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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1. INTRODUCTION

Photoassociation (PA) spectroscopy \(^1\) and \(^2\) 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 \(^3\) \( ^4 \) \( ^5 \) \( ^6 \) \( ^7 \) \( ^8 \) \( ^9 \) and generating optical Feshbach resonance \(^10\) \( ^11\) \( ^12\) \( ^13\) \( ^14\). 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 \(^17\) \( ^18\) \( ^19\) \( ^20\) \( ^21\) \( ^22\) 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 \(^23\) in rovibrational ground state have been produced. Molecules created by one- or two-color PA of ultracold atoms generally possess low-lying rotational levels \( J \leq 3 \). Motivated by recent experimental observation of excitation of higher rotational states in ultracold PA with an intense laser field \(^24\), we here expose 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 \(^24\) \(^25\) \( ^26\) \( ^27\) \( ^28\) \( ^29\) \( ^30\) \( ^31\), such as photo-ionization of excited molecules \(^24\) \(^25\) \( ^26\) \( ^27\), shielding of atomic collision \(^28\) \(^29\) \(^30\), measurement of s-wave scattering length \(^31\), etc.

In this paper 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 \( J_A = 1 \) or \( J_A = 2 \) rotational state of a particular vibrational level \( \nu \) 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 A 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 A and V-type process with continuum acting as an intermediate state for V-type transition. In the previous Raman-type PA experiments, 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 paper 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.3. Finally the paper is concluded in Sec.4.
be written as

$$H = H_{\text{elec}}(r_1, r_2; r_a, r_b) - \frac{\hbar^2}{2\mu} \nabla_r^2 \mathbf{r} - \frac{\hbar^2}{2M} \nabla_R^2 + H_{hf} + H_{\text{int}}$$

where $H_{\text{elec}}$ 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 $r_a$ and $r_b$ represent the position vectors of the nuclei of atoms $a$ and $b$, respectively; $\nabla_r$ and $\nabla_R$ denote the Laplacian operators corresponding to the relative coordinate $r = r_a - r_b$ and the center-of-mass coordinate $R = (r_a + r_b)/2$ and $H_{hf}$ stands for the hyperfine interaction of two atoms. Under 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 $(r_1, r_2; r | g) = \phi_g(r_1, r_2; r)$ and $(r_1, r_2; r | e) = \phi_e(r_1, r_2; r)$, respectively. These internal electronic states have parametrical dependence on the internuclear coordinate $r$. They satisfy the eigenvalue equations

$$H_{\text{elec}}\phi_\alpha(r_1, r_2; r) = V_a(r)\phi_\alpha(r_1, r_2; r); \quad \alpha = g, e$$

We assume that the matrix element $(e | H_{\text{int}} | g) \approx \Omega_{eg}(r)$ 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 $H_{\text{int}}$ over the electronic parts of the two molecular levels involved in free-bound transition and thus obtain molecular coupling strength $A(r)$.

The continuum-bound dressed state can be written as

$$\Psi_E(r_1, r_2; r) = \sum_{\alpha = g,e} \Phi_\alpha(r_1, r_2; r)$$

and the center-of-mass part of this wave function can also be expressed in terms of the adiabatic molecular basis $| F; S, I, \ell \rangle$. The total rotational levels $J_a (\alpha = A, B)$ 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 $J_B \geq 3$ 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 $J \geq 3$ can only be accessed from higher partial-wave ($\ell > 0$) scattering states.

## 2. 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 $\mu$ is the reduced mass) of two alkali-type homo-nuclear 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 expressed as

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

where $\hat{d}_i = -e r_i$ is the dipole moment of $i$-th atom whose valence electron’s position is given by $r_i$ 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

$$H = H_{\text{elec}}(r_1, r_2; r_a, r_b) - \frac{\hbar^2}{2\mu} \nabla_r^2 \mathbf{r} - \frac{\hbar^2}{2M} \nabla_R^2 + H_{hf} + H_{\text{int}}$$

where $H_{\text{elec}}$ 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 $r_a$ and $r_b$ represent the position vectors of the nuclei of atoms $a$ and $b$, respectively; $\nabla_r$ and $\nabla_R$ denote the Laplacian operators corresponding to the relative coordinate $r = r_a - r_b$ and the center-of-mass coordinate $R = (r_a + r_b)/2$ and $H_{hf}$ stands for the hyperfine interaction of two atoms. Under 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 $(r_1, r_2; r | g) = \phi_g(r_1, r_2; r)$ and $(r_1, r_2; r | e) = \phi_e(r_1, r_2; r)$, respectively. These internal electronic states have parametrical dependence on the internuclear coordinate $r$. They satisfy the eigenvalue equations

$$H_{\text{elec}}\phi_\alpha(r_1, r_2; r) = V_a(r)\phi_\alpha(r_1, r_2; r); \quad \alpha = g, e$$

We assume that the matrix element $(e | H_{\text{int}} | g) \approx \Omega_{eg}(r)$ 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 $H_{\text{int}}$ over the electronic parts of the two molecular levels involved in free-bound transition and thus obtain molecular coupling strength $A(r)$.

