Model study on the photoassociation of a pair of trapped atoms into an ultralong-range molecule

B. Deb[1] and L. You[2]

[1]*Physical Research Laboratory, Navrangpura, Ahmedabad 380 009, India*
[2]*School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332, USA*
(Received 21 January 2003; published 22 September 2003)

Using the method of quantum-defect theory, we calculate the ultra-long-range molecular vibrational states near the dissociation threshold of a diatomic molecular potential which asymptotically varies as $-1/R^3$. The properties of these states are of considerable interest as they can be formed by photoassociation (PA) of two ground-state atoms. The Franck-Condon overlap integrals between the harmonically trapped atom-pair states and the ultra-long-range molecular vibrational states are estimated and compared with their values for a pair of untrapped free atoms in the low-energy scattering state. We find that the binding between a pair of ground-state atoms by a harmonic trap has significant effect on the Franck-Condon integrals and thus can be used to influence PA. Trap-induced binding between two ground-state atoms may facilitate coherent PA dynamics between the two atoms and the photoassociated diatomic molecule.

I. INTRODUCTION

Photoassociation (PA) spectroscopy [1] has developed into an important tool for studying properties of cold atoms and diatomic molecules. The formation of excited diatomic molecular states through cold atom PA had been reported a long time ago [2]. Over the last decade, theoretical techniques for calculating PA rate coefficients have been developed by many groups [3]. Photoassociation spectroscopy enables a precise calibration of long range interatomic forces. It leads to the formation of translationally cold molecules and thus provides one possible route of creating a molecular Bose-Einstein condensate (BEC). Two-photon resonant Raman PA coupling can also be utilized for generating atom-molecule coherence [4,5] and massive entangled atoms [6]. In fact, many-body atom-molecule coherence was recently observed [7] through the tuning of a Feshbach resonance (FR) [8] caused by an applied magnetic field in a ^{85}Rb condensate. Quasibound molecular states can be formed by FR in ultracold atom-atom collision. FR has striking analogy with PA. In the first approximation, both are coupled two-state systems and mathematically identical. It is the magnetic field which couples the two states in the former case, while in the latter case it is the optical field. Both can be used to change the scattering length between two atoms [9]. Two-color stimulated Raman adiabatic passage (STIRAP) [10–13] via coherent PA using an appropriately tailored pair of laser pulses has been proposed for creating a molecular condensate from an atomic BEC. Stimulated PA of condensed atoms leads to "superchemistry" [14,15] where quantum statistics plays a crucial role in the production of molecules, and a superposition of macroscopic number of atoms and molecules [16]. Although there has been no explicit experimental realization of a molecular BEC, coherent production of molecules in a single rotational-vibrational state has recently been experimentally demonstrated [17]. The quantum dynamics [18] of coupled atomic and molecular condensates reveals a lot of interesting physical effects, e.g., the recently observed frequency shifts [19] contains the detailed information about the density of states of cold atoms in the quasi-

continuum regime. An alternative approach [20] for creating a molecular BEC from atoms in a Mott insulating state inside an optical lattice was also proposed recently [21].

In a PA event, two ground-state atoms, by means of a single-photon excitation during the collision, combine to form an excited diatomic molecule which can decay back to two atoms or to a different ground molecular state. Near-zero-energy vibrational states close to the dissociation threshold of an excited diatomic molecular level can be formed by PA of cold atoms. These states can extend to several hundred nanometers. PA absorption line strength and linewidth strongly depend on the overlap integral, known as Franck-Condon (FC) integral, of these states with two atoms in the ground state. For these ultralong-range states, the "reflection approximation" which is often used in molecular spectrum calculations, breaks down. The reflection approximation replaces the actual integral by an integral over a δ function. This drastically simplifies the calculation by ruling out the necessity of calculating the wave function in the entire range. Instead, it only requires to calculate the wave function at a particular interatomic separation (the turning or Condon point). This indeed seems to be a valid approximation for deeply bound molecular states with energy several tens of GHz below the dissociation threshold. For bound states with energies of the order of MHz or even kHz below the dissociation threshold, however, this approximation does not seem to work. Calculation of the actual Franck-Condon overlap integral is, therefore, inevitable for such states. This presents a significant challenge as the standard numerical techniques for calculating the wave functions of these states are not known to be reliable.

In this paper, we discuss a scheme for estimating the qualitative dependence of the required FC integrals. By using the quantum-defect theory (QDT) to find the exact solutions of molecular states in a long-range excited potential $(-1/R^3)$, we obtain near-zero-energy ($\leq$MHz) vibrational wave functions that can extend from several hundred nanometers to micrometers. We employ these wave functions to evaluate the FC overlap integral in two situations: (1) for two atoms trapped in a harmonic potential; and (2) for two free

atoms. We analyze the effect of the trapping potential and the atom scattering length on the FC integral. We also evaluate spontaneous emission linewidths of the excited molecular states.

This paper is organized as follows. In the following section, we describe the model system and the basis for our study. Then in Sec. III, we discuss the relative motional state of two ground-state (S+S) atoms trapped in a harmonic potential. In Sec. IV, we describe the method of QDT for calculating the vibrational states that can be formed by PA in the excited electronic potential which asymptotically corresponds to two (S+P) separated atoms. Photoassociation of two atoms inside an isotropic harmonic trap, with an emphasis on the usefulness of the trap-induced two-atom bound states in one- and two-color coherent PA, is discussed in Sec. V. We present and discuss the results of our study in Sec. VI. We conclude in Sec. VII.

II. THE MODEL SYSTEM

Using the Born-Oppenheimer approximation, the Hamiltonian of our model with two atoms A and B can be expressed as $H = H_{nucl} + H_{el} + V_{trap} + V_{af}$, where

$$H_{nucl} = -\frac{\hbar^2}{2M}\nabla^2_{CM} - \frac{\hbar^2}{2\mu}\nabla^2_{rel} + V(R). \quad (1)$$

M and μ are the total and the reduced mass of the two atoms, respectively. The Laplacians ∇^2_{CM} and ∇^2_{rel}, respectively, correspond to the center of mass and the relative nuclear coordinate, of the two atoms. $V(R)$ is the atom-atom interaction potential which is approximated as isotropic, i.e., as a function of the relative nuclear coordinate $R = |\mathbf{R}_A - \mathbf{R}_B|$ only. H_{el} is the electronic part of the total Hamiltonian and $V_{trap} = \Sigma_{\alpha = A,B} V^{\alpha}_{trap}$, with V^{α}_{trap} as the trapping potential for atom α. The atom-field interaction is given by the standard dipole approximation

$$V_{af} = -\sum_{\alpha = A,B}\mathbf{E}\cdot\mathbf{d}_\alpha, \quad (2)$$

where $\mathbf{E}$ represents the electric field of the applied laser field and $\mathbf{d}_\alpha$ denotes the electronic dipole moment of atom α. In the limit of a low-intensity laser, this atom-field interaction can be considered as a perturbation.

