Appendix A. The total probability amplitude of excitation $\tilde{A}_J$ for a particular J is given by

$$\tilde{A}_J = \sum_{\ell,m_\ell,M} \frac{f_{JM;\ell m_\ell}}{\hbar\delta + E - E_{vJ} + i\hbar\gamma/2 - E_J^{\text{shift}}}, \tag{10}$$

where $E_J^{\text{shift}} = \sum_{\ell,m_\ell,M} E_{J\ell}^{\text{shift}}$ is the total energy shift of the excited level. $\hbar\gamma/2$ is the natural line width of the excited molecular state, E_{vJ} is the bound state energy corresponding to the bound-state solution ϕ_{vJ}^0 of the excited state. $\delta = \omega_L - \omega_A$ is the frequency offset between the laser frequency ω_L and atomic resonance frequency ω_A. The ground-state scattering solution in the presence of PA laser is given by

$$\psi_{E\ell m_\ell}(r) = \psi_{E\ell}^{0,reg} + \sum_{\ell'm_{\ell'}M} A_{JM;\ell'm_{\ell'}}(E)$$
$$\times \int \mathcal{K}_\ell(r, r') \Lambda_{\ell m_\ell;JM}(r') \phi_{vJ}^0(r') dr'. \tag{11}$$

In the asymptotic limit ($r \to \infty$), the modified scattering wave function behaves like

$$\psi_{E\ell m_\ell} = \cos\eta_\ell^L \psi_{E\ell}^{0,reg} + \sin\eta_\ell^L \psi_{E\ell}^{0,irr}, \tag{12}$$

where $\psi_{E\ell}^{0,irr}$ is the irregular wave function of ℓ-th partial wave. Here η_ℓ^L is the phase shift due to the applied laser field and is given by

$$\tan\eta_\ell^L = -\pi \sum_{\ell'm_{\ell'}M} A_{JM;\ell'm_{\ell'}}(E) f_{\ell m_\ell;JM} \tag{13}$$

$$= -\pi \sum_{\ell',m_{\ell'},M} \frac{f_{JM;\ell'm_{\ell'}}}{\hbar\delta + E - E_{vJ} + i\hbar\gamma/2 - E_J^{\text{shift}}}$$
$$\times f_{\ell m_\ell;JM}, \tag{14}$$

where $f_{\ell m_\ell;JM} = \int_0^\infty \phi_{vJ}^0(r') \Lambda_{\ell m_\ell;JM}(r') \psi_{E\ell}^{0,reg}(r') dr'$. The two-color partial stimulated line width $\Gamma_{J_B\ell}^{(2)}$ for a particular rotational state J_B is given by

$$\Gamma_{J_B\ell}^{(2)} = 2\pi \left| \int \phi_{vJ}^0(r) \Lambda_{JM;\ell m_\ell}(r) \psi_{E\ell m_\ell}(r) dr \right|^2 \tag{15}$$

and the total stimulated line width is $\Gamma_{J_B}^{(2)} = \sum_{\ell m_\ell M} \Gamma_{J_B\ell}^{(2)}$. The excitation of particular rotational state J from the partial wave ℓ is governed by the following selection rule

$$\left| J - |\vec{L} + \vec{S}| \right| \leqslant \ell \leqslant |J + |\vec{L} + \vec{S}||, \tag{16}$$

where L is the total electronic orbital angular momentum $\vec{L} = \vec{l}_1 + \vec{l}_2$ and S is the sum of two individual atomic spin, i.e., $\vec{S} = \vec{s}_1 + \vec{s}_2$. So the lowest possible partial wave ℓ which can make the largest contribution to the excitation of rotational state $J = 1, 2, 3, 4, 5, 6$ are 0, 0, 1, 2, 3, 4, respectively. The two-color photoassociation rate $K_{PA}^{(2)}$ for $J_B > 2$ is defined as

$$K_{PA}^{(2)} = \langle v_{rel}\sigma_J \rangle = \frac{1}{hQ_T} \int_0^\infty \hbar P_{J_B}^{(2)} e^{-\beta E} dE, \tag{17}$$

