Photoassociative cooling and trapping of a pair of interacting atoms

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We show that it is possible to cool interacting pairs of atoms by a lin ⊥ lin Sisyphus-like laser cooling scheme using counterpropagating photoassociation (PA) lasers. It is shown that the center-of-mass (c.m.) motion of atom pairs can be trapped in molecular spin-dependent periodic potentials generated by the lasers. The proposed scheme is most effective for narrow-line PA transitions. We illustrate this with numerical calculations using fermionic ^{171}Yb atoms as an example.

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I. INTRODUCTION

The development of laser cooling and trapping [1–3] of atoms over the last four decades has enabled a number of breakthrough achievements such as the realization of Bose-Einstein condensation [4], Fermi degeneracy [5], Fermi superfluidity [6], superfluid-Mott transitions [7], and so on. Illumination of slowly moving atoms with multiple laser beams in a specific geometric configuration allows one to manipulate both the internal and external degrees of freedom of atoms. The internal degrees of freedom, such as the electronic configuration or the spin polarization of atoms, can be manipulated using circularly polarized resonant light as demonstrated by Kastler [8] more than 60 years ago. The external degrees of freedom such as the position and momentum of atoms can be controlled using radiative forces [9–13]. Dispersive forces, also called dipole forces, arise due to position-dependent light shifts, leading to optically generated lattice for trapping atoms in an ordered array. The techniques of laser cooling and trapping of atoms developed so far have been essentially a single-atom phenomenon, although the possibility of a collective laser cooling scheme was theoretically discussed by Vuletic and Chu [14] about 15 years ago.

Here, we propose a Sisyphus-like laser cooling scheme where interatomic interactions play an essential role. Consider the motion of two colliding atoms. The total kinetic energy of the atom pair consists of relative and the center-of-mass (c.m.) energy E and $E_{\mathrm{c.m.}}$, respectively. Cooling both atoms simultaneously implies reducing either or both of these kinetic energies. Such cooling by lasers will require photoassociative transitions [15–17] that are cyclic. In photoassociation (PA), a single photon connects the state of two interacting ground-state atoms with an excited molecular bound state via so-called free-bound dipole transitions. For PA to occur, relatively cold atoms with temperatures typically at or below millikelvin regime are required. Usually, the c.m. motion of atom pairs is not of much spectroscopic interest and hence neglected in PA spectroscopy. However, at a fundamental level, both relative and c.m. motion of atom pairs become coupled by PA process. The question then naturally arises as to whether it is possible to reduce the kinetic energies of the two coupled motion from millikelvin regime to lower temperatures by Sisyphus mechanism using photoassociative transitions. We show that it is indeed possible by coherent manipulation of the coupled motion of atom pairs with counterpropagating PA lasers in lin ⊥ lin configuration. Coherent coupling in a PA system requires that the excited molecular states to which PA lasers are tuned should have lifetime long and a relatively large Franck-Condon (FC) overlap integral with the scattering state of ground-state atoms [18,19]. The recent experimental demonstrations of Rabi oscillations in two-electron atomic systems such as Sr [18] and Yb [19] making use of ultranarrow intercombination PA transitions strongly suggest that such PA systems can be treated in a way somewhat analogous to the methods used for two-level atoms.

Sisyphus cooling of atoms, first proposed by Pritchard [20], involves an atom having degenerate sublevels in its electronic ground and excited states. It uses counterpropagating polarized lasers to produce spin-dependent and spatially modulated light shifts that eventually lead to sub-Doppler cooling. We here propose a photoassociative Sisyphus-like method with sublevels corresponding to molecular angular momenta. For two ground-state atoms in collision, the degenerate sublevels correspond to multiple scattering channels having the same asymptotic threshold. A PA system can access a single vibrational and rotational level in an electronically excited molecular potential. In narrow-line PA systems, cyclic PA transitions or Rabi oscillations between an excited molecular bound state and the continuum of ground-state scattering states are possible as can be evidenced from experiments [18,19].

For single atoms, Sisyphus cooling relies on optical pumping in multilevel atoms moving in an optical field with spatially varying polarization. Optical pumping can also be applicable for continuum-bound as well as continuum-continuum transitions in diatomic molecules as discussed by Mies [21] about 35 years ago. The "continuum" here refers to the dissociation continuum of scattering states between two free atoms. In case of PA, the initial motional state of two atoms is a scattering state which can be considered as the dissociation continuum of the ground-state molecule. Dark state resonances and optical pumping into an atom-molecule dark state in two-color PA of ultracold atoms have been experimentally observed [22,23]. The physical interpretation of dark-state resonance and optical pumping in two-photon PA of ultracold atoms has been discussed by Cohen-Tannoudji [24]. Another coherent effect related to dark-state resonance is stimulated Raman adiabatic passage (STIRAP) which has been extensively investigated by Bergman and co-workers [25] in

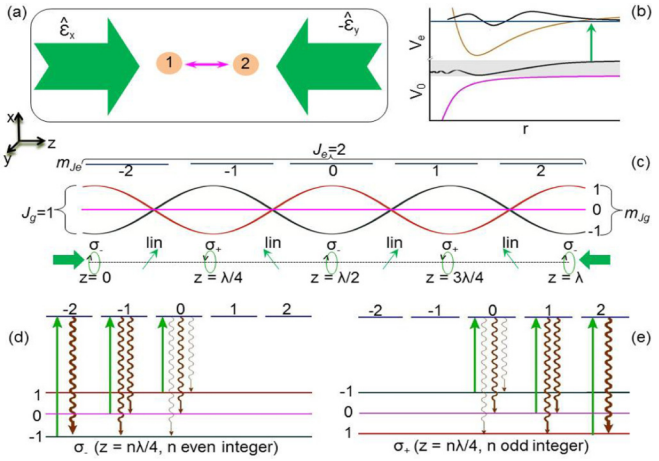

FIG. 1. (a) A pair of slowly moving atoms 1 and 2 is subjected to a pair of lin ⊥ lin counterpropagating PA lasers along z axis. (b) PA process: V_g is molecular ground-state potential and V_e is excited PLR potential. The ground-state scattering continuum state is coupled to a rovibrational state in the excited potential by the two lasers. (c) Energy-level diagram showing formation of spatially varying [w.r.t. c.m. coordinate (Z)] spin-dependent ground-state potentials under the action of applied lasers. (d) Optical pumping (green lines) and spontaneous transition (curvy brown lines having width proportional to the probability of transition) at mentioned c.m. coordinate where light is σ_- polarized. (e) Same as (d) where light is σ_+ polarized. An additional pair of counterpropagating broadband PA lasers in $\sigma_+ + \sigma_-$ configuration along the z axis may be used (not shown in the figure) as repumping lasers (see the text).

three-level atomic systems. STIRAP with a continuum as an initially populated or intermediate or a final target state has also been studied by many workers [26–30] over the years. In recent times, STIRAP using PA of ultracold atoms has been discussed and debated by many authors [31–36].

The elementary process underlying our method is schematically shown in Fig. 1. Let a pair of slowly moving atoms be subjected to a pair of lin ⊥ lin counterpropagating PA laser beams having the same frequency. Let us consider, for the sake of simplicity, two colliding ground-state atoms 1 and 2 with total energy $E_t = E + E_{\text{c.m.}}$ and total angular momentum $J_g = 1$ are being acted upon by the lin ⊥ lin counterpropagating PA lasers. Suppose the lasers are tuned near resonance to a particular excited bound state $|b\rangle \equiv |v, J_e\rangle$, with vibrational quantum number v and rotational quantum number J_e from a relative energy having significant free-bound FC factor. We here closely follow the Sisyphus method of Dalibard and Cohen-Tannoudji [37], but generalize for photoassociative transitions. The physical processes underlying our proposed photoassociative cooling of atom pairs differ from those of standard Sisyphus method of cooling of single atoms in the following respects: First, in case of standard Sisyphus method there is only one kind of external degrees of freedom of motion which is the c.m. momentum of single atoms while in our proposed photoassociative Sisyphus method, two kinds of external degrees of freedom of motion are involved: these are the relative momentum $\mathbf{p}$ and the c.m. momentum $\mathbf{P}_{\text{c.m.}}$ of the two colliding atoms.