The continuum-bound dressed state can be written as

$$\Psi_E(r_1, r_2; r) = \sum_{\alpha = g,e} \Phi_\alpha(r_1, r_2; r)$$

and the center-of-mass part of this wave function can also be expressed in terms of the adiabatic molecular basis $| F; S, I, \ell \rangle$. The total rotational levels $J_a (\alpha = A, B)$ 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 $J_B \geq 3$ 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 $J \geq 3$ can only be accessed from higher partial-wave ($\ell > 0$) scattering states.
\( \Omega \) 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. \( D^{\ell\Omega}_{\ell M}(\hat{r}) \) is the rotational matrix element. For ground electronic configuration, we have \( J = \ell, M = m_\ell \) and \( \Omega = 0 \); thereby, \( D^{\ell\Omega}_{\ell M}(\hat{r}) \) reduces to spherical harmonics \( Y_{\ell m_\ell} \). We thus express the ground state \( \Phi_g(\mathbf{r}) \) in the following form

\[
\Phi_g(\mathbf{r}) \propto r^{-1} \sum_{\ell, m_\ell} \left[ \int E' \beta E' \psi_{E'\ell m_\ell}(r) dE' \right] \tag{4}
\]

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

\[
\Phi_e(\mathbf{r}) \propto r^{-1} \sum_{M} [\phi_{e,\ell}(r) \mid J \Omega M] \tag{5}
\]

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 \( \phi_{e,\ell}(r) \) can be expressed as

\[
\phi_{e,\ell}(r) = \int E' \beta E' \sum_{\ell, m_\ell} A_{J, M; \ell m_\ell} \psi_{E'\ell m_\ell}(r) dE' \tag{6}
\]

where \( \psi_{E'\ell m_\ell}(r) \) is the excited molecular state (unit-normalized) in the absence of laser field and

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

is the probability amplitude of excitation of \( J \) from a particular partial wave \( \ell \). Here

\[
f_{J, M; \ell m_\ell} = \int \phi_{e,\ell}^0(r') \Lambda_{J, M; \ell m_\ell}(r') \psi_{E'\ell m_\ell}^0(r') dr' \tag{8}
\]

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

\[
E^{\text{shift}} = \pi \int dr'' \psi_{e,\ell}^0(r') \Lambda_{J, M; \ell m_\ell}(r') \times |\mathcal{K}_\ell(r', r')| \Lambda_{\ell m_\ell; J M}(r) \psi_{e,\ell}^0(r) \tag{9}
\]

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

\[
\tilde{A}_J = \sum_{\ell, m_\ell} f_{J, M; \ell m_\ell} \frac{\hbar \delta + E - E_{e, \ell} + i \hbar \gamma / 2}{E_{J, \ell}^{\text{shift}}} \tag{10}
\]

where

\[
E_{J, \ell}^{\text{shift}} = \sum_{\ell, m_\ell} f_{J, M; \ell m_\ell} \frac{\hbar \delta + E - E_{e, \ell} + i \hbar \gamma / 2 - E_{J, \ell}^{\text{shift}}}{f_{J, M; \ell m_\ell}} \tag{11}
\]

is the total stimulated line width for transformation from body-fixed to space-fixed frame. \( \Omega \) are the z-component of \( J \) in the absence of laser field and \( \Delta J = E_{e, \ell} - E_{e, \ell-1} \) in the unit of GHz for a few lowest \( J \) values.