where $P_{J_B}^{(2)} = \gamma \Gamma_J^{(2)}/[(\hbar\delta_B + E - E_{v,J_B} - E_{J_B}^{\text{shift}})^2 + (\gamma + \Gamma_J^{(2)})^2/4]$ and $v_{rel} = \hbar k/\mu$ is the relative velocity of two atoms, $\sigma_J = \hbar P_{J_B}^{(2)}/k^2$ is the inelastic cross section due to loss of atoms. Here $\langle\cdots\rangle$ implies an averaging over the distribution of initial velocities, $Q_T = (2\pi\mu K_B T/h^2)^{3/2}$ is the translational partition function and $\beta = (K_B T)^{-1}$. In the next section, we apply this formalism to a model system and obtain numerical results.

III. RESULTS AND DISCUSSION

For numerical illustration, we consider a model system of two cold ground-state ($S_{1/2}$) ^{23}Na atoms undergoing PA transition from ground state $^3\Sigma_u^+$ to the vibrational state $v = 48$ of the excited molecular 1_g state [23]. At large internuclear distance this 1_g potential correlates to $^2S_{1/2} + ^2P_{3/2}$ free atoms and at short range to $1\,^1\Pi_g$ Born-Oppenheimer potential. In Ref. [23] higher rotational lines up to $J = 6$ have been clearly observed in PA with an intense laser field. The centrifugal barrier of $\ell > 0$ of the two atoms lies at $r > 50\,a_0$ ($a_0 = $ Bohr radius), whereas PA excitations occur at $r \sim 27\,a_0$. Therefore, the higher rotational states will be unlikely to be populated by PA transitions from $\ell > 0$ partial-wave scattering states at ultracold temperatures in the weak-coupling regime. Previously, higher rotational levels have been excited in PA spectroscopy due to resonant dipole-dipole interaction with transition occurring at large internuclear separations [33,34]. The numerically calculated rotational energies E_{vJ}, energy shifts E_J^{shift} and the corresponding energy difference $\Delta_J = E_{vJ} - E_{vJ-1}$ for six lowest J values are given in Table I. To demonstrate the working of our proposed scheme, we resort

TABLE I. Numerically calculated rotational energies E_{vJ} (in unit of GHz) and total shift E_J^{shift} (in unit of MHz) for one-color laser intensity $I = 1$ kW/cm^2 for vibrational state $v = 48$ of 1_g excited state. Also given are the rotational energy spacings $\Delta_J = E_{vJ} - E_{vJ-1}$ (in unit of GHz) for a few lowest J values.

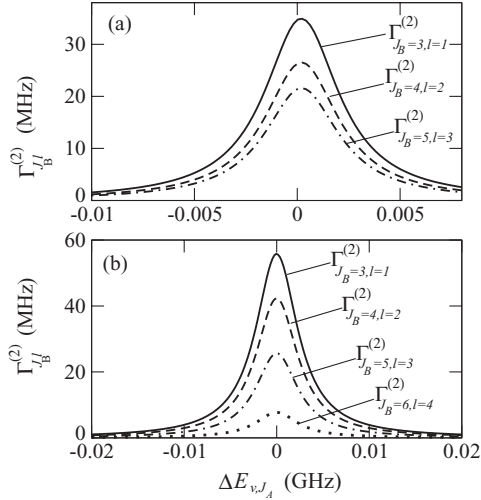| $J \longrightarrow$	1	2	3	4	5	6
E_{vJ} (GHz)	0.57	2.13	4.77	8.55	13.03	18.34
Δ_J (GHz)	–	1.56	2.64	3.78	4.48	5.31
$-E_J^{\text{shift}}$ (MHz)	19.69	22.79	17.36	11.61	6.83	2.22