In an elementary process of PA where one photon from PA laser is absorbed followed by spontaneous emission of one photon from the excited molecular state, the momentum conservation dictates that the change in c.m. momentum $\Delta\mathbf{P}_{\text{c.m.}} = \mathbf{P}^{\text{final}}_{\text{c.m.}} - \mathbf{P}^{\text{initial}}_{\text{c.m.}}$, where $\mathbf{P}^{\text{initial (final)}}_{\text{c.m.}}$ denotes the initial (final) CM momentum, should satisfy

$$\Delta\mathbf{P}_{\text{c.m.}} = \hbar[\mathbf{k}_{\text{PA}} - \mathbf{k}_{\text{spon}}] \tag{1}$$

with $\mathbf{k}_{\text{PA}}$ and $\mathbf{k}_{\text{spon}}$ being the momentum of PA laser photon and spontaneously emitted photon, respectively. Since the relative motion of the two atoms occurs under the influence of molecular potentials, the relative momentum $\mathbf{p}$ is not a good quantum number to specify the conservation of momentum in this situation. Second, in case of standard Sisyphus method, energy exchange between the atoms and photons occurs at the expense of the c.m. motional energy of single atoms, but in our proposed scheme energy exchange can happen between photons and the total motional energy E_t which is a sum of $E = p^2/2\mu$ and $E_{\text{c.m.}} = P^2/2M$ where μ and M denote the reduced and total mass of the atom pair. This means that energy transfer can happen to both the c.m. and relative motions of the atom pair from the photonic fields. This is because PA process couples both relative and c.m. motion. Recently, coupling between the relative and c.m. motion of exactly two atoms in an anharmonic trap has been experimentally demonstrated by Sala *et al.* [38]. These experimental results and the recent observation of Rabi oscillations in PA [18,19] indicate that a two-level type treatment of a free-bound system is possible. Third, by standard Sisyphus method one can trap single atoms, while by our proposed method one can trap the c.m. motion of atom pairs. In this context, it is to be noted that, unless PA occurs in a tightly confined trap, the trapping potential has practically no influence over PA transitions since PA occurs near the trap center where trapping potential is negligible. The interatomic separations at which PA transitions take place are typically far below or of the order of a nanometer. So, unless trapping size is reduced to a nanometer or less, PA process will not be affected by the trapping potential [19]. So, to subject a pair of cold atoms into counterpropagating PA lasers, one can prepare pairs of atoms in a two-atom Mott insulator where each lattice site is occupied by two atoms as is done in the recent experiment by Taie *et al.* [19]. PA lasers will then act almost independently on separated atom pairs in optical lattice. In that case, the lasers that generate the lattice should be far off PA resonance so that they do not disturb the PA process. Once the atom pairs are cooled enough for their c.m. motion to be trapped by dipole forces, the lattice lasers may be switched off since the c.m. motion of the pairs is trapped in the periodic dipole potentials generated by PA lasers.

In contrast to Sisyphus cooling of single atoms where only one kind of external motional energy scale is involved, in the present case there are two external energy scales: c.m. and relative motional energy. The change in c.m. momentum of the atom pair is governed by the principle of momentum conservation of light scattering. The energy conservation is maintained by a decrease in total energy E_t when the spontaneously emitted photon carries away the excess energy that is released from the coupled relative and c.m. motion. Two atoms colliding with opposite momenta will have maximum probability to come closer to each other and so to couple with

PA laser. This means that an atom pair with zero or very small c.m. energy is most likely to be influenced by PA laser. We assume that the c.m. kinetic energy $E_{\text{c.m.}}$ is much smaller than the relative motional energy E, PA resonance is then primarily determined by E when the lasers are tuned close to an excited molecular bound level from the threshold of ground-state continuum. The PA detuning parameter $\delta_E = E/\hbar + \omega_L - \omega_b$ is an explicit function of E, where $\hbar\omega_b$ is the bound-state energy measured from the continuum threshold and ω_L is the angular frequency of the PA laser.

The strength of PA coupling is given by Frank-Condon (FC) overlap factor. In the low-energy regime, the FC factor as a function of E shows a prominent peak at a particular energy $E = \bar{E}$. Let $\delta_{E=\bar{E}} = 0$ if $\omega_L = \bar{\omega}_L$. So, $\bar{E}$ and $\bar{\omega}_L$ can be termed as resonance energy corresponding resonance laser frequency $\bar{\omega}_L$. In the weak-coupling limit, Sisyphus cooling remains effective so long as the laser detuning $|\delta| \leqslant \gamma$ or $|\delta| \simeq \gamma$, where γ is the spontaneous linewidth. So, the spontaneous emission into the continuum from the excited bound state may lead to continuum states with an energy spread of the order of $\hbar\gamma$. If the final energy E_f after the spontaneous emission is less than $\bar{E}$, we have cooling effect.

On the other hand, if E_f is greater than $\bar{E}$, the atoms may go out of cooling cycle. Therefore, we need a repumping mechanism to bring back the atoms that acquire higher relative energy as a result of spontaneous emission. This can be accomplished by applying counterpropagating broadband PA lasers in $\sigma_+ + \sigma_-$ configuration, in addition to the monochromatic Sisyphus cooling lasers. These broadband repumping lasers should have the same central frequency $\bar{\omega}_L - \gamma$ such that the pair of atoms having energy $E \simeq \bar{E} + \hbar\gamma$ comes to PA resonance with the central frequency and are repumped into the cooling cycle. We consider $\sigma_+ + \sigma_-$ configuration for repumping lasers, that is, one laser with σ_+ and the other σ_- polarization, because this configuration leads to space-independent light shift of the Zeeman sublevels, redistributing the population in both ground- and excited-state sublevels [39]. In the present context, the Zeeman sublevels refer to the total magnetic quantum number of the two atoms because the two atoms are correlated and the photoassociative transitions occur between the correlated two-atom state and the molecular bound state.

Since the repumping lasers give a space-independent shift for all the sublevels, there is no additional optical force resulting from this light shift. Regarding the bandwidth of the repumping lasers, the bandwidth may be set at a few times of γ or one order of magnitude larger than γ. If γ is in the kHz regime as in the case of metastable excited states or spin-forbidden intercombination transitions in Yb and Sr atoms, the bandwidth of the repumping lasers would be in MHz regime. For larger γ, the bandwidth of the repumping lasers has to be large enough. The repeating cycles of the repumping laser pulses should be much smaller than γ so that once the atom pair is excited to the bound state, the pair can quickly decay back to the ground-state continuum without any memory effect of the pulse [40].

Broadband laser cooling [41,42] with $\sigma_+ + \sigma_-$ scheme is theoretically described by Parkins and Zoller [43]. Doppler cooling of atoms or atomic ions with broadband or pulsed lasers has been experimentally demonstrated [40,44]. In recent times, broadband laser cooling methods have been successfully applied for vibrational or rotational cooling of some specific molecules [45–48]. Our proposed scheme may be compared to Sisyphus laser cooling of diatomic molecules [46,49,50]. The c.m. and relative motion of atom pairs are equivalent to translational and vibrational motion of a diatomic molecule. In general, laser cooling of molecules is extremely difficult due to the presence of a plethora of rovibrational levels hindering cyclic transitions that are needed for laser cooling. Nevertheless, direct laser cooling of some specific molecules [46,51] has been successfully demonstrated in recent times.

The optical pumping has been used to demonstrate vibrational cooling of molecules in a recent experiment [46]. These recent advances towards laser cooling of diatomic molecules and coherent PA [18,19] motivate us to explore Sisyphus-like scheme to cool and trap an analogous system of a pair of atoms in a state of slow collision. This will allow one to optically control both the relative and c.m. motions between two atoms.