We choose molecular states as our basis functions. Initially, the two atoms A and B are in their ground s electronic states. Thus their initial molecular state notation is $|\Phi_i\rangle = |ns,ns,^{2S+1}\Lambda_{g,u},\epsilon_i,J_i,M_i\rangle|\Psi_i(R)\rangle$, where Λ is the projection of the total electronic orbital angular momentum on the molecular axis and ϵ_i is the relative energy of the two atoms. $|\Psi_i(R)\rangle$ is the initial relative nuclear wave function. The final molecular state can be represented by $|\Phi_f\rangle = |ns,np,\Omega_{u,g},\epsilon_v,J_f,M_f\rangle|\Psi_v(R)\rangle$, where v denotes the vibrational quantum number, the energy E_v of the vibrational state v lies at an energy $\epsilon_v = D_f - E_v$ below the dissociation threshold D_f. Here $\Omega_{u,g}$ refers to Hund's case c of the interatomic potential; $J_{i(f)}$ is the total angular momentum (consisting of electronic orbital, spin, and molecular orbital an-

gular momenta) of the initial (final) state with respect to a laboratory axis and $M_{i(f)}$ is its projection on that axis. $|\Psi_v(R)\rangle$ is the relative vibrational nuclear wave function. These basis states are similar to those used in Ref. [22]. In this representation of the basis states, we have neglected the hyperfine interaction for the sake of simplicity. The dipole interaction term (2) in this molecular basis, in the center-of-mass frame of the two atoms, then takes the form

$$V_{af} \simeq -\hat{\boldsymbol\epsilon}\cdot\hat{\boldsymbol\mu}ED(R)\cos(\mathbf{k}_L\cdot\mathbf{R}/2), \quad (3)$$

where $D(R)$ is the molecular dipole matrix element between the molecular states $\Lambda_{g,u}$ and $\Omega_{u,g}$, $\mathbf{k}_L$ and $\hat{\boldsymbol\epsilon}$ are the wave vector and the polarization unit vector, respectively, of the laser field, and $\hat{\boldsymbol\mu}$ is the unit vector of the dipole moment. For two homonuclear alkali-metal atoms, $D(R)$ has been calculated by Marinescu and Dalgarno [23]. To leading order, it asymptotically varies as $1/R^3$ in the form of $D(R) = D_0 + D_1/R^3$. For the $3S_{1/2}$-$3P_{3/2}$ transition in Na$_2$, in atomic units $D_0 = -3.5007$ and $D_1 = 142.13$ [23]. Therefore, for R larger than $100a_0$ in unit of Bohr radius a_0, the R dependence of $D(R)$ of Na$_2$ can safely be neglected and $D(R)$ can be approximated as a constant D_0. All ultralong-range excited vibrational states of Na$_2$ we report here have negligible amplitude in $R < 100$; instead, their major amplitude lies at a separation much greater than a 1000 Bohr radii.

To illustrate our study with concrete results, we specifically consider the transition $^3\Sigma_u \to 0^-_g$ of Na$_2$. The initial and the final internal states are assumed to be $|ns,ns,^3\Sigma_u,\epsilon_i,0,0\rangle$ and $|ns,np,0^-_g,\epsilon_v,1,0\rangle$, respectively. The potential of the 0^-_g and 1_u states of Na$_2$ has been explicitly tabulated by Stwalley $et\ al.$ [24]. These states have their equilibrium positions at a separation larger than $60a_0$. Compared to the size of a ground diatomic molecule whose equilibrium position ranges in general between 2 and 10 Bohr radius, these 0^-_g and 1_u molecular states are truly long ranged. The PA spectrum for some vibrational states of 0^-_g of Na$_2$ have already been observed experimentally [25].

III. TWO-ATOM STATE IN A TRAP

We can choose the initial state of two ground-state (S) atoms in two different ways depending on whether the two atoms are trapped or are moving freely. The corresponding PA spectrum for these two cases can become markedly different. For two free ground-state atoms colliding under the interatomic interaction, their asymptotic relative motion scattering wave function is given by

$$\Psi_\epsilon = \sqrt{\frac{k}{\pi\epsilon}}\sin[k(R - a_{sc})], \quad (4)$$

which is an energy-normalized scattering state. $\epsilon = \hbar^2 k^2/(2\mu)$ is the asymptotic collision energy. At low energies, for $|R - a_{sc}| \ll k^{-1}$ this wave function can be approximated as a straight line. Care should be taken to calculate the

TABLE I. The energy eigenvalues E_ν of the lowest three harmonic trap-bound s-wave vibrational atom-pair states and their outer turning point R_t for two values of harmonic frequencies.

$n_t(\nu)$	$\omega_t = 2\pi \times 10$ kHz		$\omega_t = 2\pi \times 100$ kHz	
	E_ν (MHz)	R_t (nm)	E_ν (MHz)	R_t (nm)
0	0.095	515.44	0.96	164.25
1	0.221	786.35	2.23	249.89
2	0.347	985.28	3.49	312.78

FIG. 1. Two ^{23}Na atom s-wave bound-state wave functions (in units of nm$^{-1/2}$) in a harmonic trap with $\omega_t = 2\pi \times 100$ kHz (a) and $\omega_t = 2\pi \times 10$ kHz (b). The individual curves are specified by the trap quantum number n_t.

free-bound FC factor of ultralong-range molecular states, since the range of the vibrational state can exceed k^{-1} even at very low energies.

For two atoms in an isotropic harmonic trap, their wave function is separable into the center of mass and the relative motion [26]. Approximating the atom-atom interaction $V(R)$ by a regularized contact potential $4\pi\hbar^2 a_{sc}\delta^3(\mathbf{R})/(2\mu)$ (with a_{sc} as the s-wave scattering length), the bound state of two atoms in a harmonic trap (of frequency ω_t) was first derived analytically by Busch *et al.* [26]. Let us define a characteristic length scale of an isotropic harmonic trap as $a_t = \sqrt{\hbar/(\mu\omega_t}$ and introduce a dimensionless quantity $\bar{R} = R/a_t$. Let $\Psi_{n_t} = R\Phi_{n_t}$ represent the relative motional bound-state wave function in the harmonic trap, with n_t (which we will define below) being an integer quantum number related to the three-dimensional isotropic harmonic trap. We can then express the bound state as

$$\Phi_{n_t} = \tfrac{1}{2}\pi^{-3/2}A\exp(-\bar{R}^2/2)\Gamma(-\nu)U(-\nu,\tfrac{3}{2},\bar{R}^2), \quad (5)$$

where A is a normalization constant having the dimension of inverse of square root of volume and

$$\nu = \frac{1}{2\hbar\omega_t}\epsilon - \frac{3}{4}, \quad (6)$$

an effective quantum number for the relative motional eigenstate. $U(.,.,.)$ is the confluent hypergeometric function. The energy spectrum for such trap-bound two-atom states has been analyzed in detail before [26]. The energy eigenvalue is given by the roots of the equation

$$\frac{\Gamma(-x/2+3/4)}{\Gamma(-x/2+1/4)} = \frac{1}{\sqrt{2}\,\xi_s}, \quad (7)$$

where $x = \epsilon/(\hbar\omega_t)$.