FIG. 2. Two-color partial stimulated line widths $\Gamma_{J_B\ell}^{(2)}$ (in unit of MHz) as a function of $\Delta E_{v,J_A}$ (in unit of GHz) at collisional energy $E = 10\ \mu$K. The intensity I_A of laser L_A tuned near $J_A = 1$ (a) and $J_A = 2$ (b) is 40 kW/cm^2 and the intensity I_B of weak laser L_B is 1 W/cm^2. The total shift $E_{J_A}^{\text{shift}}$ of the rotational state $J_A = 1$ and $J_A = 2$ are -0.79 GHz and -0.91 GHz, respectively.

to a simplified two-state calculation. We consider only one ground hyperfine channel with $F = 4$, $f_a = 2$, and $f_b = 2$ in the absence of any external magnetic field. In the excited molecular state, we neglect the hyperfine interaction. The two-color partial stimulated line width $\Gamma_{J_B\ell}^{(2)}$ is plotted as a function of detuning $\Delta E_{v,J_A} = \hbar\delta_A + E - E_{v,J_A} - E_{J_A}^{\text{shift}}$ in Fig. 2 for J_B ranging from 3 to 6. The strong laser L_A is tuned near $J_A = 1$ [Fig. 2(a)] and $J_A = 2$ [Fig. 2(b)]. From Fig. 2 we note that $\Gamma_{J_B\ell}^{(2)}$ strongly depends on the detuning $\Delta E_{v,J_A}$ of the strong laser from PA resonance of the rotational level J_A. The maximun of $\Gamma_{J_B\ell}^{(2)}$ occurs at $\Delta E_{v,J_A} = 0$. For lower J_B values, the probability of rotational excitation is higher.

For comparison, we also calculate one-color partial stimulated line widths $\Gamma_{J\ell}^{(0)}$ for $J > 2$ from the expression $\Gamma_{J\ell}^{(0)} = 2\pi|f_{JM;\ell m_\ell}|^2$. The one-color total stimulated line width is $\Gamma_J^{(0)} = \sum_{\ell,m_\ell,M} \Gamma_{J\ell}^{(0)}$. At 10 μK energy and at laser intensity 1 W/cm^2, the one-color partial stimulated line widths $\Gamma_{J=3,\ell=1}^{(0)} = 15.46$ Hz, $\Gamma_{J=4,\ell=2}^{(0)} \simeq 0$, $\Gamma_{J=5,\ell=3}^{(0)} \simeq 0$. A

TABLE II. Tabulated are one- and two-color partial stimulated line widths $\Gamma_{J\ell}^{(0)}$ and $\Gamma_{J_B\ell}^{(2)}$ at $E = 10\ \mu$K for two δ_A values. Here laser L_A is tuned near $J_A = 1$ rotational state. The intensities of the two lasers are $I_B = 1$ W/cm^2 and $I_A = 40$ kW/cm^2.

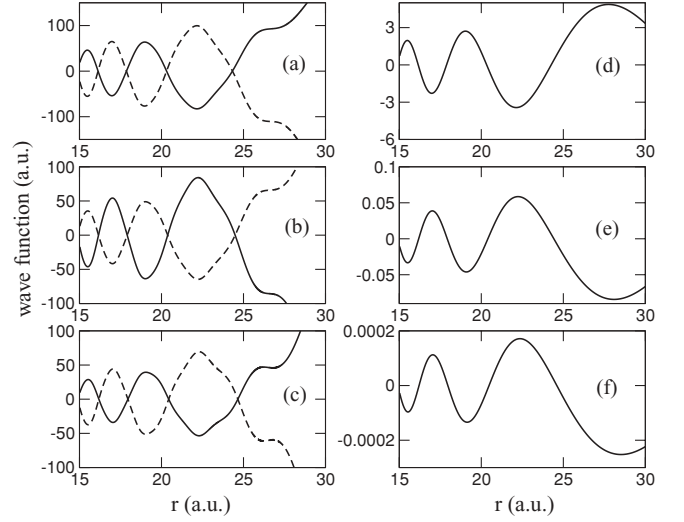|			$\delta_A = -1.25$ GHz	$\delta_A = -1.48$ GHz
J	ℓ	$\Gamma_{J\ell}^{(0)}$ (MHz)	$\Gamma_{J_B\ell}^{(2)}$ (MHz)	$\Gamma_{J_B\ell}^{(2)}$ (MHz)
3	1	1.55×10^{-05}	0.0158	0.0107
3	2	0.0000	0.0111	0.0065
3	3	0.0000	0.0085	0.0051
4	2	0.0000	0.0128	0.0075
4	3	0.0000	0.0072	0.0047
5	3	0.0000	0.0103	0.0061