In our proposed scheme, we have two coupled and competing variables involved: relative and c.m. momentum. The relative momentum is a fast variable and the c.m. momentum is a slow one. For narrow PA linewidth, one can thus adiabatically eliminate relative motion leaving c.m. motion to follow an optical potential obtained by averaging over E near $\bar{E}$. Since the c.m. energy $E_{\text{c.m.}}$ is much smaller than the depth of the optical potential, the c.m. motion of the pair will eventually be trapped. Since the optical pumping will preferentially bring the atom pair at the bottom of the potential well with the release of mostly relative kinetic energy, by successive absorption-emission cycles the pair will be cooled. In case of single atoms, Sisyphus or other sub-Doppler cooling and trapping methods such as velocity selective coherent population trapping (VSCPT) make use of a number of optical coherent effects such as Rabi oscillations, dressed states, optical pumping, saturation effects, light shifts, dark-state resonances, etc., at the backdrop of randomness introduced by spontaneous emission [39]. As we embark to extend Sisyphus method to photoassociative continuum-bound systems, the question naturally arises as to whether similar coherent effects can be obtained using continuum-bound optical transitions. The problem of coherent coupling, Rabi oscillations, and dressed states in continuum-bound coupled systems had been addressed by a number of workers in the 1980s [52–54] and early 1990s [55], particularly in the context of autoionization or photoionization. It was theoretically shown that Rabi oscillations in a continuum-bound system are possible provided the continuum-bound matrix element is strong and the continuum has a narrow resonance [54]. In fact, fulfillment of exactly such conditions have enabled experimental demonstrations of Rabi oscillations in PA [18,19]. Saturation effects in PA have also been studied experimentally by many groups [56–58].

A class of excited molecular bound states known as purely long-range (PLR) states [59] will play a particularly useful role in our proposed method. These states are localized at nanometer scale separations at which electronic charge overlap of the two atoms may be negligible. As a result, the number of rovibrational levels or scattering channels that can be optically coupled to PLR states is drastically reduced. Furthermore, in some cases, PLR states can be accessible by photoassociative transitions from a single scattering channel [60–62] only.

PLR potentials are usually quite shallow, and so capable of supporting only a small number of vibrational levels. As a consequence, the free-bound FC factor at ultralow collision energy can be large. At ultralow temperatures, the collision energy of the initially two free atoms is quite low. This can lead to a narrow PA resonance, providing a unique advantage for generating coherent photoassociative coupling.

The remainder of the paper is organized in the following way. In the next section, we present theory of generating molecular spin-dependent periodic optical potentials for cooling and trapping an atom pair. In Sec. III, we discuss the implementation of our proposed scheme and present numerical results using a pair of fermionic ^{171}Yb atoms and their photoassociative coupling to a PLR state. The paper is concluded in Sec. IV.

II. THEORETICAL METHOD

We now present general mathematical formalism of a simple one-dimensional scheme of photoassociative cooling and trapping (PACT) as schematically depicted in Fig. 1. In the center-of-mass (c.m.) frame, we can express the Hamiltonian of our system in terms of c.m. and relative coordinates $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ and $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, respectively. The Hamiltonian describing the interaction of a pair of cold atoms with the PA lasers is $\hat{H} = \hat{H}_0^{\text{c.m.}} + \hat{H}_0^{\text{rel}} + \hat{H}_I$, where

$$\hat{H}_0^{\text{rel}} = \int_0^\infty E^{'}|E^{'}\rangle\langle E^{'}|dE^{'} + \hbar\omega_b|b\rangle\langle b| \tag{2}$$

describes relative motion between the two atoms with $|E\rangle$ representing the continuum of ground-state scattering states in the relative energy (E') basis and $|b\rangle$ being an excited molecular bound state. Here,

$$\hat{H}_0^{\text{c.m.}} = \hat{P}^2_{\text{c.m.}}/2M = -[\hbar^2/2M]\nabla_R^2 \tag{3}$$

is the kinetic term of c.m. motion. The interaction part

$$\hat{H}_I = \left[\int_0^\infty \Lambda_{bE'} e^{-i\omega_L t}|b\rangle\langle E^{'}|dE^{'} + \text{H.c.}\right], \tag{4}$$

where $\Lambda_{bE} = -\langle b|\mathbf{d_1}\cdot\mathcal{E}(\mathbf{r_1}) + \mathbf{d_2}\cdot\mathcal{E}(\mathbf{r_2})|E\rangle$ is molecular dipole coupling, $\mathbf{d_1}$ and $\mathbf{d_2}$ are atomic dipole moments with $\mathbf{r_1}$ and $\mathbf{r_2}$ being the position vectors of atoms 1 and 2, respectively. We can then write Λ_{bE} in terms of molecular dipole operator $\mathbf{D}(\mathbf{r})$ in the form

$$\Lambda_{bE} = -\langle b|\mathbf{D}\cdot\hat{\epsilon}(\mathbf{R})\sqrt{2}\mathcal{E_0}\cos(\mathbf{k}_L\cdot\mathbf{r}/2)|E\rangle, \tag{5}$$

where $\hat{\epsilon}(\mathbf{R}) = [\hat{\sigma}_-\cos(\mathbf{k}_L\cdot\mathbf{R}) - i\hat{\sigma}_+\sin(\mathbf{k}_L\cdot\mathbf{R})]$ is the polarization vector. Since $\hat{H}_I$ depends both on relative and c.m. coordinates, the relative and c.m. motion becomes coupled. The optically generated force is given by

$$\mathbf{F} = \nabla_R\int_0^\infty\{\rho_{E'b}[\Lambda_{bE'}(R)e^{-i\phi(r,R)}]e^{-i\omega_L t} + \text{c.c.}\}dE', \tag{6}$$

where ρ_{Eb} is the density matrix element representing continuum-bound coherence and $\phi(r,R)$ is the position-dependent phase part of the applied laser field. This force $\mathbf{F}$ is a sum of two forces: one is dipole force $\mathbf{F}_{\text{dip}}$ and another is dissipative force $\mathbf{F}_{\text{dis}}$.

Here, we consider the simplest one-dimensional (1D) model of Sisyphus cooling. A pair of PA lasers are applied along the z axis, so we have $\mathbf{k}_L\cdot\mathbf{R} = k_L Z$. At $Z = n\lambda/4$ (n is an integer) the polarization is σ_- for even n and σ_+ for odd n. After having done a lengthy calculation (see Appendixes A and B), we derive the expression for dipole force as given by

$$\mathbf{F}_{\text{dip}}(Z) = -\frac{\hbar\delta_{\bar{E}}}{\pi}\left\{\frac{\frac{d}{dZ}\left[\int_0^\infty\mathcal{G}_E(Z)d\omega_E\right]}{\delta^2_{\bar{E}} + \frac{\gamma^2}{4} + \frac{2}{2\pi}\int_0^\infty\mathcal{G}_E(Z)d\omega_E}\right\}, \tag{7}$$

where $\delta_E = [\omega_L - (\omega_b - \frac{E}{\hbar})]$ and γ is the spontaneous linewidth of the bound state. Here, the spontaneous emission is taken into account by a master-equation approach as elaborated in Appendix B. It is worth mentioning that the master-equation approach to discrete systems such as two-level atoms or a single-mode cavity field is well known. However, the master-equation approach to a coupled continuum-bound system is not adequately addressed in the literature. Unlike discrete systems, master-equation formalism for continuum-bound systems leads to integrodifferential equations which are in general difficult to solve analytically.

As derived in Appendix A, the optical potential can be expressed as

$$U_{\text{opt}} = \hbar\delta_{\bar{E}}\ln\left[1 + \frac{\frac{1}{\pi}\int_0^\infty\mathcal{G}_E(Z)d\omega_E}{\delta^2_{\bar{E}} + \frac{\gamma^2}{4}}\right]. \tag{8}$$

In weak-intensity limit (as mentioned in Appendix A)

$$U_{\text{opt}} = \hbar\delta_{\bar{E}}\frac{\frac{1}{\pi}\int_0^\infty\mathcal{G}_E(Z)d\omega_E}{\delta^2_{\bar{E}} + \frac{\gamma^2}{4}}. \tag{9}$$