We here define a dimensionless quantity $\xi_s = a_{sc}/a_t$. If $\xi_s \ll 1$, then the eigenenergies can be approximated as

$$\epsilon_{n_t} \simeq \left[\frac{3}{2} + 2n_t + \sqrt{2/\pi}\,\xi_s C_{n_t}^{n_t+1/2}\right]\hbar\omega_t, \quad n_t = 0,1,2,\ldots. \quad (8)$$

Selected numerical results are presented in Table I and Fig. 1. Recently, the energy spectrum of two atoms in a harmonic trap has also been analyzed in detail in two papers [27] where it was shown that the validity of the solutions found in R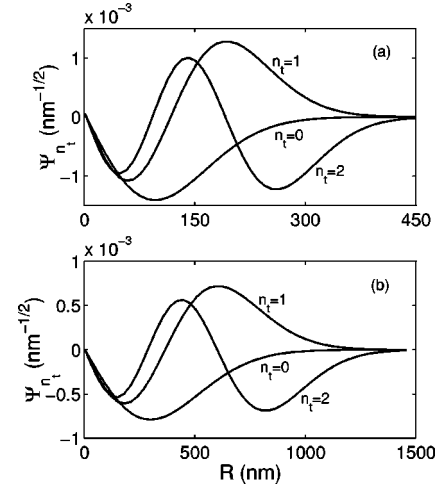ef. [26] critically depends on a characteristic length scale of the interatomic potential. This length scale is defined by $\beta_6 = (2\mu C_6/\hbar^2)^{1/4}$, where C_6 is van der Waal's coefficient and $\mu = m/2$ is the reduced mass of the two atoms. If both $\beta_6 \ll a_t$ and $a_{sc} \ll a_t$, then the solutions of Ref. [26] are physically valid. If these validity conditions are not satisfied, then the use of an energy-dependent scattering length in the pseudopotential improves the solution as demonstrated in Ref. [27]. For a trap frequency $\omega_t = 2\pi \times 100$ kHz and for ^{23}Na atoms, we find $\xi_s = a_{sc}/a_t = 0.042$ and $\beta_6/a_t = 0.13$. Thus for our model system pursued in this study as described in Sec. II, we can safely use the solutions of Ref. [26] for very strong traps with frequency $\omega_t \lesssim 2\pi \times 100$ kHz.

IV. BOUND STATES IN THE $-C_3/R^3$ POTENTIAL

In order to compute the PA spectrum, one first needs to find the vibrational wave functions of the excited diatomic molecule. It turns out, however, that it is not always necessary to find vibrational states for the entire range—the knowledge of wave functions near the vicinity of an outer turning point sometimes allows one to make a good estimate of the FC factor. In such cases, the FC factor can be approximated as the product of the two vibrational amplitudes at the outer turning point. This approximation, known as reflection approximation, relies on the fact that the molecule has its major probability of existence at the semiclassical outer turning point. Barring the ground state, this is true for most of the low-lying vibrational states of a molecule. But, for the vibrational states near dissociation threshold, the probability can be distributed over a wide range. Therefore, for those states, the validity of this approximation becomes questionable. This was examined in the past by many authors for the case of bound-free transitions [28] that defy the reflection approximation.

In this study, we concentrate on near-threshold vibrational bound states in a potential that varies asymptotically as $-1/R^3$, which corresponds to a S+P excited molecular state

between two atoms in the separated atom limit. Recently, these states have become very important in view of their wide accessibility in various PA processes. It is widely appreciated that there exists a class of pure long-range excited molecules whose equilibrium position is at a large separation [24]. The binding energies of these vibrational states can range from a few Hz to several hundred GHz. The lower the binding energy is, the longer the spatial extension of the states is. In calculating the FC factor for these states with respect to the state of two ground-state atoms moving either freely or in a trap, use of the reflection approximation becomes questionable, particularly so for the vibrational states with sub-GHz energies. Therefore, it is necessary to calculate the vibrational states in the entire range or at least in a broader range near the outer turning point.

In practice, it is difficult to accurately compute wave functions for vibrational states just below the dissociation threshold by the standard numerical integration procedure such as the Numerov method. Therefore, alternative procedures such as the semianalytic approach offered by the method of QDT need to be explored. While QDT has been successfully employed over the years for computing Rydberg-atom-like energy spectrum, its application to the problem of PA has not yet been fully explored. For Rydberg-atom-like systems, the relevant potential is the Coulomb potential that admits analytic solutions known as Coulomb functions which forms the basis for the application of QDT. For the excited state in the single-photon PA process as discussed here, the potential is of an attractive $-1/R^3$ type. Fortunately, a semianalytic QDT [29] of PA has recently been developed which is based on the semiclassical WKB-type solutions of a $-1/R^3$ potential. Exact quantum solutions of this potential have also been found recently [30,31]. For some diatomic molecules, the spacings of near-zero-energy vibrational states can be as small as a few kHz or even a few Hz, which leads to the interesting possibility that the free-bound PA linewidth of these states can exceed the spacings by several times even at a temperature as low as one 1 μK. Such a situation prevents the resolution of individual spectral lines. One naive suggestion to overcome this problem is to place two atoms inside a single trap, and to photoassociate them for different trap frequencies. Although PA in a trap may lead to a diffused continuous absorption spectrum, as we will show below, the use of different trap frequencies results in shifts of the peak of the spectrum. The energies of the different vibrational levels can be estimated from these shifts.

We now briefly outline the use of QDT for computing near-threshold ultralong-range vibrational states. The exact scattering solution of a repulsive $1/R^3$ was first obtained by Gao [32], and the exact analytic solutions of an attractive $1/R^3$ have been applied to a QDT formulation of diatomic molecular excited vibrational energy calculations before [30]. The scattering solutions of an attractive $1/R^3$ potential has also been used before for a multichannel QDT formulation of atom-atom interactions in the presence of a dc electric field [31].