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

| \( J \rightarrow \) | 1 | 2 | 3 | 4 | 5 | 6 |
|-----------------|---|---|---|---|---|---|
| \( E_{e, \ell} \) (GHz) | 0.57 | 2.13 | 4.77 | 8.55 | 13.03 | 18.34 |
| \( \Delta J \) (GHz) | -1.56 | 2.64 | 3.78 | 4.48 | 5.31 |   |
| \( -E_{J, \ell}^{\text{shift}} \) (MHz) | 19.69 | 22.79 | 17.36 | 11.61 | 6.83 | 2.22 |

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

\[
\psi_{E\ell m_\ell} = \cos \eta^L_{E\ell} \psi_{E\ell}^0 + \sin \eta^L_{E\ell} \psi_{E\ell}^{0\text{irr}} \tag{12}
\]

where \( \psi_{E\ell}^{0\text{irr}} \) is the irregular wave function of \( \ell \)-th partial wave. Here \( \eta^L_{E\ell} \) is the phase shift due to the applied laser field and is given by

\[
\tan \eta^L_{E\ell} = -\pi \sum_{\ell', m_{\ell'}} A_{J, M; \ell' m_{\ell'}} (E) f_{\ell m_\ell; J M} \tag{13}
\]

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

$$|J - |\mathbf{T} + \mathbf{S}|| \leq \ell \leq |J + |\mathbf{T} + \mathbf{S}||$$

(16)

where $L$ is the total electronic orbital angular momentum $\mathbf{T} = \mathbf{T}_1 + \mathbf{T}_2$ and $S$ is the sum of two individual atomic spin, i.e. $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$. So the lowest possible partial wave $\ell$ 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

$$K_{PA}^{(2)} = \langle v_{rel} \sigma_J \rangle = \frac{1}{\hbar Q_T} \int_0^\infty hP_E^{(2)} e^{-\beta E} dE$$

(17)

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

### 3. 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 $^{25}$. At large internuclear distance this $1_g$ potential correlates to $^2S_{1/2} + ^2P_{3/2}$ free atoms and at short range to $^1\Pi_g$ Born-Oppenheimer potential. In Ref. $^{25}$ 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 $r > 50a_0$ ($a_0$ = Bohr radius) whereas PA excitations occur at $r \sim 27a_0$. Therefore, the higher rotational states will be unlikely to be populated by PA transitions from $\ell > 0$ partial-wave scattering states at ultra-cold 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 in-
ternuclear separations \[^{33,34}\]. The numerically calculated rotational energies \(E_{\ell J}\), energy shifts \(E_{\ell J}^{\text{shift}}\) and the corresponding energy difference \(\Delta J = E_{\ell J} - E_{\ell J-1}\) for six lowest \(J\) values are given in Table I. To demonstrate the working of our proposed scheme, we resort 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 \(\Gamma_{\ell J_{\ell \ell}}^{(2)}\) is plotted as a function of detuning \(\Delta E_{\ell J_{\ell-1}}\) at laser intensity \(1\) W/cm\(^2\) and they are \(0.02229\) MHz, \(0.0122\) MHz and \(0.0061\) MHz, respectively for \(J_a = 2\) at laser intensity \(1\) W/cm\(^2\) and \(E = 10\) \(\mu\)K.

![Fig. 4](image-url) FIG. 4: \(\tan \eta^f_J\) (\(\eta^f_J\) is the light induced phase-shift) is plotted as a function of detuning \(\Delta E_{\ell J_{\ell-1}}\) (MHz) when \(L_a\) is tuned near \(J_a = 2\). The total shift \(E_{\ell J_{\ell-1}}^{\text{shift}}\) at 40 kW/cm\(^2\) is -0.91 GHz. The other parameters are \(I_A = 40\) kW/cm\(^2\) and \(E = 10\) \(\mu\)K.

For comparison, we also calculate one-color partial stimulated line widths \(\Gamma_{\ell J}^{(0)}\) for \(J > 2\) from the expression \(\Gamma_{\ell J}^{(0)} = 2\pi f_{J M; t m}\) \(J_{\ell-1}\). The one-color total stimulated line width \(\Gamma_{\ell J}^{(2)}\) is plotted as a function of detuning \(\Delta E_{\ell J_{\ell-1}}\) at laser intensity \(1\) W/cm\(^2\) and \(E = 10\) \(\mu\)K for \(J_{\ell-1}\) ranging from 3 to 6. The strong laser \(L_A\) is tuned near \(J_A = 1\) (Fig.2a) and \(J_A = 2\) (Fig.2b). From Fig.2 we notice that \(\Gamma_{\ell J_{\ell}}^{(2)}\) strongly depends on the detuning \(\Delta E_{\ell J_{\ell}}\) of the strong laser from PA resonance of the rotational level \(J_A\). The maximum of \(\Gamma_{\ell J_{\ell}}^{(2)}\) occurs at \(\Delta E_{\ell J_{\ell} = 0}\). For lower \(J_B\) values, the probability of rotational excitation is higher.

![Fig. 5](image-url) FIG. 5: The Two-color total stimulated line width \(\Gamma_{J_{\ell B}}^{(2)}\) (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\(^2\).