FIG. 3. The subplots (a), (b), and (c) show the light-induced scattering wave functions $\psi_{E\ell m_\ell}$ (in unit of Bohr radius$^{-1/2} \times$ Hartree$^{-1/2}$) for p ($\ell = 1$), d ($\ell = 2$), and f waves ($\ell = 3$), respectively. The solid and dashed curves correspond to the detuning $\delta_A = -1.25$ GHz and $\delta_A = -1.48$ GHz, respectively. The plots (d), (e), and (f) exhibit the corresponding field-free regular wave functions $\psi_{E\ell}^{0,reg}$. All the wave functions are plotted at collisional energy of 10 μK and intensity $I_A = 40$ kW/cm^2.

comparison between one- and two-color partial stimulated line widths has been made in Table II for $J_B > 2$ at collisional energy 10 μK. The two-color total line widths $\Gamma_{J_B=3}^{(2)}$, $\Gamma_{J_B=4}^{(2)}$, $\Gamma_{J_B=5}^{(2)}$ are 0.03537, 0.0200, and 0.0103 MHz, respectively, when $\delta_A = -1.25$ GHz and they are 0.02229, 0.0122, and 0.0061 MHz, respectively, for $\delta_A = -1.48$ GHz. The corresponding one-color weak-coupling partial as well as total stimulated line widths $\Gamma_{J\ell}^{(0)}$ and $\Gamma_J^{(0)}$ for the same rotational states with laser intensity of 1 W/cm^2 are vanishingly small while the two-color partial $\Gamma_{J_B\ell}^{(2)}$ and total $\Gamma_{J_B}^{(2)}$ exceed $\Gamma_{J\ell}^{(0)}$ and $\Gamma_J^{(0)}$ by several orders of magnitude. We find the energy shift $|E_{J_A=1}^{\text{shift}}|$ is 0.79 GHz which exceeds the spontaneous line width γ (say, 2 MHz for the model calculation) by two orders of magnitudes.

In order to trace the origin of increment of $\Gamma_{J_B\ell}^{(2)}$ we plot perturbed $\psi_{E\ell m_\ell}$ for $\ell \neq 0$ when laser L_A is tuned near $J_A = 1$ and the corresponding field-free regular functions $\psi_{E\ell}^{0,reg}$ in

TABLE III. Tabulated are the $\tan\eta_\ell^L$ when the laser L_A is tuned near $J_A = 2$ at $E = 10\ \mu$K for three values of δ_A. The parameters are $I_A = 40$ kW/cm^2, $E_{vJ_A=2} = -2.138$ GHz, and $E_{J_A=2}^{\text{shift}} = -0.91$ GHz. In the field-free case, $\tan\eta_{\ell=1}^0 = -1.57 \times 10^{-4}$, $\tan\eta_{\ell=2}^0 = 1.20 \times 10^{-6}$, $\tan\eta_{\ell=3}^0 \simeq 0$, and $\tan\eta_{\ell=4}^0 \simeq 0$.