We next concentrate on the bound solutions of a $-1/R^3$ potential. The asymptotic form of linearly independent base

functions f_l and g_l satisfying the Schrödinger equation with this potential for energy $E<0$ can be expressed as

$$
\begin{pmatrix} f_l(R\to\infty) \\ g_l(R\to\infty) \end{pmatrix} = \begin{pmatrix} W_{f-} & W_{f+} \\ W_{g-} & W_{g+} \end{pmatrix} \begin{pmatrix} \exp(\kappa R) \\ \exp(-\kappa R) \end{pmatrix}, \quad (9)
$$

where W's are chosen to be real functions

$$
W_{f\mp} = \frac{\exp(\pm i\theta)}{D(\nu)} \sqrt{\frac{2}{\pi\kappa}} \left[\frac{C_+(\nu)}{G(-\nu)} \xi_\mp - \frac{C_+(-\nu)}{G(\nu)} \eta_\mp \right],
$$

$$
W_{g\mp} = \frac{\exp(\pm i\theta)}{D(\nu)} \sqrt{\frac{2}{\pi\kappa}} \left[-\frac{C_-(\nu)}{G(-\nu)} \xi_\mp + \frac{C_-(-\nu)}{G(\nu)} \eta_\mp \right],
$$
$$(10)$$

with $\theta = \pi\nu/2 + \pi/4$ and

$$
\xi_\mp = \sum_{m=-\infty}^{\infty} b_m \exp(\pm im\pi/2), \quad (11)
$$

$$
\eta_\mp = \sum_{m=-\infty}^{\infty} (-1)^m b_m \exp(\mp im\pi/2). \quad (12)
$$

Following standard conventions, we take $\hbar^2\kappa^2/(2\mu) = -E$, the bound-state energy. The other parameters $C_\pm(\nu)$, $D(\nu)$, $G(\nu)$, and b_m are as defined in Appendix A of Ref. [31]. The condition for bound states is given by

$$
\chi - K^0 = 0, \quad (13)
$$

where K^0 is the short-range K matrix determined by matching the solutions of short- and long-range potentials at a judiciously chosen separation and χ is given by

$$
\chi = -W_{f-}/W_{g-}. \quad (14)
$$

With the help of QDT, the short-range K matrix is extrapolated from the positive-energy scattering solutions near the dissociation threshold. The bound-state wave function at discrete energy E_i can then be expressed as

$$
\Psi_i(R) = f_l - K^0 g_l. \quad (15)
$$

Selected numerical results for the ultralong-range molecular states are given in Table II and Fig. 2.

V. PHOTOASSOCIATION IN A HARMONIC TRAP

A key factor of the PA spectrum strength is the FC integral. Ever since its introduction more than 70 years ago [33], the FC principle remains a paradigm in molecular spectroscopy, particularly for the spectra of diatomic molecules. The essence for this principle relies on the wave mechanical property of molecules. The underlying idea is that when a molecule undergoes electronic transition from one state to another, the transition occurs much faster than the time scale of the vibrational motion of its constituent atomic nuclei. Therefore, just before and after the transition, the relative nuclear position remains almost the same. The wave mechanics of the molecule comes into the picture when one

TABLE II. The energy E_v of the last seven molecular vibrational levels of the 0_g^- state of Na_2 for rotational quantum number $l = 0$ and their outer turning point R_t and the separation R_{max} at which the probability $|\Psi_v(R)|^2$ peaks.

v	E_v (kHz)	R_t (nm)	R_{max} (nm)
33	1460	162.3	139.3
34	550	224.8	190.2
35	170	332.3	275.4
36	39.5	540.3	431.5
37	5.7	1000	794.0
38	0.3017	2700	1900
39	0.0003	28200	14200

calculates the transition probability between the two states. In view of the FC principle, the strength of the transition is determined by an integral over the overlap of initial and final wave functions of the nuclear motion. The line strength and the linewidth of molecular spectrum are proportional to this overlap integral. The ground vibrational state of a molecule has the maximum probability at its equilibrium position, while the excited vibrational states have their maximum probability near outer turning points. Accordingly, the relative location of the equilibrium positions is also important in determining which vibrational transition would have a given intensity.

For two atoms initially in a harmonic trap, we can define a Rabi frequency

$$\Omega_{n_t - v} = \frac{1}{\hbar} |\langle n_t | V_{af} | v \rangle| \qquad (16)$$

between the trap-induced bound state $|n_t\rangle$ of the two atoms and the excited molecular vibrational state $|v\rangle$ due to the interaction of the two-atom system with the PA laser field. The Rabi frequency, Eq. (16), is proportional to the rate of coherent population transfer between the two-atom state $|n_t\rangle$ and the molecular state $|v\rangle$. Clearly, it is proportional to overlap integral
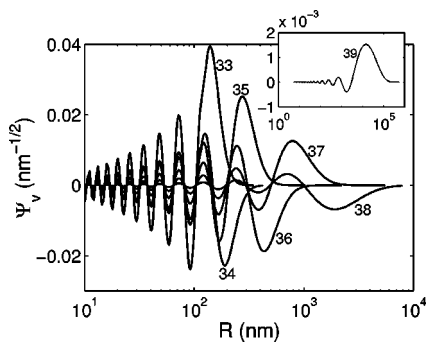

FIG. 2. The last seven (from 33 to 39) s-wave vibrational wave functions (in $nm^{-1/2}$) of the 0_g^- state of Na_2. The numbers assigned to the curves refer to the vibrational quantum numbers. The range of the last bound state ($v = 39$) shown in the inset is so long that it exceeds 1 μm by two orders of magnitude.

$$\eta_{v - n_t} = \int \Psi_v \Psi_{n_t} \cos(\mathbf{k}_L \cdot \mathbf{R}) dR, \qquad (17)$$

which is the FC factor between the two states. Since both states $|v\rangle$ and $|n_t\rangle$ are discrete (bound) and unit normalized, the FC factor in this case is dimensionless.

Here we wish to stress that the dynamics of photoassociation of two trapped atoms is strikingly different from that of two free atoms. Since two trapped atoms form discrete relative motional states, there exists a well-defined Rabi frequency and the associated coherent dynamics. In contrast, for two freely moving atoms, the definition of free-bound Rabi frequency is not so straightforward, since Rabi frequency is usually defined between two discrete states. Instead, for low laser power, applying Fermi's golden rule, one can define free-bound stimulated transition rate

$$\Gamma_{st}^{v - \epsilon} = \frac{2\pi}{\hbar} |\langle v | V_{af} | \epsilon \rangle|^2, \qquad (18)$$

which is proportional to the square of the free-bound FC factor

$$\eta_{v - \epsilon} = \int \Psi_v \Psi_\epsilon \cos(\mathbf{k}_L \cdot \mathbf{R}) dR, \qquad (19)$$

having the dimension of $1/\sqrt{\epsilon}$, i.e., $|\eta_{v - \epsilon}|^2$ has dimension of per unit energy. $\Gamma_{st}^{v - \epsilon}$ is the free-bound stimulated decay rate and does not characterize any coherent PA. In order to describe free-bound coherent PA dynamics, a quasicontinuum model [12] has been proposed. In this model, quasicontinuum is assumed to consist of many discrete equally spaced levels and thus enables to define a photoassociative Rabi frequency. Then the continuum limit is taken by allowing the energy spacing between the levels to approach zero. With this model analysis, it was shown [12] that the free-bound Rabi frequency is proportional to the square root of the collision energy. Thus in the zero energy limit, the free-bound Rabi frequency vanishes and so there is no coherent photoassociative dynamics. Alternatively, the quasicontinuum model can be supplemented [10] by introducing two-atom scattering states normalized within a sphere of arbitrary volume $\mathcal{V}$. After all the calculations are done, the continuum limit can be taken by allowing the volume $\mathcal{V}$ to go to infinity. It is thus argued that for a nondegenerate gas, free-bound Rabi frequency is much smaller than the corresponding bound-bound Rabi frequency. To transfer atoms into molecules by STIRAP, one of the necessary and sufficient conditions is the swapping of the bound-bound Rabi frequency into free-bound Rabi frequency in a counterintuitive way, i.e., for an initial duration of the STIRAP pulse, bound-bound Rabi frequency should be much larger than the free-bound one, and later it should be just the opposite. Therefore, according to the arguments put forward in Refs. [10,12], the STIRAP condition in a nondegenerate gas would not be satisfied and so there is no STIRAP in a nondegenerate gas; although, there has been a debate [34] on the possibility of STIRAP in a nondegenerate gas. However, it is also argued [10] that, for Bose condensed atoms and in the thermody-