### Table III: Tabulated are the \(\tan \eta^J_\ell\) when the laser \(L_A\) is tuned near \(J_A = 2\) at \(E = 10\) \(\mu\)K for three values of \(\delta A\). The parameters are \(I_A = 40\) kW/cm\(^2\), \(E_{\ell J_{\ell = -2}} = -2.138\) GHz and \(E_{\ell J_{\ell = -2}}^{\text{shift}} = -0.91\) GHz. In the field-free case, \(\tan \eta_{\ell = 1}^J = -1.57 \times 10^{-4}\), \(\tan \eta_{\ell = 2}^J = 1.20 \times 10^{-6}\), \(\tan \eta_{\ell = 3}^J \approx 0\) and \(\tan \eta_{\ell = 4}^J \approx 0\).

| \(\delta A\) | \(\tan \eta_0^J \times 10^4\) | \(\tan \eta_1^J \times 10^4\) | \(\tan \eta_2^J \times 10^4\) |
| --- | --- | --- | --- |
| -2.95 GHz | 263.00 | 36900.00 | -229.00 |
| -3.049 GHz | 4.93 | 659.00 | -4.09 |
| -3.17 GHz | 0.01 | 2.01 | -0.01 |
| -3.295 GHz | 0.00 | 0.01 | 0.00 |

stimated line widths \(\Gamma_{J_{\ell B}}^{(0)}\) and \(\Gamma_{J_{\ell B}}^{(2)}\) for the same rotational states with laser intensity of 1 W/cm\(^2\) are vanishingly small while the two-color partial \(\Gamma_{J_{\ell B}}^{(2)}\) and total \(\Gamma_{J_{\ell B}}^{(2)} > \Gamma_{J_{\ell B}}^{(0)}\) exceed \(\Gamma_{J_{\ell B}}^{(0)}\) and \(\Gamma_{J_{\ell B}}^{(2)}\) by several orders of magnitude. We find the energy shift \(|E_{J_{\ell B = 1}}^{\text{shift}}|\) is 0.79 GHz which exceeds the spontaneous line width \(\gamma\) (say 2 MHz for model calculation) by two orders of magnitudes.

In order to trace the origin of increment of \(\Gamma_{J_{\ell B}}^{(2)}\) we plot perturbed \(\psi_{E_{\ell m}\ell}^{(0)}\) for \(\ell \neq 0\) when laser \(L_A\) is tuned near \(J_A = 1\) and the corresponding field-free regular functions \(\psi_{E_{\ell m}\ell}^{(0)}\) in Fig.3. It is clear from this figure that the amplitudes of \(\psi_{E_{\ell m}\ell}^{(0)}\) are greatly enhanced by several orders of magnitude than that of \(\psi_{E_{\ell m}\ell}^{(0)}\). Next, we calculate \(\tan \eta^J_\ell\) by using Eq. \[^{[13]}\] when laser \(L_A\) is tuned near \(J_A = 2\). These are given in Table III for \(\delta A = -2.95\) GHz, -3.17 GHz and -3.049 GHz. The first two \(\delta A\)
values correspond to off-resonant and the last one to resonant condition. The variation of $\tan \eta$ with $\Delta E_{v,J_B}$ is plotted in Fig.4 which exhibits resonance for higher partial waves induced by strong-coupling PA. The enhancement of the partial $(J_B = 4,5)$ rotational states can not be populated for higher rotational states $(J_B > 4)$ 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.

4. CONCLUSION

In the present paper we have developed a two-color PA scheme for the excitation 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 and 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 A

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 the two state basis can be expressed as

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

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

$$[-\frac{\hbar^2}{2\mu} \nabla^2 + V_\text{ex}(r) - E]\Phi_\text{ex}(r) = -\Omega_{ge}(r)\Phi_e(r) $$ (A2)

$$[-\frac{\hbar^2}{2\mu} \nabla^2 + V_\text{ex}(r) - E - i\hbar\gamma] \Phi_\text{ex}(r) = -\Omega_{eg}(r)\Phi_g(r)$$ (A3)