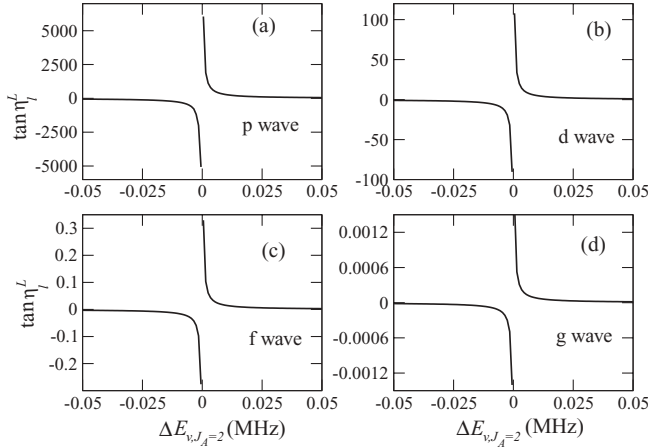|	$\delta_A = -2.95$ GHz	$\delta_A = -3.049$ GHz	$\delta_A = -3.17$ GHz
ℓ	$\tan\eta_\ell^L$ (units of 10^4)	$\tan\eta_\ell^L$ (units of 10^4)	$\tan\eta_\ell^L$ (units of 10^4)
1	263.00	36900.00	-229.00
2	4.93	659.00	-4.09
3	0.01	2.01	-0.01
4	0.00	0.01	0.00

FIG. 4. $\tan \eta_\ell^L$ (η_ℓ^L is the light induced phase shift) is plotted as a function of detuning $\Delta E_{v, J_A=2}$ (MHz) when L_A is tuned near $J_A = 2$. The total shift $E_{J_A=2}^{\text{shift}}$ at 40 kW/cm^2 is -0.91 GHz. The other parameters are $I_A = 40$ kW/cm^2 and $E = 10$ μK.

Fig. 3. It is clear from this figure that the amplitudes of $\psi_{E\ell m_\ell}$ are greatly enhanced by several orders of magnitude compared to those of $\psi_{E\ell}^{0,reg}$. Next, we calculate $\tan \eta_\ell^L$ by using Eq. (14) when laser L_A is tuned near $J_A = 2$. These are given in Table III for $\delta_A = -2.95$, -3.17, and -3.049 GHz. The first two δ_A values correspond to off-resonant and the last one to resonant condition. The variation of $\tan \eta_\ell^L$ with $\Delta E_{v, J_A=2}$ is plotted in Fig. 4 which exhibits resonance for higher partial waves induced by strong-coupling PA. The enhancement of the partial ($\ell \neq 0$) wave amplitude is due to the term $\sum_{\ell' m_{\ell'} M} A_{JM; \ell' m_{\ell'}}(E)$ of Eq. (11). In Fig. 5, the two-color total stimulated line width $\Gamma_{J_B}^{(2)}$ is plotted as a function of collisional energy E for two off-resonant δ_A values when L_A is tuned near $J_A = 1$. The magnitude of $\Gamma_{J_B}^{(2)}$ for higher rotational
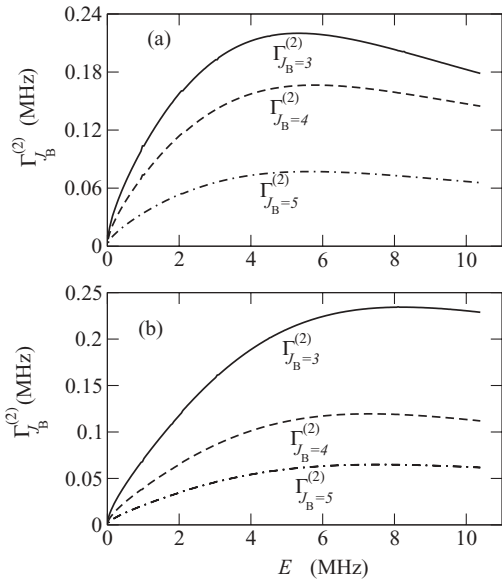

FIG. 5. The two-color total stimulated line width $\Gamma_{J_B}^{(2)}$ (in unit of MHz) for different J_B (as indicated in the plots) is plotted as a function of collisional energy E (in unit of MHz) when L_A is tuned near $J_A = 1$ for $\delta_A = -1.25$ GHz (a), $\delta_A = -1.48$ GHz (b) with $I_A = 40$ kW/cm^2 and $I_B = 1$ W/cm^2.