Separating out $\mathcal{G}_E(Z)$ in the form $\mathcal{G}_E(Z) = \Gamma(E)\Theta(Z)$, we obtain $U_{\text{opt}} = \hbar\delta_{\bar{E}}S_0\Theta(Z)$, where

$$S_0 = \frac{\frac{1}{\pi}\int_0^\infty\Gamma(E)d\omega_E}{\delta^2_{\bar{E}} + \frac{\gamma^2}{4}} \tag{10}$$

is a parameter that describes saturation effect in PA. In terms of S_0 the excited bound-state population ρ_{bb} in steady state can be written as

$$\rho_{bb} = \frac{S_0\Theta(R)}{2 + 2S_0\Theta(R)}. \tag{11}$$

S_0 can be considered as the photoassociative counterpart of saturation parameter of a two-level atom. The saturation intensity in TLA is the intensity at which the parameter becomes unity at resonance. Equation (10) shows that for $\delta_{\bar{E}} = 0$, $S_0 = 1$ when $(4/\pi\hbar)\int_0^\infty\Gamma(E)dE = \gamma^2$. Note that $\Gamma(E)$ is proportional to laser intensity. It is now clear that the saturation intensity in PA will depend on FC factor: the larger the FC factor, the lower is the saturation intensity. The amount of FC factor depends primarily on the amplitude of the scattering wave function at internuclear separations near the outer or inner turning point of the excited bound state, rather than the scattering phase shift. In this context, an interesting question is the effect of unitarity regime of scattering on the saturation. The unitarity happens when the scattering phase shift is $\pi/2$ and, as a consequence, the magnitude of scattering T-matrix element attains its maximum value of unity. As the phase shift goes through $\pi/2$ as a function

of energy, scattering cross section shows a resonance structure. Whether this unitarity-limited scattering will maximize FC factor depends on whether the most prominent antinode of the scattering wave function at unitarity appears near the outer turning point of the excited molecular bound state. For instance, in case of cold collision between bosonic atoms or between two-component fermionic atoms, the scattering is predominantly of s wave and so the unitarity-limited scattering wave function $\psi_0(r)$ asymptotically behaves as $\psi_0(r) \sim \sin(kr + \delta_0) \sim \cos(kr)$, where we have put the value of the s-wave phase shift $\delta_0 = \pi/2$. So, in the limit $k \to 0$, the scattering wave function will maximize at asymptotically large separations. Now, on the question as to whether this will lead to the maximization of FC factor obviously depends on the location of outer turning point. If the outer turning point lies at such large separations where the scattering wave function attains its asymptotic behavior, then the FC factor will maximize for a fixed laser intensity. On the other hand, for p-wave scattering, the reverse effect will happen since the p-wave scattering wave function $\psi_{\ell=1}(r)$ behaves as $\psi_{\ell=1}(r) \sim \sin(kr)$ at large separations. The behavior of scattering wave function at short separations can not be analytically predicted *a priori*, and hence no definite relationship of unitarity regime with saturation effect in PA can be established. One can notice from Eq. (2) that for large saturation parameter, the population of the excited bound states ρ_{bb} approaches $\frac{1}{2}$. This means that the other half of the total population is contained in the ground continuum states when the saturation parameter is large. However, we work much below the saturation limit, i.e., $S_0 \ll 1$.

Let $J_e = 2$ as in Fig. 1. The form of $\Theta(Z)$ is then given by

$$\begin{aligned} \Theta(Z)_{m_{J_g}=\pm 1} &= -A \pm B\cos(2k_L Z), \\ \Theta(Z)_{m_{J_g}=0} &= \text{const}, \end{aligned} \tag{12}$$

where A and B are constants that depend on Clebsch-Gordon (CG) coefficients. We thus obtain light-shifted periodic potentials for c.m. motion for different magnetic quantum numbers, that is, we get spin-dependent potentials for c.m. motion. The c.m. momentum changes due to absorption of a photon from one plane wave and its subsequent emission into another plane wave. Let us consider a point $Z = \lambda/4$ where the field is circularly polarized in positive sense. For such polarization, three possible transition pathways may arise in Fig. 1(e): (1) The continuum state with at $m_{J_g} = 1$ can couple to bound state $m_{J_e} = 2$. This state can decay to $m_{J_g} = 1$ and all other transitions are forbidden. (2) The state with $m_{J_g} = -1$ can be excited to $m_{J_e} = 0$ state and it can decay to $m_{J_g} = 1$ or $m_{J_g} = -1$ or $m_{J_g} = 0$ state. (3) The state with $m_{J_g} = 0$ can be excited to $m_{J_e} = 1$ state and it can decay to state $m_{J_g} = 1$ or $m_{J_g} = 0$ state. All the spontaneous transition lines shown here have widths proportional to the square of the corresponding CG coefficients. The net effect is the maximum occupation probability happens for the state $m_{J_g} = 1$ having the lowest c.m. energy at the potential minima. This argument applies similarly for locations where the field is circularly polarized in the negative sense as shown in Fig. 1(d). Now, as an atom pair moves up the hill from lower potential energy side, it loses its c.m. kinetic energy. After reaching the top of the hill and just about to start gliding down, the optical pumping intervenes, transferring the pair into a state which is at the potential minima where the probability of downward bound-free transition by spontaneous emission is maximum due to the largest CG coefficient. The previously gained potential energy is carried away by the emitted photon. As a consequence, the atom pair loses its total kinetic energy. Now, if $\mathbf{k}_{\text{c.m.}} \simeq 0$, most of the energy lost is the relative energy. The c.m. motion now repeats climbing up the next hill and so on. In this process, eventually the atom pairs become cooled and trapped in the minima of the potential.

III. RESULTS AND DISCUSSIONS

Next, we discuss practical implementation of our proposed scheme. A set of good internal states (molecular angular momenta) of two colliding atoms represent a scattering channel. It is preferable to have only one ground-state scattering channel that can be subjected to Sisyphus cooling cycle so that atoms have no chance to be transferred to other ground-state channel by spontaneous emission [63,64]. Alternatively, the energy difference between asymptotic thresholds of different ground-state channels should be large enough compared to bound-free spontaneous linewidth so that atoms can be cycled only between the chosen (cooling) channel and the excited bound state. Although Sisyphus mechanism will predominantly bring the atom pair into the potential minima reducing the kinetic energy, there is still finite probability of transitions to two free atoms into the continuum with higher energies due to spontaneous emission. In order to recycle these higher-energy atoms back into cooling cycles, the linewidth of PA lasers should be larger than the spontaneous linewidth γ.

For numerical illustration, we consider fermionic ^{171}Yb atoms which have p-wave PLR excited states that are recently used to demonstrate p-wave optical Feshbach resonance [63–65]. For these PLR molecular states, the projection Φ of the total angular momentum $\mathbf{F} = \mathbf{J} + \mathbf{I}$ on the internuclear axis is a good quantum number. Further, when one includes the rotation ℓ of the relative motion between the two atoms, the good quantum numbers are $\mathbf{T} = \mathbf{F} + \vec{\ell}$ and its projection m_T on the space-fixed axis. We consider 0^- ($\Phi_e = 0$) PLR state for which only odd T_e are allowed [65–67]. These PLR states are accessible by PA transitions only from odd partial waves (odd ℓ) and nuclear spin triplet ($I = 1$). Let the two counterpropagating PA lasers be tuned near resonance to $T_g = 2 \leftrightarrow T_e = 3$ transition that is dominated by p-wave ($\ell = 1$) contribution at low energy. We choose vibrational quantum number $v = 1$ for $T_e = 3$ having binding energy -355.4 MHz below the threshold of the corresponding PLR potential. By selection rules, $T_e = 3$ is accessible via PA only from $T_g = 2$ at low energy. Because, from the consideration of fermionic symmetry of the two ground-state ^{171}Yb atoms, s and d and all higher even partial-wave ground-state scattering states will be associated with nuclear spin-triplet state ($I = 0$). Optical dipole transitions to $T_e = 3$ from these two states will be forbidden since the molecular electronic wave functions (molecular orbitals) of these two ground states and the excited state belong to the same symmetry (even) under reflection at the midpoint of the internuclear axis. On similar arguments, spontaneous emission from $T_e = 3$ to all even partial-wave ground-state channels (i.e, s and d wave) is forbidden [65]. The molecular dipole moment $\mathbf{D}$ will couple ground and excited

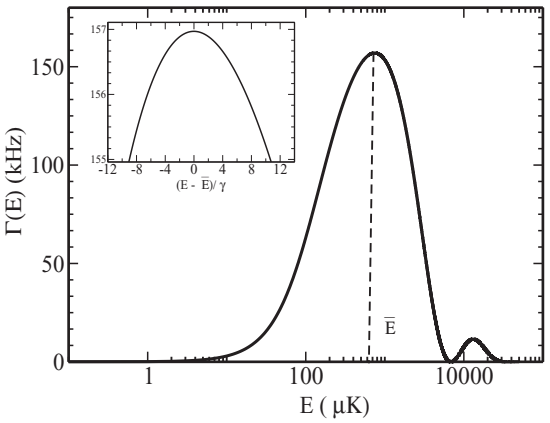

FIG. 2. $\Gamma(E)$ as a function of relative kinetic energy E.