Here $V_\text{ex}$ is assumed to include hyperfine interaction of the chosen channel. Substituting Eqs. (1) and (4) into the Schrödinger equations (A2) and (A3) we get two coupled equations

$$-rac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + B_J(r) + V_\text{ex}(r) - h\delta - E - i\hbar\gamma \sum_{\ell m_\ell} \Lambda_{\ell M;\ell m_\ell} \tilde{\psi}_{E\ell m_\ell}$$ (A4)

$$-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + B_\ell(r) + V_\text{ex}(r) - E \tilde{\psi}_{E\ell m_\ell} = -\sum_{\ell m_\ell} \Lambda_{\ell M;\ell m_\ell} \tilde{\psi}_{E\ell m_\ell}$$ (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. $B_\ell(r) = \hbar^2/(2\mu r^2)(\ell + 1)$ is the centrifugal term in collision of two ground state (S) atoms,
\[ \psi_{Em}(r) = \int E \beta_E \psi_E \psi_{Em}(r) dE' \]. The above two equations are solved by the green’s function method by setting \( A_{JM;\ell m} = A_{\ell m;JM} = 0 \). The single channel scattering equation becomes

\[ \left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + B_\ell(r) + V_g(r) - E \right] \psi_{\ell m}^0 = 0. \] (A6)

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

\[ K_\ell(r, r') = -\pi \psi_{\ell m}^{0,\text{reg}}(r) \psi_{\ell m}^{0,\text{irr}}(r') \quad (r' > r) \] (A7)

\[ K_\ell(r, r') = -\pi \psi_{\ell m}^{0,\text{reg}}(r') \psi_{\ell m}^{0,\text{irr}}(r) \quad (r' < r) \] (A8)

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

\[ \psi_{\ell m}^{0,\text{reg}} = \sqrt{\frac{2\mu}{\pi \hbar^2 k}} \sin(kr - \frac{\ell \pi}{2} + \eta_0^\ell), \quad r \to \infty \] (A9)

\[ \psi_{\ell m}^{0,\text{irr}} = \sqrt{\frac{2\mu}{\pi \hbar^2 k}} \cos(kr - \frac{\ell \pi}{2} + \eta_0^\ell), \quad r \to \infty \] (A10)

where \( \eta_0^\ell \) is the phase-shift of \( \ell \)-th partial wave in the absence of PA coupling. The homogeneous part of (A4) with \( \gamma = 0 \) is

\[ \left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + B_\ell(r) + V_{\text{ex}}(r) \right] \phi_{\ell m}^0 = (\hbar \delta + E) \phi_{\ell m}^0 = E_{\ell m} \phi_{\ell m}^0 \] (A11)

The Green function corresponding to these rovibrational states \( \phi_{\ell m}^0 \) can be written as

\[ G_v(r, r') = -\frac{1}{\delta + E - E_{\ell m} + i\hbar \gamma/2} \phi_{\ell m}^0(r) \phi_{\ell m}^0(r') \] (A12)

Using this Green’s function, we can write down the solution of equation (A3) in the form

\[ \phi_{\ell m}(r) = -\sum_{\ell'm} \int dr' A_{\ell m;\ell'm} (r') G_v(r, r') \psi_{\ell m}(r') \]

\[ = \int dr' \beta_E \sum_{\ell m} A_{\ell m;\ell m} \phi_{\ell m}^0(r) dE' \] (A13)

where

\[ A_{\ell m;\ell m} = \sum_{\ell'm} \int dr' A_{\ell m;\ell'm} (r') \phi_{\ell m}^0(r') \psi_{\ell m}(r') \]

Substituting equation (A13) into equation (A5) we obtain

\[ \psi_{\ell m}(r) = \sum_{\ell'm} A_{\ell m;\ell'm} \Lambda_{\ell m;\ell'm} \phi_{\ell m}^0(r) \] (A15)

The scattering solution can now be expressed as

\[ \psi_{\ell m}(r) = \psi_{\ell m}^{0,\text{reg}} + \sum_{\ell'm} A_{\ell m;\ell'm} \Lambda_{\ell m;\ell'm} \phi_{\ell m}^0(r) \]

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

\[ A_{\ell m;\ell m} = \frac{1}{\delta + E - E_{\ell m} + i\hbar \gamma/2} \left[ \sum_{\ell'm \neq \ell} A_{\ell m;\ell'm} + E_{\ell m}^{\text{shift}} \right] \] (A17)

summing over all possible \( \ell, m, M \) we can evaluate \( A_{\ell} \). Having done all these algebra, we can explicitly express

\[ A_{\ell m;\ell m} = \frac{1}{\delta + E - E_{\ell m} + i\hbar \gamma/2} \] (A18)
and

$$\hat{A}_J = \sum_{\ell, m \ell, M} \frac{f_{J M; \ell m}}{\hbar \delta + E - E_{0 J} + i\hbar \gamma/2 - E_{\text{shift}}^J}$$  (A19)

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