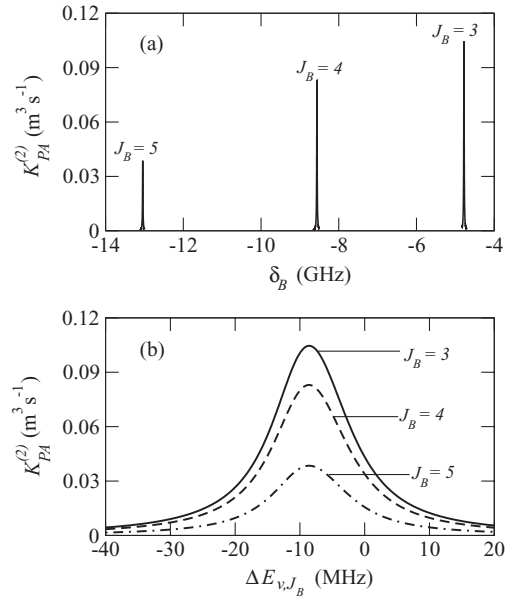

FIG. 6. The upper panel (a) shows two-color photoassociation rate $K_{PA}^{(2)}$ (in unit of m^3 s^{-1}) as a function of atom-field detuning δ_B (in unit of GHz) for three higher rotational levels J_B (as indicated in the plots) for $\delta_A = -1.25$ GHz when the laser L_A is tuned near $J_A = 1$. The lower panel (b) shows the same but as a function of detuning $\Delta E_{v, J_B} = \hbar \delta_B - E_{v, J_B} - E_{J_B}^{\text{shift}}$ (in unit of MHz) from PA resonance. The other parameters for both the panels are $I_A = 40$ kW/cm^2, $I_B = 1$ W/cm^2, and $T = 100$ μK.

states ($J_B = 4, 5$) is less than that of $J_B = 3$. This is due to the fact that the lowest possible partial-wave contribution to the excitation of rotational states $J_B = 4$ and $J_B = 5$ are d and f, respectively, while $J_B = 3$ state can be populated from p wave which has rotational barrier lower than that of d and f wave. The two-color photoassociation rate $K_{PA}^{(2)}$ as defined in Eq. (17) has been plotted as a function of δ_B [Fig. 6(a)] and $\Delta E_{v, J_B}$ [Fig. 6(b)]. The spectra in Fig. 6(b) are red shifted due to the presence of the term $\Gamma_{J_B}^{(2)}$ in Eq. (17). From the selection rule, it is obvious that $J_B = 3, 4, 5$ rotational states cannot be populated by a PA transition from s-wave scattering state. But the appearance of the $J_B = 3, 4, 5$ lines in PA spectra is an indication of the significant modification of the partial-scattering wave functions by intense light field.

IV. CONCLUSION

In the present article we have developed a two-color PA scheme for the excitations of higher ($J_B > 2$) rotational levels which are generally suppressed in the Wigner threshold law regime. We have calculated two-color stimulated line width (for $J_B > 2$) by fixing strong laser either near $J_A = 1$ or $J_A = 2$ state and tuning another weak laser to higher rotational ($J_B = 3, 4, 5$) states. Then we have compared these with one-color line widths. The enhancement of stimulated line width is a result of strong-coupling photoassociative dipole interaction which in turn modifies the continuum states. This proposed method may be important for coherent control of rotational excitations and manipulation of optical Feshbach resonance of higher partial waves.