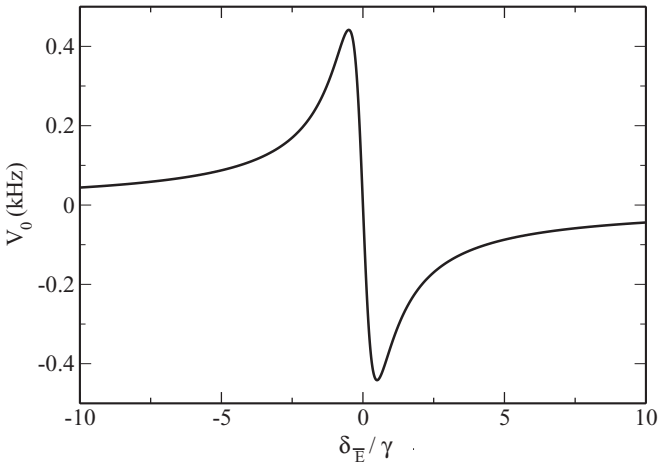

FIG. 3. Strength V_0 (in kHz) of the potential $U_{\rm opt}$ is plotted against detuning $\delta_{\bar{E}}$.

molecular electronic states of opposite electronic center of symmetry. Since the excited electronic state we consider here 0^- ($\Phi_e = 0$) has positive symmetry [65], the ground electronic state of negative symmetry only will be coupled to this excited state. The molecular ground state of all even partial waves has positive symmetry due to fermionic symmetry of the two nuclei with $I = 0$, and therefore spontaneous emission from excited state to s, d, and higher even partial-wave channels are ruled out. f-wave channel is not dominant at low energy and so can be ignored.

The dependence of stimulated linewidth $\Gamma(E)$ on E is shown in Fig. 2. $\Gamma(E)$ is proportional to the square of FC factor. Figure 2 exhibits that $\Gamma(E)$ attains a prominent maximum near $E \simeq 750\ \mu$K with a broad width. This feature can be attributed to the nature of PLR bound state which can be accessible from almost asymptotic regime of ground-state continuum. From Fig. 2, we notice that at $E = 3$ mK, the FC factor reduces to about one tenth of its peak value near $E = 0.75$ mK. As discussed in the preceding section, successive absorption-spontaneous emission cycles will on an average reduce the relative kinetic energy. Therefore, the spontaneous emission will not be a major hindrance to cooling as long as there are no other states except the single-channel continuum to which the atom pair can decay. Suppose initial relative energy is 750 μK at which the PA coupling is maximized as Fig. 2 shows. Although the atom pair will be preferentially transferred towards lower relative energy side, there will be still some finite probability that spontaneous emission will push two atoms to higher-energy side. To bring them back into cooling cycle, a pair of broadband PA lasers (see the Introduction section). Since $\gamma \simeq 364$ kHz, repumping lasers with bandwidth of a few MHz will suffice the purpose. The inset to Fig. 2 shows that the peak structure of PA coupling at $E = \bar{E}$ is sufficiently broad compared to γ. At energies $E = \bar{E} \pm 10\gamma$, the stimulated PA linewidth (or equivalently square of the FC factor) changes by about 1% only from its peak value at $E = \bar{E}$. This weak dependence of PA couping on E near the resonance energy $\bar{E}$ when the laser is tuned to the resonance frequency $\bar{\omega}_L$ [$= (\bar{E}/\hbar + \omega_b$] facilitates us to obtain an approximate analytical solution of the master equation in the steady state as discussed in Appendix B. Figure 2 further shows that for $E < 8\ \mu$K, PA coupling is vanishingly small. This is due to threshold effect. In the limit $E \to 0$, FC factor goes to zero. As PA coupling goes to zero, cooling will stop.

As a result of photoassociative Sisyphus process, we get five spin-dependent c.m. potentials of pair of ^{171}Yb atoms for ground state $T_g = 2$ as given by

$$
\begin{aligned}
U_{\rm opt}\big(m_{T_g} = \pm 2\big) &= -\frac{V_0}{2}\left[-\frac{8}{7} \pm \cos(2k_L Z)\right],\\
U_{\rm opt}\big(m_{T_g} = \pm 1\big) &= -\frac{V_0}{4}\left[-\frac{13}{7} \pm \cos(2k_L Z)\right],\\
U_{\rm opt}\big(m_{T_g} = 0\big) &= -\frac{6}{14}V_0,
\end{aligned}
\qquad (13)
$$

where $V_0 = -\frac{14}{75}\hbar\delta_{\bar{E}} S_0$. The c.m. motion can be trapped in $m_{T_g} = \pm 2, \pm 1$ state provided $\delta_{\bar{E}}$ is negative as can be seen from Fig. 3 which shows that the $U_{\rm opt}$ is attractive (repulsive) when $\delta_{\bar{E}} < 0$ (>0). We take laser intensity 10 mW/cm^2. Figure 3 shows that V_0 varies with $\delta_{\bar{E}}$ reaching a maximum of about 440 Hz at $\delta_{\bar{E}} = 0.5\gamma$, where we have set $\gamma = 364$ kHz which is taken to be double the atomic linewidth of 182 kHz [68]. When $\delta_{\bar{E}}$ is negative V_0 is positive, implying the existence of trapping potential, but when $\delta_{\bar{E}}$ is positive V_0 becomes negative, showing no trapping is possible. The c.m. recoil limit for ^{171}Yb$_2$ is $E_r^{\rm c.m.} = 1.3$ kHz. The parameter $S_0 = 0.013$ and 0.0006 for $\delta_{\bar{E}}/\gamma = -0.5$ and -10, respectively. In near-resonant case ($\delta_{\bar{E}} \sim \gamma$), the c.m. motion will be subjected to cooling due to Sisyphus process while for far-off resonant case ($|\delta_{\bar{E}}| \gg \gamma$) the c.m. motion will be trapped in shallow potentials. With the given intensity of PA laser we can cool the atom pairs to about a few microkelvin.

IV. CONCLUSION

In conclusion, we have proposed a Sisyphus-like method with photoassociative transitions for optically cooling and trapping an atom pair by optical dipole force that acts on the c.m. of the pair. As in the case of molecules, laser cooling of a pair of interacting atoms is a challenging problem. There is no general method of laser cooling of molecules due to the existence of a large number of closely lying rovibrational

levels. Only in some specific cases of favorable level structure, laser cooling of molecules is possible. Similarly, to cool an interacting pair of atoms by photoassociative Sisyphus-like laser cooling technique, one has to look for some favorable atomic systems which have a single asymptotic collision channel with degenerate molecular magnetic sublevels and narrow-line PA transitions. The atoms should be precooled so that the c.m. momentum is small enough to be subjected to Sisyphus mechanism with counterpropagating PA lasers. We have shown that fermionic ^{171}Yb is one such favorable PA system due to the existence of narrow-line PA transitions. Our method critically depends on the strength and nodal structure of the free-bound overlap integral at low energy. In this context, we have shown PLR states play an important role. We have also discussed repumping of the atom pair with relatively high energy into the cooling cycle by using broadband PA lasers in $\sigma_+ + \sigma_-$ polarization configuration. The use of spectrally filtered broadband lasers [45,47] will be particularly useful for our purpose. For instance, suppose all frequency components higher than the resonant frequency $\bar{\omega}_L$ are filtered out from the repumping lasers. Then, the repumping lasers will recycle into the cooling cycles those atom pairs which have energies higher than the resonant energy $\bar{E}$. In this context, it is to be born in mind that while Sisyphus lasers will optically pump the atom pairs in different ground-state sublevels, broadband repumping lasers are needed only to recycle the atom pairs which go far-off resonant on the higher side of the energy due to spontaneous emission. Apart from cooling and trapping of atom pairs, our proposed method will be particularly important for preparing a system of spatially isolated ultracold atom pairs for conversion into molecules with spatial control over association process. This method will also be applicable for manipulating interactions between two atoms with trapped c.m. motion. Particularly important prospect for our method will be a scenario where one can simultaneously cool and manipulate onsite interactions in a Mott insulator of atoms in optical lattice, and thereby to explore new aspects of many-body physics with ultracold atoms. By this way, in the near future it might be possible to explore p-wave or d-wave pairing or superfluidity with fermionic ^{171}Yb or ^{40}K atoms in an optical lattice. In essence, our proposed scheme and theoretical method will stimulate further studies, opening new perspectives in research with cold atoms and molecules.