namic limit, the collective free-bound Rabi frequency becomes proportional to the number density of atoms and so it regains a finite (nonzero) value. Therefore, for condensed atoms, STIRAP becomes possible because of the symmetric state bosonic stimulation [14]. In passing, we note that the possible effect of a trap on nondegenerate free-bound-bound STIRAP was earlier pointed out in Ref. [12].

We emphasize that with trap-induced two-atom bound states, unlike in the case two free atoms, two-photon Raman-type photoassociative coherent dynamics is possible. The conditions for STIRAP can also be satisfied for a sufficiently dilute nondegenerate atomic gas in a harmonic trap due to the existence of trap-induced two-atom bound states. However, the mean-field energy shift and inelastic collisions such as the three-body interaction may limit the efficiency of the STIRAP.

VI. RESULTS AND DISCUSSION

Having discussed in the preceding section the advantages we may possibly derive from trap-induced atom-pair binding in performing two-color photoassociative STIRAP in a nondegenerate atomic gas to produce cold molecules, we now turn our attention to the effects of this pair binding on incoherent one-color photoassociative processes such as spontaneous and stimulated linewidths. The spontaneous linewidth for a transition $v \rightarrow n_t$ is given by

$$\gamma_{\text{sp}}^{v \rightarrow n_t} = \frac{4}{3\hbar c^3} \omega_{vn_t}^3 |D_0|^2 |\eta_{v-n_t}|^2 + \gamma_v^{\text{bound-bound}}, \quad (20)$$

where $\omega_{vn_t} = \omega_A - (\omega_v + \omega_{n_t})$, ω_A is the frequency of the bare atom transition, $\hbar \omega_v = E_v$ is the energy of the bound molecular level v, $\hbar \omega_{n_t} = E_{n_t}$ is the energy of the trap-bound level n_t, and

$$\gamma_v^{\text{bound-bound}} \propto \sum_{v_g} \omega_{vv_g}^3 |\langle v | D(R) | v_g \rangle|^2 \quad (21)$$

is the rate of spontaneous emission for transition from the vibrational state v in the excited molecular potential to the bound levels in the ground molecular potential. $\omega_{vv_g} = \omega_A - (\omega_v + \omega_{v_g})$, with v_g as the vibrational quantum number of the bound state $|v_g\rangle$ in the electronic ground molecular potential. For a bound-free transition

$$\gamma_{\text{sp}}^{v \rightarrow \epsilon} = \frac{4}{3\hbar c^3} \int \omega_{v\epsilon}^3 |D_0|^2 |\eta_{v-\epsilon}|^2 d\epsilon + \gamma_v^{\text{bound-bound}}, \quad (22)$$

where $\omega_{v\epsilon} = \omega_A - (\omega_v + \epsilon/\hbar)$. The integration on the right-hand side of the above equation is over the distribution of collision energy ϵ.

The contribution to the total spontaneous linewidth due to transitions from the ultralong-range bound states in the excited molecular potential to bound states in the ground molecular potential is negligible. Because the turning points of even the least-bound state (longest range) in a typical ground molecular potential that asymptotically becomes a van der

Waals interaction of the form $-C_6/R^6$, are of the order of 1 nm, as can be estimated from the binding energies of such states for Li_2 and Na_2 as calculated in Refs. [35,36]. In contrast, the excited ultralong-range vibrational states, as calculated here by the QDT method in Sec. IV, have their turning points at a much larger distance of the order of 100 nm. We further note from the plots of the wave functions of these ultralong-range vibrational states (Fig. 2) that, below 10 nm, the amplitude of these wave functions is vanishingly small. Therefore, the FC overlap integral of these excited ultralong-range states with the bound states in the ground electronic manifold would be negligible in comparison to that with the two-atom scattering states as well as trap-induced bound atom-pair states. We henceforth calculate the spontaneous emission width for a transition from a particular ultralong-range vibrational level in the excited molecular potential only to the trap-induced bound atom-pair states and to the two free-atom states (scattering states) while neglecting all other molecular bound-bound transitions. In this context, a pertinent question that may arise is whether such tight traps would have any influence on the molecular bound states in the ground molecular electronic manifold. As we have already mentioned, the least-bound or the nearest-to-zero-energy molecular bound states supported by van der Waal's potential $-C_6/R^6$ have their outer turning point at a typical separation of 1 nm. If we now estimate, for a typical value of $C_6 = 1500$ a.u., the van der Waal potential energy at $R = 1$ nm, and compare this with the relative harmonic trap energy of two atoms at the same separation in an isotropic harmonic trap with harmonic frequency 100 kHz, we find that this trapping potential energy is smaller than the van der Waal potential by at least two orders of magnitude. So, for harmonic trapping frequency $\omega_t \leq 2\pi \times 100$ kHz, the trap has negligible influence on the molecular bound states in the ground electronic molecular potential. This is why in writing the expressions for $\gamma_{sp}^{v \rightarrow n_t}$ and $\gamma_{sp}^{v \rightarrow \epsilon}$ in Eqs. (20) and (22), respectively, we have retained the same $\gamma_v^{\text{bound-bound}}$ in both expressions.

In Sec. III, we have described two-atom bound states $\Psi_{n_t}(R)$ formed inside a harmonic trap. Unlike the free-bound case, the FC factor for two trapped atoms can be controlled by tuning the trap parameters. The lower the trap frequency is, the longer the extension of the trap-induced two-atom bound state. Thus, by lowering the trapping frequency, the FC factor for the higher molecular vibrational states can be increased. Therefore, the trap-induced bound state can facilitate probing of ultralong-range molecular states. Figure 1 exhibits the lowest three Ψ_{n_t} for two values of trapping frequency $\omega_t = 2\pi \times 100$ or $2\pi \times 10$ kHz. Since $\xi_s \ll 1$, they deviate very little from the harmonic-oscillator states. The bound-state energies and the outer turning point of these states are given in Table I.