APPENDIX

The mathematical treatment given here is closely related to our earlier work [14]. Treating the laser field classically, the effective interaction Hamiltonian under rotating wave approximation in the two state basis can be expressed as

$$H_{\text{eff}}^{\text{int}} = \exp(-i\delta t)\Omega_{eg}(r)|e\rangle\langle g| + \text{H.c.} \qquad (A1)$$

From time-independent Schrödinger equation $H\Psi_E = E\Psi_E$, we obtain two coupled equations

$$\left[-\frac{\hbar^2}{2\mu}\nabla_r^2 + V_{\text{g}}(r) - E\right]\Phi_g(\mathbf{r}) = -\Omega_{ge}(r)\Phi_e(\mathbf{r}) \qquad (A2)$$

$$\left[-\frac{\hbar^2}{2\mu}\nabla_r^2 + V_{\text{ex}}(r) - E - \hbar\delta\right]\Phi_e(\mathbf{r}) = -\Omega_{eg}(r)\Phi_g(\mathbf{r}). \qquad (A3)$$

Here V_{g} is assumed to include hyperfine interaction of the chosen channel. Substituting Eqs. (4) and (5) into the Schödinger equations (A2) and (A3) we get two coupled equations

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + B_J(r) + V_{\text{ex}}(r) - \hbar\delta - E - i\hbar\frac{\gamma}{2}\right]\phi_{vJ}$$
$$= -\sum_{\ell m_\ell}\Lambda_{JM;\ell m_\ell}\tilde{\psi}_{E\ell m_\ell} \qquad (A4)$$

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + B_\ell(r) + V_{\text{g}}(r) - E\right]\tilde{\psi}_{E\ell m_\ell}(r)$$
$$= -\sum_M \Lambda_{\ell m_\ell;JM}\phi_{vJ}, \qquad (A5)$$

where $B_J(r) = \hbar^2/(2\mu r^2)[J(J+1) - \Omega^2]$ is the rotational term of excited molecular bound state in the absence of nuclear spin, $B_\ell(r) = \hbar^2/(2\mu r^2)\ell(\ell+1)$ is the centrifugal term in collision of two ground state (S) atoms, $\tilde{\psi}_{E\ell m_\ell}(r) = \int_{E'}\beta_{E'}\psi_{E'\ell m_\ell}(r)dE'$. The above two equations are solved by the Green's function method by setting $\Lambda_{JM;\ell m_\ell} = \Lambda_{\ell m_\ell;JM} = 0$. The single channel scattering equation becomes

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + B_\ell(r) + V_{\text{g}}(r) - E\right]\psi_{E\ell}^0 = 0. \qquad (A6)$$

Let $\psi_{E\ell}^{0,\text{reg}}(r)$ and $\psi_{E\ell}^{0,\text{irr}}(r)$ represent the regular and irregular solutions of the above equation. The appropriate Green's function for the scattering wave function can be written as

$$\mathcal{K}_\ell(r,r') = -\pi\psi_{E\ell}^{0,\text{reg}}(r)\psi_{E\ell}^{0,\text{irr}}(r')(r' > r) \qquad (A7)$$

$$\mathcal{K}_\ell(r,r') = -\pi\psi_{E\ell}^{0,\text{reg}}(r')\psi_{E\ell}^{0,\text{irr}}(r)(r' < r). \qquad (A8)$$

The regular function, $\psi_{E\ell}^{0,\text{reg}}(r)$ vanishes at $r = 0$ and the irregular solution $\psi_{E\ell}^{0,\text{irr}}(r)$ is defined by boundary only at $r \to \infty$. The energy normalized asymptotic form of both regular and irregular wave function is

$$\psi_{E\ell}^{0,\text{reg}} = \sqrt{\frac{2\mu}{\pi\hbar^2 k}}\sin\left(kr - \frac{\ell\pi}{2} + \eta_\ell^0\right), \quad r \to \infty \qquad (A9)$$

$$\psi_{E\ell}^{0,\text{irr}} = \sqrt{\frac{2\mu}{\pi\hbar^2 k}}\cos\left(kr - \frac{\ell\pi}{2} + \eta_\ell^0\right), \quad r \to \infty, \qquad (A10)$$

where η_ℓ^0 is the phase shift of ℓ-th partial wave in the absence of PA coupling. The homogeneous part of (A4) with $\gamma = 0$ is