ACKNOWLEDGMENT

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APPENDIX A: CENTER-OF-MASS DIPOLE FORCE

The equation of motion for c.m. momentum ($P_{\text{c.m.}}$) is given by $dP_{\text{c.m.}}/dt = \frac{i}{\hbar}[H_I, P_{\text{c.m.}}]$ which yields $dP_{\text{c.m.}}/dt = \nabla_R[\int_0^\infty \Lambda_{bE'}(E',R)e^{-i\phi(r,R)}e^{-i\omega_L t}|b\rangle\langle E'|dE' + \text{H.c.}]$. As a result, the c.m. of the two atoms experiences an optical force $F = \langle dP_{\text{c.m.}}/dt\rangle$, where $\langle \dots \rangle$ implies averaging over initial states. The c.m. and relative motions of the system of two atoms become coupled due to photoassociative coupling. We are dealing with cold atoms for which the time scale of evolution of c.m. motion can be assumed to be much less than that of relative motion. We can then safely decouple the two degrees of motions and obtain

$$\mathbf{F} = \int_0^\infty \nabla_R\{\langle|b\rangle\langle E'|\rangle_{\text{rel}}\langle[\Lambda_{bE'}(R)e^{-i\phi(r,R)}]e^{-i\omega_L t}\rangle_{\text{c.m.}}dE' + \text{c.c.}\}. \tag{A1}$$

One can relate $\langle|b\rangle\langle E'|\rangle_{\text{rel}}$ to density matrix element $\rho_{E'b}$ as derived in Appendix B. So, the optically generated force is given by Eq. (6). It is convenient to express Eq. (6) in a frame rotating at the frequency ω_L of the laser field. This is achieved by introducing the variable $\rho_{Eb} = \rho_{Eb}e^{i\omega_L t}$. We can thus write $F = F_{\text{dip}} + F_{\text{dis}}$, where

$$\mathbf{F}_{\text{dip}} = \int_0^\infty [e^{-i\phi(r,R)}\nabla_R\{\Lambda_{bE'}(R)\rho_{E'b}\} + e^{i\phi(r,R)}\nabla_R\{\Lambda_{E'b}\rho_{bE'}(R)\}]dE', \tag{A2}$$

$$\mathbf{F}_{\text{dis}} = \int_0^\infty i\{\nabla_R\phi(r,R)\}[\rho_{bE'}e^{i\phi(r,R)}\Lambda_{E'b}(R) - \rho_{E'b}e^{-i\phi(r,R)}\Lambda_{bE'}(R)]dE'. \tag{A3}$$

For plane wave only dissipative force and for standing wave only dipole force exists. In the latter case, $\phi(r,R) = 0$. We are interested in conservative dipole force, hence, we consider standing wave [$\phi(r,R) = 0$].

In order to calculate the forces, we need to evaluate the free-bound density matrix element ρ_{Eb}. With relaxation processes included, the atomic density matrix is given by the solution of the master equation for the density matrix. For an all discreet atomic system, the master equation is well known. For a coupled discrete-continuum system such as in the present case, density matrix approach is not adequately addressed in the literature.

Let $\rho_c = \hbar\int \rho_{EE}d\omega_E$ and $\rho_{bc} = \int_0^\infty \Lambda_{Eb}(R)\rho_{bE}d\omega_E$. Using the normalization condition $\rho_{bb} + \rho_c = 1$, we can write

$$\dot{\rho}_c = i\rho_{bc} - i\rho_{cb} - \gamma\rho_{bb}. \tag{A4}$$

Now, we get from density matrix equation (Appendix B)

$$\dot{\rho}_{bc} = \left(i\Delta - \frac{\gamma}{2}\right)\rho_{bc} + i\hbar\int_0^\infty \Lambda_{Eb}(R)\rho_{bE}\omega_E d\omega_E + \int_0^\infty \Lambda_{bE}(R)\left\{\int_0^\infty \Lambda_{bE'}(R)\rho_{E'E}d\omega_{E'}\right\}d\omega_E - \frac{i}{2\pi}\int_0^\infty \mathcal{G}_E\rho_{bb}d\omega_E. \tag{A5}$$

The solution of density matrix (Appendix B) equation of $\dot{\rho}_{E'E}(t)$ can be formally written as

$$\rho_{E'E}(t) = \rho_{E'E}(0)e^{i\omega_{EE'}t} + \frac{i}{\hbar}e^{i\omega_{EE'}t}\left[\Lambda_{E'b}\int_0^t \rho_{bE}e^{i\omega_{E'E}t'}dt' - \Lambda_{bE}\int_0^t \rho_{E'b}(R)e^{i\omega_{E'E}t}dt'\right] + \gamma_0\eta^*_{bE'}\eta_{bE}\int_0^t \rho_{bb}(t')e^{i\omega_{E'E}(t'-t)}dt', \tag{A6}$$

where $\omega_{EE'} = \frac{E-E'}{\hbar}$.

Putting the expression $\rho_{E'E}(t)$ in Eq. (A5),

$$\dot{\rho}_{bc} = \left(i\Delta - \frac{\gamma}{2}\right)\rho_{bc} + i\hbar\int_0^\infty \Lambda_{Eb}(R)\rho_{bE}\omega_E d\omega_E - \frac{i}{2\pi}\int_0^\infty \mathcal{G}_E\rho_{bb}d\omega_E$$
$$+i\int_0^\infty \Lambda_{Eb}(R)\left\{\int_0^\infty \Lambda_{bE'}(R)\left[\rho_{E'E}(0)e^{i\omega_{EE'}t} + \gamma_0\eta^*_{bE'}\eta_{bE}\int_0^t \rho_{bb}(t')e^{i\omega_{E'E}(t-t')}dt'\right]d\omega_{E'}\right\}d\omega_E$$
$$+\frac{1}{\hbar}\int_0^t\left[\int_0^\infty |\Lambda_{Eb}|^2\left(\int_0^\infty \Lambda_{bE'}\rho_{E'b}e^{i\omega_{E'E}(t-t')}d\omega_{E'}\right)d\omega_E\right]dt'$$
$$-\frac{1}{\hbar}\int_0^t\left[\int_0^\infty \Lambda_{Eb}\rho_{bE}\left(\int_0^\infty |\Lambda_{E'b}|^2 e^{i\omega_{E'E}(t-t')}d\omega_{E'}\right)d\omega_E\right]dt'. \quad \text{(A7)}$$

We assume $\rho_{E'E}(0) = \rho_c(0)\delta(E'-E)$. While doing the energy integrals, we have assumed that $\delta_E \simeq \delta_{\bar{E}}$. This approximation can be justified in the following way. Since the coherence term ρ_{bE} has the linewidth γ which is quite small compared to the scale of energy variation of PA coupling $\Lambda(E)$ near the resonant energy $\bar{E}$ as discussed in the theory section (see Fig. 2), ρ_{bE} can be taken as rapidly varying function of energy compared to all other energy-dependent quantities:

$$\dot{\rho}_{bc} = \left(i\delta_{\bar{E}} - \frac{\gamma}{2}\right)\rho_{bc} - \frac{i}{2\pi}\int_0^\infty \mathcal{G}_E(R)d\omega_E[2\rho_{bb}-1]. \quad \text{(A8)}$$

After doing some algebra, we get the steady-state solutions

$$\rho_{bb} = \frac{\frac{1}{2\pi}\int_0^\infty \mathcal{G}_E(R)d\omega_E}{\delta^2_{\bar{E}} + \frac{\gamma^2}{4} + \frac{2}{2\pi}\int_0^\infty \mathcal{G}_E(R)d\omega_E}, \quad \text{(A9)}$$

$$\rho_{bc} = -\frac{\frac{1}{2\pi}\int_0^\infty \mathcal{G}_E(R)d\omega_E\left(\delta_{\bar{E}} - i\frac{\gamma}{2}\right)}{\delta^2_{\bar{E}} + \frac{\gamma^2}{4} + \frac{2}{2\pi}\int_0^\infty \mathcal{G}_E(R)d\omega_E}. \quad \text{(A10)}$$

From the dipole force from Eq. (A2) we get

$$F_{\rm dip} = -\frac{\hbar\delta_{\bar{E}}}{\pi}\left\{\frac{\nabla_R\int_0^\infty \mathcal{G}_E(R)d\omega_E}{\delta^2_{\bar{E}} + \frac{\gamma^2}{4} + \frac{2}{2\pi}\int_0^\infty \mathcal{G}_E(R)d\omega_E}\right.$$
$$\left. - \frac{\frac{2\hbar}{2\pi}\int_0^\infty \mathcal{G}_E(R)d\omega_E\left[\nabla_R\int_0^\infty \mathcal{G}_{E'}(R)d\omega_{E'}\right]}{\left[\delta^2_{\bar{E}} + \frac{\gamma^2}{4} + \frac{2}{2\pi}\int_0^\infty \mathcal{G}_E(R)d\omega_E\right]^2}\right\}, \quad \text{(A11)}$$

where $\mathcal{G}_E(R) = \frac{2\pi}{\hbar}|\Lambda_{bE}(R)|^2 = \Gamma(E)\Theta(R)$.