The wave functions $\Psi_v(R)$ of the last seven vibrational states from $v = 33$ to $v = 39$ calculated by the QDT method as outlined in Sec. IV are plotted in Fig. 2. Their vibrational energies E_v, outer turning points R_t, and the internuclear distances R_{max} at which $|\Psi_v|^2$ attains maximum are given in Table II. To evaluate E_v, we employ Eq. (15) with a constant

TABLE III. Square of Franck-Condon integral $|\eta_{vn_t}|^2$ between molecular bound v and trap-bound states n_t.

| v | $\omega_t = 2\pi \times 10$ kHz | | | $\omega_t = 2\pi \times 100$ kHz | | |
	$n_t = 0$	$n_t = 1$	$n_t = 2$	$n_t = 0$	$n_t = 1$	$n_t = 2$
33	0.075	0.074	0.059	0.221	0.122	0.009
34	0.102	0.080	0.039	0.024	0.066	0.019
35	0.116	0.004	0.033	0.000	0.214	0.021
36	0.009	0.022	0.000	0.000	0.013	0.093

$K^0 = 0.623$. The vibrational energies of these states have also been calculated previously by a similar method [30]. From Table II, it is clear that the molecule in these states would spend most of its time at an internuclear distance larger than 100 nm. In terms of typical molecular scale, this length scale is enormous. Now, a question naturally arises: is it possible to probe these states by PA? To seek an answer to this question, we carry out an explicit calculation of the FC factors in two different cases: (1) both atoms being trapped in a single harmonic potential and (2) the two atoms are in a free-scattering state.

In Table III, we tabulate the values of the square of the FC factor for selected states. Why and how much these values differ from one pair of states to another can be naively understood from the positions of their outer turning points and the shape of the respective wave functions.

For example, from Tables I and II, we note that the states $\Psi_{n_t=0}$ [for $\omega_t = 2\pi \times 100$ kHz] and $\Psi_{v=33}$ have their outer turning points at a comparable distance. Therefore, these two states should have maximum overlap.

In Figs. 3 and 4, we display the variations of the bound-bound FC factor as a function of the positive and negative scattering length, respectively. Although as discussed earlier that for a large positive a_{sc}, energy-dependent pseudopotential should be used in the calculation of trap-induced atom-atom bound states, we simply took the energy-independent pseudopotential for all the calculations. This approximation underestimates the actual eigenenergies and hence underestimates the actual range of those states. Therefore, for large positive a_{sc}, the actual value of the FC factor should be
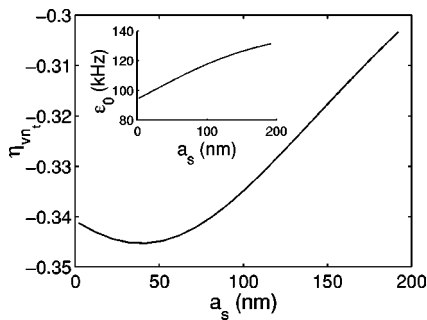

FIG. 3. Dimensionless Franck-Condon integral η_{vn_t} between molecular bound $v = 35$ and the trap-bound $n_t = 0$ (ground) states as a function of positive scattering length a_{sc} in nanometers for a trap frequency of $\omega_t = 2\pi \times 10$ kHz. The inset shows the variation of trap-bound ground-state energy ϵ_0 ($2\pi\nu_0$) as a function of a_{sc}.
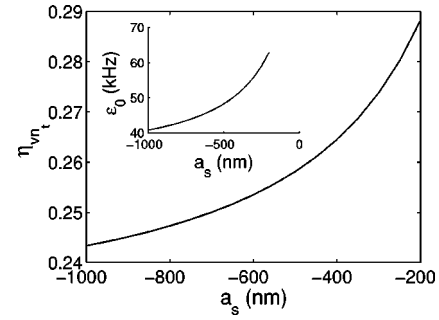

FIG. 4. The same as in Fig. 3 but for a negative scattering length.

somewhat larger. However, we took this approximation for our model calculation and comparison because the overall pattern of variation of the FC factor as a function of a_{sc} should remain the same.

When two atoms are not trapped, the FC factor becomes strikingly different. Since the FC factor in the two cases have different dimensionality, it is not easy to have a direct comparison between the two. However, we can make a comparison by comparing their spontaneous linewidth which is proportional to the respective FC factor. For the sake of this comparison with the bound-bound $v \to n_t$ transition, we have assumed that the the velocity of the free atoms follow a Maxwellian distribution at a temperature $T = E_{n_t}/k_B$ in calculating the corresponding free-bound transitions, where k_B is the Boltzmann constant. The results are tabulated in Table IV. The free-bound FC factor of Eq. (19) depends critically on the locations of the antinodes of the sinusoidal scattering state of the two atoms relative to the outer turning point of the molecular bound state. If the first antinode is located near the turning point, then the free-bound FC factor would be greater than if it is located far away from the turning point.

From Table IV, we note that the tabulated bound-bound spontaneous linewidths are much smaller than their respective free-bound values. This suggests that if we PA two trapped atoms, and if the resulting ultralong-range excited molecule remains trapped under the same or a different trap-

TABLE IV. Spontaneous linewidths $\gamma_{sp}^{v \to n_t}$ for transitions from excited molecular bound states v to trap-bound states n_t are compared with corresponding linewidth $\gamma_{sp}^{v \to \epsilon}$ for molecular bound-free transition. The frequency of the harmonic trap is $\omega_t = 2\pi \times 100$ kHz.

| v | $\gamma_{sp}^{v \to n_t}/(2\pi)$ and $\gamma_{sp}^{v \to \epsilon}/(2\pi)$ (kHz), $k_B T = \hbar\omega_{n_t}$ | | | | | |
| | $n_t = 0$ | | $n_t = 1$ | | $n_t = 2$ | |
	$v \to n_t$	$v \to \epsilon$	$v \to n_t$	$v \to \epsilon$	$v \to n_t$	$v \to \epsilon$
33	4278	28985	2883	40422	2359	47139
34	464	26591	5532	37216	1282	43467
35	0.002	23248	276	30781	4150	34831
36	0.011	6449	40.0	9434	245	11007
37	0.001	3429	6.3	4106	29.6	4249
38	0.000	599	0.5	623.7	2.4	735.2
39	0.000	10.2	0.002	7.8	0.009	7.4

ping potential, then the spectral line associated with the formation of the molecule may be resolved.

The trap frequencies we have considered for our numerical illustration correspond to very tight traps. In this section, so far we have restricted our treatment to an elementary PA process of only two atoms inside an isotropic harmonic trap. Now, the question obviously arises how the tight traps would affect the PA of an ensemble of atoms in a trap, in particular of an atomic BEC for its potential use in forming a molecular BEC by collective photoassociative STIRAP. In this regard, it becomes necessary to consider various effects due to mean-field interactions and inelastic three-body recombination processes [11,17]. Let us first discuss the possible effect of a tight trap on the efficiency of STIRAP. The presence of a trap introduces an additional length scale in the system, namely, the size of the harmonic-oscillator ground state a_t. For a typical magnetic trap in use today with Rb or Na atoms, trap frequency ω is of the order of $2\pi \times 100$ Hz. The frequencies we have considered here are 10–100 kHz, usually associated with strong far-off-resonant optical dipole traps. A condensate in such traps would typically have dimensions smaller than an order of magnitude of that in a magnetic trap. One can then argue that, for a typical number of atoms $N \sim 10^6$, the number density of atoms in such a tight trap would also be higher by two to three orders of magnitude. Therefore, the strength of the mean-field interactions between atoms and also between atoms and STIRAP-produced molecules will be greatly enhanced. This increased mean-field interaction will lead to large frequency shifts and broadening in two-photon STIRAP PA spectrum, it also leads to a dramatically increased loss of atoms or molecules due to density dependent three-body collisions. Therefore, as already suggested in Ref. [37], our study applies to cases of modest atom number densities associated with condensates of smaller numbers of atoms, of the order of 1000 or fewer.