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + B_J(r) + V_{\text{ex}}(r)\right]\phi_{vJ}^0 = (\hbar\delta + E)\phi_{vJ}^0 = E_{vJ}\phi_{vJ}^0. \qquad (A11)$$

The Green function corresponding to these rovibrational states ϕ_{vJ}^0 can be written as

$$G_v(r,r') = -\frac{1}{\hbar\delta + E - E_{vJ} + i\hbar\gamma/2}\phi_{vJ}^0(r)\phi_{vJ}^0(r'). \qquad (A12)$$

Using this Green's function, we can write down the solution of equation (A4) in the form

$$\phi_{vJ}(r) = -\sum_{\ell m_\ell}\int dr'\Lambda_{JM;\ell m_\ell}(r')G_v(r,r')\tilde{\psi}_{\ell m_\ell}(r')$$
$$= \int_{E'}\beta_{E'}\sum_{\ell m_\ell}A_{JM;\ell m_\ell}\phi_{vJ}^0(r)dE', \qquad (A13)$$

where

$$A_{JM;\ell m_\ell} = \sum_{\ell m_\ell}\int dr'\Lambda_{JM;\ell m_\ell}(r')\phi_{vJ}^0(r')\psi_{E\ell m_\ell}(r')$$
$$\times \frac{1}{\hbar\delta + E - E_{vJ} + i\hbar\gamma/2}. \qquad (A14)$$

Substituting Eq. (A13) into Eq. (A5) we obtain

$$\left[\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} - B_\ell(r) - V_g(r) + E\right]\psi_{E\ell m_\ell}(r)$$
$$= \sum_{\ell' m_{\ell'} M}A_{JM;\ell' m_{\ell'}}\Lambda_{\ell m_\ell:JM}(r)\phi_{vJ}^0(r). \qquad (A15)$$

The scattering solution can now be expressed as

$$\psi_{E\ell m_\ell}(r) = \psi_{E\ell}^{0,\text{reg}} + \sum_{\ell' m_{\ell'} M}A_{JM;\ell' m_{\ell'}}(E)$$
$$\times \int \mathcal{K}_\ell(r,r')\Lambda_{\ell m_\ell;JM}(r')\phi_{vJ}^0(r')dr'. \qquad (A16)$$

On substitution of Eq. (A16) into (A14) and after some algebra, we obtain

$$A_{J,M;\ell,m_\ell} = \frac{1}{\hbar\delta + E - E_{vJ} + i\hbar\gamma/2 - E_J^{\text{shift}}}$$
$$\times \left[f_{JM:\ell m_\ell} + E_{J\ell}^{\text{shift}}\sum_{\ell' \neq \ell, m_{\ell'} M'}A_{JM':\ell' m_{\ell'}}\right]. \qquad (A17)$$

Let $D = \hbar\delta + E - E_{vJ} - E_{J\ell}^{\text{shift}} + i\hbar\gamma/2$. Now, adding a term $D^{-1}E_{J\ell}^{\text{shift}}A_{J,M;\ell,m_\ell}$ on both sides of Eq. (A17), we can express $A_{J,M;\ell,m_\ell}$ in terms of quantity $\tilde{A}_J = \sum_{\ell m_\ell M}A_{J,M;\ell,m_\ell}$ as well as other parameters. On summing over all possible ℓ, m_ℓ, M we can evaluate $\tilde{A}_J$. Having done all these algebra, we can

explicitly express

$$A_{J,M;\ell,m_\ell} = \frac{\left[f_{J,M;\ell m_\ell} + E_{J\ell}^{\text{shift}} \tilde{A}_J \right]}{\hbar\delta + E - E_{vJ} + i\hbar\gamma/2} \qquad (A18)$$

and

$$\tilde{A}_J = \sum_{\ell,m_\ell,M} \frac{f_{JM;\ell m_\ell}}{\hbar\delta + E - E_{vJ} + i\hbar\gamma/2 - E_J^{\text{shift}}}. \qquad (A19)$$

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