We define the saturation parameter $S_0 = \frac{\frac{1}{\pi}\int_0^\infty \Gamma(E)d\omega_E}{\delta^2_{\bar{E}} + \frac{\gamma^2}{4}}$. At the weak-intensity limit, the second term on the right side $F_{\rm dip}$ [Eq. (A11)] can be neglected. At weak intensity (i.e., $S_0 \ll 1$) the dipole force becomes

$$F_{\rm dip}(R) = -\frac{\hbar\delta_{\bar{E}}}{\pi}\left[\frac{\nabla_R\int_0^\infty \mathcal{G}_E(R)d\omega_E}{\delta^2_{\bar{E}} + \frac{\gamma^2}{4} + \frac{2}{2\pi}\int_0^\infty \mathcal{G}_E(R)d\omega_E}\right]. \quad \text{(A12)}$$

The optical potential is

$$U_{\rm opt} = -\int F_{\rm dip}(R)dR$$
$$= \hbar\delta_{\bar{E}}\ln\left[1 + \frac{\frac{1}{\pi}\int_0^\infty \mathcal{G}_E(R)d\omega_E}{\delta^2_{\bar{E}} + \frac{\gamma^2}{4}}\right]. \quad \text{(A13)}$$

At weak intensity ($S_0 \ll 1$) the optical potential is

$$U_{\rm opt} = \hbar\delta_{\bar{E}}\frac{\frac{1}{\pi}\int_0^\infty \mathcal{G}_E(R)d\omega_E}{\delta^2_{\bar{E}} + \frac{\gamma^2}{4}}. \quad \text{(A14)}$$

In terms of S_0, Eq. (A9) can be written as

$$\rho_{bb} = \frac{S_0\Theta(R)}{2 + 2S_0\Theta(R)}. \quad \text{(A15)}$$

When $S_0 \to \infty$, $\rho_{bb} \to \frac{1}{2}$.

APPENDIX B: DERIVATION OF THE MASTER EQUATION FOR PA SYSTEM

To incorporate spontaneous decay in the continuum-bound system under consideration, we derive the master equation of the the system from first principles. The excited molecular bound state can spontaneously decay to the continuum scattering states of two ground-state atoms due to coupling of the system with a reservoir of electromagnetic vacuum modes. The Hamiltonian is $H = H_S + H_R + H_{SR}$, where $H_S \equiv \hat{H}_0^{\rm rel}$, the system Hamiltonian as given in Eq. (2). $H_R = \sum_{\kappa\sigma}\hbar\omega_{\kappa\sigma}\hat{a}^\dagger_{\kappa\sigma}\hat{a}_{\kappa\sigma}$ represents the Hamiltonian for the reservoir of the infinite number of electromagnetic modes denoted by the wave number κ and the polarization σ with $\hat{a}_{\kappa\sigma}$ ($\hat{a}^\dagger_{\kappa\sigma}$) denoting photon annihilation (creation) operator for the $(\kappa\sigma)$ mode. Here, we are considering the incoherent interaction of the vacuum modes only. We have dropped PA laser interaction part of the Hamiltonian for the sake of simplicity. The system-reservoir interaction Hamiltonian can be expressed as

$$H_{SR} = \left[\sum_{\kappa\sigma}\hat{a}_{\kappa\sigma}e^{-i\omega_{\kappa\sigma}t}\int dE\,\mathcal{V}_E(\kappa\sigma)S^+_E e^{i\omega_{bE}} + \text{H.c.}\right], \quad \text{(B1)}$$

where $\omega_{bE} = E/\hbar + \omega_b$, with ω_b being the frequency of the bound state measured from the threshold of the continuum. $\mathcal{V}_E(\kappa\sigma) = -E_{\rm vac}(\kappa)(\vec{D}\cdot\hat{\epsilon}_\sigma)\eta_{bE}$ is the vacuum-induced continuum-bound coupling with $E_{\rm vac}(\kappa) = \sqrt{\frac{\hbar\omega_\kappa}{2\epsilon_0 V}}$, $\hat{\epsilon_\sigma}$ being the unit vector of polarization and V is the volume, $\vec{D}$ is the molecular dipole moment operator, and $\eta_{bE} = \int_0^\infty d^3r\,\phi_b(\vec{r})\psi_E(\vec{r})$ is the bound-free overlap integral, $\phi_b(\vec{r})$ and $\psi_E(\vec{r})$ being, respectively, the bound and free wave functions.

The equation for the incoherent part of the reduced density matrix of the system [70] is

$$\dot{\rho}_{\rm inc} = -\int_0^t dt' {\rm Tr}_R\{[H_{SR}(t),[H_{SR}(t'),\rho(t')R_0]]\}. \tag{B2}$$

R_0 is an initial reservoir density operator. Substituting Eq. (B1) in (B2), and expanding the commutator, we have

$$\begin{aligned}
\dot{\rho}_{\rm inc} = &-\sum_{\kappa\sigma\kappa'\sigma'}\int_0^\infty dE\int_0^\infty dE'\int_0^t dt' {\rm Tr}_R(\{[\mathcal{V}_E^*(\kappa\sigma)\mathcal{V}_{E'}^*(\kappa'\sigma')S_E S_{E'}\rho(t')R_0 \\
&-\mathcal{V}_E^*(\kappa\sigma)\mathcal{V}_{E'}^*(\kappa'\sigma')S_E\rho(t')S_{E'}R_0]e^{-i(\omega_{bE}t+\omega_{bE'}t')}\hat{a}^+_{\kappa\sigma}\hat{a}^+_{\kappa'\sigma'}e^{i(\omega_{\kappa\sigma}t+\omega_{\kappa'\sigma'}t')} + {\rm H.c.}\} \\
&+\{[\mathcal{V}_E(\kappa\sigma)\mathcal{V}_{E'}(\kappa'\sigma')S_E^+S_{E'}^+\rho(t')R_0 - \mathcal{V}_E(\kappa\sigma)\mathcal{V}_{E'}(\kappa'\sigma')S_E^+\rho(t')S_{E'}^+R_0] \\
&\times e^{i(\omega_{bE}t+\omega_{bE'}t')}\hat{a}_{\kappa\sigma}\hat{a}_{\kappa'\sigma'}e^{-i(\omega_{\kappa\sigma}t+\omega_{\kappa'\sigma'}t')} + {\rm H.c.}\} + \{[\mathcal{V}_E(\kappa\sigma)\mathcal{V}_{E'}^*(\kappa'\sigma')S_E S_{E'}^+\rho(t')R_0 \\
&-\mathcal{V}_E^*(\kappa\sigma)\mathcal{V}_{E'}(\kappa'\sigma')S_E^+\rho(t')S_{E'}R_0]e^{-i(\omega_{bE}t-\omega_{bE'}t')}\hat{a}^+_{\kappa\sigma}\hat{a}_{\kappa'\sigma'}e^{-i(\omega_{\kappa\sigma}t-\omega_{\kappa'\sigma'}t')} + {\rm H.c.}\} \\
&\times\{[\mathcal{V}_E^*(\kappa\sigma)\mathcal{V}_{E'}(\kappa'\sigma')S_E^+S_{E'}\rho(t')R_0 - \mathcal{V}_E(\kappa\sigma)\mathcal{V}_{E'}^*(\kappa'\sigma')S_E\rho(t')S_{E'}^+R_0] \\
&\times e^{i(\omega_{bE}t-\omega_{bE'}t')}\hat{a}_{\kappa\sigma}\hat{a}^+_{\kappa'\sigma'}e^{-i(\omega_{\kappa\sigma}t-\omega_{\kappa'\sigma'}t')} + {\rm H.c.}\}).
\end{aligned} \tag{B3}$$