The enhancement of the Franck-Condon integral due to trap-induced binding between two ground-state atoms depends on the location of the outer turning point in the excited (S + P) molecular potential relative to the value of a_t. Our calculations reveal that the amplitude of the ground state of the two-atom (S-S) bound state attains a maximum at about $a_t/2$. Therefore, the Franck-Condon integral will be maximal for transitions to states in the excited potential whose outer turning points lie close to $a_t/2$. For a typical magnetic trap of 100 Hz, a_t is about 1 μm, while the outer turning point of the excited vibrational state used in Refs. [11,17] is at about 3 nm. The finding of Drummond et al. [11] that a weak trap reduces the efficiency of STIRAP, we believe therefore, is due to this huge mismatch between a_t and the outer turning point. They have used the excited vibrational state whose free-bound transition frequency is 23 cm^{-1} below the dissociation threshold. This state is far off the dissociation threshold in comparison to the ultralong-range states we have described in the paper. To achieve a significant enhancement, the free-bound transition should involve the highest-lying excited vibrational states, so that their outer turning points lie close to $a_t/2$. Normally, the excited ultralong-range vibrational states have their outer turning points at about tens to several hundred nanometers. In order to have large FC overlaps between these states and the trap-induced two-atom bound states, the trap frequencies should be much larger than 100 Hz, i.e., we should use very tight traps. As long as the condition ($na_{sc}^3 \ll 1$) remains fulfilled, the mean-field effects and three-body recombinations do not lead to substantial degradation of the efficiency of the STIRAP, as the gas remains sufficiently dilute and the interactions would be mainly of a two-body type, and only a small fraction of atoms will be pair correlated with trap-induced binding, they will experience enhanced FC coupling in a STIRAP. Presently, the nature of collision interaction between photoassociated excited or STIRAP-produced ground molecules and individual atoms is not precisely known. Therefore, we will omit a detailed study of how three-body recombination will affect the efficiency of the STIRAP. Intuitively it can be understood that with a high number density, the increased three-body recombination will lead to increased inelastic losses, which counteract any enhancement effect by tight trap. However, it can also be intuitively argued that for a very low density of atoms and molecules, such three-body recombination losses may perhaps be overcome in achieving a considerably efficient STIRAP.

In view of the foregoing discussion, it now appears that the best way out to avoid mean-field shifts and three-body effects is to photoassociate atoms in a Mott insulating state of atoms in an optical lattice [21]. In such a structured state of atoms, a pair of atoms can be arranged to occupy a single site of an optical lattice.

Before concluding this section, we would like to discuss another important application of the ultralong-range excited vibrational states in coherent laser spectroscopy of yet a different type of potentially ultralong-range molecules, namely, molecules that can be formed in a controlled crossing of a Feshbach resonance [7]. These exotic molecules are produced in magnetic-field-induced Feshbach resonance by the nonadiabatic coupling between two close molecular potential curves, one of which acts as an energetically closed channel while the other as an open asymptotic collision channel. Coherent transfer of atoms into a molecular vibrational state close to the open-channel threshold occurs through the tuning of a magnetic field. Recently, these vibrational states have been numerically calculated [38] and shown to have an extent ranging from many tens to many hundreds of nanometers. Although, these molecules are translationally cold, they are not generally cold in their vibrational states. Obviously, any two-photon resonant coherent Raman spectroscopy of these molecules would involve higher-lying excited vibrational states as we have calculated by the QDT method. Thus, in addition to our finding of the trap enhancement in coherent PA, our study of the QDT approach in finding ultralong-range wave functions is important for applying the STIRAP to the newly attained capability of a controlled crossing of a Feshbach resonance, and the attempt to produce translationally as well as vibrationally cold molecules.

VII. CONCLUSIONS

We have developed a scheme for estimating the FC factor involved in a single-photon PA of two atoms into an

ultralong-range molecular state. In this approach, we have made two simplifications: first, the initial state of the atoms are based only on the asymptotic form at a large interatomic separation, which in the low-energy limit, only depends on the *s*-wave scattering length and second, for the excited molecular state (corresponding to a S+P asymptote), we have used the exact solutions of the asymptotic long-range molecular potential $-1/R^3$, taking advantage of the QDT formulation. We have calculated the wave functions of the molecular states that are very close to dissociation threshold. We have calculated the FC overlap integrals between these molecular states and the initial states of the two ground-state atoms. We have shown that when two atoms are trapped in a single harmonic potential well, the trap frequency can significantly affect the integral and hence the PA rate. We suggest that the ultralong-range excited molecule can be formed by PA of two ground-state atoms inside a trap and simultaneously switching on another trap that can confine photoassociated molecules. In this way, the damping of the excited molecule can be minimized. We have also demonstrated the dependence of the FC integral on both the sign and the magnitude of the atomic scattering length. To form a ground-state molecule by stimulated Raman PA, the excited vibrational state should have sufficient amplitude in the short-range region such that it can possess a significant overlap with the ground molecular vibrational state. For the model system studied in this paper, this seems practically impossible. However, since trap potentials have a significant effect on the overlap integral as well, it can perhaps also be adjusted to affect stimulated Raman PA. In particular, when performing coherent PA in a nondegenerate gas, we have shown that a tight trap does offer an advantageous situation in comparison to atoms in free-scattering state. However, as discussed in the preceding section, the mean-field shifts and three-body recombination effects may ultimately limit the efficiency for employing the STIRAP process to form a molecular BEC, and it appears that the best way to exploit the trap-induced enhancement of coherent coupling for producing a molecular BEC by STIRAP with no adverse effects from three body recombination and mean-field shifts is to photoassociate atoms in the Mott insulating state with more than one atom per well of an optical lattice as first investigated in Ref. [20]. To this end, we would also need an accurate method for calculating the ultralong-range excited molecular vibrational states. Very recently, far-off-resonance trap for atoms inside a cavity in the strong-coupling regime has been experimentally demonstrated [39]. This trap is insensitive to the internal atomic states and has strong or tight trapping capability. Only a few number of atoms can be captured in such a trap for a considerable duration. Trap-induced enhancement may be experimentally studied in photoassociation inside such a tight trap without any side effects of mean-field interaction and three-body recombination. Apart from the usual PA spectroscopy, our study can also find applications in the future studies of coherent laser spectroscopy of the recently discovered ultralong-range Feshbach molecules [7].

[1] For recent reviews on photoassociation spectroscopy, see F. Masnou-Seeuws and P. Pillet, Adv. At. Mol. Phys. **47**, 53 (2001); J. Weiner, V.S. Bagnato, S. Zilio, and P.S. Julienne, Rev. Mod. Phys. **71**, 1 (1999).

[2] H.R. Thorsheim, J. Weiner, and P.S. Julienne, Phys. Rev. Lett. **58**, 2420 (1987).

[3] R. Napolitano, J. Weiner, C.J. Williams, and P.S. Julienne, Phys. Rev. Lett. **73**, 1352 (1994); R. Côte, A. Dalgarno, Y. Sun, and R.G. Hulet, *ibid.* **74**, 3581 (1995); R. Côte and A. Dalgarno, Phys. Rev. A **58**, 498 (1998).

[4] P.D. Drummond, K.V. Kheruntsyan, and H. He, Phys. Rev. Lett. **81**, 3055 (1998).

[5] J. Javanainen and M. Mackie, Phys. Rev. A **59**, R3186 (1999).

[6] K. Helmerson and L. You, Phys. Rev. Lett. **87**, 170402 (2001).

[7] E.A. Donley, N.R. Claussen, S.T. Thompson, and C.E. Wieman, Nature (London) **417**, 529 (2002).

[8] S. Inouye *et al.*, Nature (London) **392**, 151 (1998); J. Stenger *et al.*, Phys. Rev. Lett. **82**, 4569 (1999); E. Timmermans, P. Tommasini, M. Hussein, and A. Kerman, Phys. Rep. **315**, 199 (1999).

[9] F.K. Fatemi, K.M. Jones, and P.D. Lett, Phys. Rev. Lett. **85**, 4462 (2000); P.O. Fedichev, Y. Kagan, G.V. Shlyapnikov, and J.T.M. Walraven, *ibid.* **77**, 2913 (1996).

[10] M. Mackie, R. Kowalski, and J. Javanainen, Phys. Rev. Lett. **84**, 3803 (2000); M. Kostrun, M. Mackie, and R. Côte, Phys. Rev. A **62**, 063616 (2000).

[11] P.D. Drummond, K.V. Kheruntsyan, D.J. Heinzen, and R.H. Wynar, Phys. Rev. A **65**, 063619 (2002).

[12] J. Javanainen and M. Mackie, Phys. Rev. A **58**, R789 (1998); M. Mackie and J. Javanainen, *ibid.* **60**, 3174 (1999).

[13] J.J. Hope, M.K. Olsen, and L.I. Plimak, Phys. Rev. A **63**, 043603 (2001).

[14] D.J. Heinzen, R. Wynar, P.D. Drummond, and K.V. Kheruntsyan, Phys. Rev. Lett. **84**, 5029 (2000).

[15] J.J. Hope and M.K. Olsen, Phys. Rev. Lett. **86**, 3220 (2001).

[16] J. Calsamiglia, M. Mackie, and K.-A. Suominen, Phys. Rev. Lett. **87**, 160403 (2001).

[17] R. Wynar, R.S. Freeland, D.J. Han, C. Ryu, and D.J. Heinzen, Science **287**, 1016 (2000); C.J. Williams and P.S. Julienne, *ibid.* **287**, 986 (2000).

[18] A. Vardi, V.A. Yurovsky, and J.R. Anglin, Phys. Rev. A **64**, 063611 (2001); M.K. Olsen, J.J. Hope, and L. Plimak, *ibid.* **64**, 013601 (2001).

[19] J.M. Gerton, D. Strekalov, I. Prodan, and R.G. Hulet, Nature (London) **408**, 692 (2000); J.M. Gerton, B.J. Frew, and R.G. Hulet, Phys. Rev. A **64**, 053410 (2001); C. McKenzie *et al.*, Phys. Rev. Lett. **88**, 120403 (2002).

[20] D. Jaksch, V. Venturi, J.I. Cirac, C.J. Williams, and P. Zoller, Phys. Rev. Lett. **89**, 040402 (2002); M. Greiner, O. Mandel, T. Esslinger, T.W. Hänsch, and I. Bloch, Nature (London) **415**, 39 (2002).

[21] M. Greiner, O. Mandel, T. Esslinger, T.W. Hänsch, and I. Bloch, Nature (London) **415**, 39 (2002).

[22] P. Pillet, A. Crubellier, A. Bleton, O. Dulieu, P. Nosbaum, I. Mourachko, and F. Masnou-Seeuws, J. Phys. B **30**, 2801 (1997).

[23] M. Marinescu and A. Dalgarno, Phys. Rev. A **52**, 311 (1995).

[24] W.C. Stwalley, Y.-H. Uang, and G. Pichler, Phys. Rev. Lett. **41**, 1164 (1978).

[25] L.P. Ratliff, M.E. Wagshul, P.D. Lett, S.L. Rolston, and W.D. Phillips, J. Chem. Phys. **101**, 2638 (1994).

[26] T. Busch, B.-G. Englert, K. Rzazewski, and M. Wilkens, Found. Phys. **28**, 549 (1998).

[27] D. Blume and C.H. Greene, Phys. Rev. A **65**, 043613 (2002); E.L. Bolda, E. Tiesinga, and P.S. Julienne, *ibid.* **66**, 013403 (2002).

[28] H.M. James and A.S. Coolidge, Phys. Rev. **55**, 184 (1939); R.O. Doyle, J. Quant. Spectrosc. Radiat. Transf. **8**, 1555 (1968); J. Tellighuisen, Adv. Chem. Phys. **60**, 299 (1985).

[29] J.L. Bohn and P.S. Julienne, Phys. Rev. A **60**, 414 (1999).

[30] B. Gao, Phys. Rev. Lett. **83**, 4225 (1999).

[31] B. Deb and L. You, Phys. Rev. A **64**, 022717 (2001).

[32] B. Gao, Phys. Rev. A **59**, 2778 (1999).

[33] J. Franck, Trans. Faraday Soc. **21**, 536 (1925); E.U. Condon, Phys. Rev. **28**, 1182 (1926); E.U. Condon, *ibid.* **32**, 858 (1928).

[34] A. Vardi, M. Shapiro, and J.R. Anglin, Phys. Rev. A **65**, 027401 (2002); J. Javanainen and M. Mackie, *ibid.* **65**, 027402 (2002).

[35] R. Cote, A. Dalgarno, and M.J. Jamieson, Phys. Rev. A **50**, 399 (1994).

[36] P.S. Julienne, J. Res. Natl. Inst. Stand. Technol. **101**, 487 (1996).

[37] M. Mackie and J. Javanainen, e-print physics/0212111.

[38] T. Kohler, T. Gasenger, P.S. Julienne, and K. Burnett, e-print cond-mat/0302082.

[39] J. McKeever *et al.*, e-print quant-ph/0211013.