Tracing over the vacuum modes [69] and using

$$\begin{aligned}
&{\rm Tr}\{R_0\hat{a}_{\kappa\sigma}\hat{a}^+_{\kappa'\sigma'}\} = \delta_{\kappa\kappa'}\delta_{\sigma\sigma'}, \quad {\rm Tr}\{R_0\hat{a}^+_{\kappa\sigma}\hat{a}_{\kappa'\sigma'}\} = 0, \\
&{\rm Tr}\{R_0\hat{a}_{\kappa\sigma}\hat{a}_{\kappa'\sigma'}\} = {\rm Tr}\{R_0\hat{a}^+_{\kappa\sigma}\hat{a}^+_{\kappa'\sigma'}\} = 0,
\end{aligned} \tag{B4}$$

we are left with the last term containing $\hat{a}_{\kappa\sigma}\hat{a}^+_{\kappa'\sigma'}$. After making the change of variable $\tau = t - t'$, Eq. (B3) reduces to

$$\begin{aligned}
\dot{\rho}_{\rm inc} = &-\sum_{\kappa\sigma}\int_0^\infty dE\int_0^\infty dE'\int_0^t d\tau\{\mathcal{V}_E^*(\kappa\sigma)\mathcal{V}_{E'}(\kappa\sigma)S_E^+S_{E'}\rho(t-\tau) \\
&-\mathcal{V}_E(\kappa\sigma)\mathcal{V}_{E'}^*(\kappa\sigma)S_E\rho(t-\tau)S_{E'}^+\}e^{i\omega_{EE'}t}e^{i\omega_{bE'}\tau}e^{-i\omega_{\kappa\sigma}\tau} + {\rm H.c.}
\end{aligned} \tag{B5}$$

Under Markov approximation, we get

$$\begin{aligned}
\dot{\rho}_{\rm inc} = &-\sum_{\kappa\sigma}\int_0^\infty dE\int_0^\infty dE' e^{i\omega_{EE'}t}\Big\{S_E^+S_{E'}\rho(t)\mathcal{V}_E^*(\kappa\sigma)\mathcal{V}_{E'}(\kappa\sigma)\int_0^t d\tau e^{i(\omega_{bE'}-\omega_{\kappa\sigma})\tau} \\
&-\mathcal{V}_E(\kappa\sigma)\mathcal{V}_{E'}^*(\kappa\sigma)S_E\rho(t)S_{E'}^+\int_0^t d\tau e^{i(\omega_{bE'}-\omega_{\kappa\sigma})\tau}\Big\} + {\rm H.c.}
\end{aligned} \tag{B6}$$

We can write $\mathcal{V}_{E'}(\kappa\sigma) = g_{\kappa\sigma}\eta_{bE}$ where $g_{\kappa\sigma} = -E_{\rm vac}(\kappa)(\vec{D}\cdot\hat{\epsilon}_\sigma)$ and $\mathcal{V}_E(\kappa\sigma)\mathcal{V}_{E'}^*(\kappa\sigma) = |g_{\kappa\sigma}|^2\eta_{bE}\eta^*_{bE'}$. Now, we convert the sum $\sum_{\kappa\sigma}$ into an energy integral using the relation

$$\sum_{\kappa\sigma}|g_{\kappa\sigma}|^2 = \int\frac{D^2}{6\pi^2\epsilon_0\hbar c^3}\omega_\kappa^3 d\omega_\kappa. \tag{B7}$$

For bound-continuum system, the spontaneous linewidth can be defined as $\gamma = \gamma_0\int_0^\infty dE|\eta_{bE}|^2$, where $\gamma_0 = \frac{D^2}{3\pi\epsilon_0\hbar c^3}\omega_b^3$.

As the time of interest $t \gg 1/\omega_{bE}$, where ω_{bE} is generally in the optical frequency domain, we can take upper limit of above time integral to ∞. Writing the integral as

$$\begin{aligned}
\int_0^\infty d\tau\, e^{i(\omega_{bE'}-\omega_{\kappa\sigma})\tau} &= \lim_{\epsilon\to0}\int_0^\infty d\tau\, e^{i(\omega_{bE'}-\omega_{\kappa\sigma}+i\epsilon)\tau} \\
&= -\lim_{\epsilon\to0}\frac{1}{i(\omega_{bE'}-\omega_{\kappa\sigma}+i\epsilon)} \\
&= \pi\delta(\omega_{\kappa\sigma}-\omega_{bE'}) + i{\rm P}\left(\frac{1}{\omega_{\kappa\sigma}-\omega_{bE'}}\right),
\end{aligned} \tag{B8}$$

where P represents the Cauchy principal part which leads to Lamb shift. This is quite small and so can be ignored for the present purpose. So, we write Eq. (B6) as

$$\begin{aligned}
\dot{\rho}_{\rm inc} = &-\int_0^\infty dE\int_0^\infty dE' e^{i\omega_{EE'}t}\frac{\gamma_0}{2}\{S_E^+S_{E'}\rho(t)\eta^*_{bE}\eta_{bE'} - S_E\rho(t)S_{E'}^+\eta^*_{bE'}\eta_{bE}\} \\
&-\int_0^\infty dE\int_0^\infty dE' e^{-i\omega_{EE'}t}\frac{\gamma_0}{2}\{\rho(t)S_{E'}^+S_E\eta^*_{bE'}\eta_{bE} - S_{E'}\rho(t)S_E^+\eta^*_{bE}\eta_{bE'}\}.
\end{aligned} \tag{B9}$$

Using Eq. (B9) we get

$$\begin{aligned}(\dot{\rho}_{bb})_{\text{inc}} &= -\gamma\rho_{bb},\\ (\dot{\rho}_{bE})_{\text{inc}} &= -\frac{\gamma}{2}\rho_{bE},\\ (\dot{\rho}_{EE'})_{\text{inc}} &= \gamma_0\rho_{bb}\eta^*_{bE'}\eta_{bE}.\end{aligned} \tag{B10}$$

The complete master equation for our system is $\dot{\rho} = \dot{\rho}_{\text{coh}} + \dot{\rho}_{\text{inc}}$, where

$$\dot{\rho}_{\text{coh}} = -\frac{i}{\hbar}\left[H_I^{\text{coh}},\rho\right] \tag{B11}$$

with $H_I^{\text{coh}} = [\int_0^\infty \Lambda_{bE'}|b\rangle\langle E'|dE' + \text{H.c.}]$ is the interaction Hamiltonian in the interaction picture due to PA laser only. Thus, for continuum-bound coupled system as in the present case, the density matrix elements are given by

$$\hbar\dot{\rho}_{bE} = \left(i\hbar\delta_E - \frac{\hbar\gamma}{2}\right)\rho_{bE} + i\left[\int_0^\infty \Lambda_{bE'}(R)\hbar\rho_{E'E}dE' - \Lambda_{bE}(R)\rho_{bb}\right], \tag{B12}$$

$$\hbar\dot{\rho}_{E'E} = -i(E' - E)\rho_{E'E} + i[\Lambda_{E'b}(R)\rho_{bE} - \rho_{E'b}\Lambda_{bE}(R)] + \gamma_0\rho_{bb}\eta^*_{bE'}\eta_{bE}, \tag{B13}$$

$$\hbar\dot{\rho}_{bb} = \left[i\int_0^\infty \rho_{E'b}\Lambda_{bE'}(R)dE' + \text{c.c.}\right] - \hbar\gamma\rho_{bb}, \tag{B14}$$

where $\delta_E = \Delta + \omega_E$ and $\Delta = \omega_L - \omega_0$ (ω_L,ω_0) is laser and atomic frequency, respectively ($\omega_E = E/\hbar$).

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