

## Laser-Induced Photoassociation of Ultracold Sodium Atoms

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(Received 2 March 1987)

We present the theory of laser-induced radiative association in terms of a scattering resonance formalism and apply this theory to the specific case of Na-atom collisions at a temperature of 10 mK. Use of ultracold atoms permits a new kind of high-resolution free-bound spectroscopy for the study of near-threshold collisions and excited-state energy levels which are difficult to study by conventional bound-state spectroscopy.

PACS numbers: 32.80.-t, 32.80.Pj, 33.8C.-b, 33.80.Ps

Recent developments in laser cooling and trapping of atoms<sup>1-4</sup> have opened the possibility of studying an entirely new regime of heavy-particle collision dynamics at ultracold temperatures,  $T \ll 1$  K. The salient features of this new regime are the following: (1) The heavy-particle de Broglie wavelength becomes much longer than the collision interaction range, (2) the kinetic energy spread can become comparable to the natural linewidth of the atomic resonance transition, and (3) the orbital angular momentum is so low that only a few partial waves contribute to the scattering event. Thus, many conventional ideas characterizing heavy-particle collision dynamics have to be reexamined. For example, at a temperature of 1 mK, a Na-atom kinetic energy of  $kT$  corresponds to a de Broglie wavelength of about 400 a.u. Therefore, the semiclassical picture in which nuclear motion is treated as a classical particle moving in an adiabatic potential breaks down and must be replaced by a treatment fully quantum mechanical in both the nuclear and electronic motion. Since the velocity distribution function narrows with decreasing temperature, the photoassociation spectrum exhibits lines of sharpness comparable to those normally associated with bound-bound spectroscopy:  $kT$  at 1 mK corresponds to 21 MHz. Furthermore, the photoassociation rate can be much larger for very small collision energy than for room-temperature collision energy because of large near-threshold free-bound Franck-Condon factors.<sup>5</sup> The rate may also be greatly enhanced if a shape resonance should occur in which the colliding atoms are trapped behind a centrifugal barrier of the lower-state potential. Cold-atom photoassociative collisions are important not only for their intrinsic interest as a novel bond-forming mechanism and spectroscopic tool, but also for the role they may play in other phenomena at low temperature such as ion or neutral cluster formation stabilized without third-body collisions.

This paper demonstrates some of the basic features of

cold-atom photoassociation by specific calculations for Na-atom collisions. The basic photoassociation experiment is the following: Two ground-state atoms collide in the presence of a photoassociation laser tuned to a frequency  $\nu_1$  different from that of the cooling or trapping laser. The colliding atoms can absorb a photon to produce a bound excited-state molecule which then decays by spontaneous fluorescence:



By measuring the total fluorescence intensity in the  $\nu_2$  spectrum (or the intensity of some subset of the fluorescence) as a function of the frequency  $\nu_1$  of the photoassociation laser, the photoassociation absorption spectrum can be mapped out. This experiment is analogous to a standard laser-induced fluorescence (LIF) experiment, except the initial state is free rather than bound. Two important differences from normal  $\text{Na}_2$  LIF are (1) since the absorbing molecular states are formed by collisions of two atoms, both singlet and triplet states can be probed and (2) the Franck-Condon principle favors excitation of high rather than low excited vibrational levels.

Although the basic Franck-Condon expression for free-bound absorption has long been known,<sup>6</sup> we prefer to use the more general results from the theory of collisions in a radiation field.<sup>5,7</sup> In this picture the excited molecule-field state  $|r\rangle = |v'J'\rangle|(n-1)h\nu\rangle$  becomes a resonance coupled to the initial-state continuum  $|i\rangle = |\epsilon''J''\rangle|nh\nu\rangle$  through radiative coupling. The excited-state resonance also decays irreversibly to fluorescence channels with total spontaneous-emission rate  $A_f$ . Standard Breit-Wigner resonance scattering theory<sup>8</sup> can be used to give the fluorescence production rate if the photoassociation laser field is not too strong and if  $kT$  is large compared with the spontaneous decay width  $\hbar A_f$  of the resonance. In order to illustrate the

basic features of cold-atom photoassociation without undue complexity in this brief Letter, let us assume that photoassociation occurs from a single initial adiabatic Born-Oppenheimer (ABO) state to a single final ABO state without fine and hyperfine structure. Pure Hund's-case-(b) coupling is assumed. The photoassociation rate coefficient is

$$\langle\sigma v\rangle=(g'/g''Q_T)\sum_r(2N_r'+1)(A_rA_f/A_t)e^{-\epsilon_r''/kT}. \quad (3)$$

Here  $Q_T$  is the translational partition function  $(2\pi\mu kT/h^2)^{3/2}$ ; the resonance collision energy is  $\epsilon_r''=E_r'-h\nu_1$ , where the zero of energy is the initial-state threshold, and  $E_r'$  is the energy of the excited vibrational-rotational level above this threshold; the  $g''$  and  $g'$  factors give the respective ground and excited electronic degeneracy factors;  $N_r'$  is the upper-state Hund's-case-(b) rotational quantum number.

The stimulated-emission decay rate of an excited-state resonance back into the initial photoassociation channels is

$$A_r=\sigma_r\phi=(8\pi^3/3\lambda)\sum_{N''}\ell(N',N'')|\langle v'N'|\mu(R)|\epsilon_r''N''\rangle|^2\phi, \quad (4)$$

where  $\phi$ =photon flux,  $\mu(R)$  is the electronic transition dipole,  $\ell$  is the Hönl-London factor, and  $|v'N'\rangle$ ,  $|\epsilon_r''N''\rangle$  are the respective bound and free (energy-normalized) radial functions for the potentials including the centrifugal term;  $\sigma_r$  is the stimulated-emission cross section for the upper level. For  $\Sigma$ - $\Sigma$  transitions the sum in (4) is over  $P$ - and  $R$ -type transitions with  $N''=N'+1$  and  $N'-1$ , respectively. The two branches need to be treated separately at low temperature due to large centrifugal-barrier effects on the near-threshold integrals.

The spontaneous-emission rate of a resonance  $v'$  is

$$A_f(v')=(64\pi^3/3hc^3)\sum_{v''}\left[v_v^3v''|\langle v'|\mu(R)|v''\rangle|^2+\int v_v^3\epsilon''|\langle v'|\mu(R)|\epsilon''\rangle|^2d\epsilon''\right], \quad (5)$$

where the effect of rotation may be safely ignored. The coefficient  $A_f$  separates into contributions from bound-bound and bound-free fluorescence,  $A_f=A_f(\text{bb})+A_f(\text{bf})$ , in accordance with the two terms in (5). Since the total decay rate of the resonance is  $A_t=A_r+A_f$ , we see that the Breit-Wigner rate expression (3) expresses the competition between decay to the collisional and fluorescence channels. If the photoassociation laser intensity is low, the stimulated-emission rate  $A_r$  which couples the resonance to the incoming channel

will be much less than the spontaneous-emission decay rate  $A_f$ . In this case, the  $A_f/A_t$  factor in (3) is unity and the association rate is linear in laser flux  $\phi$ . Saturation occurs when  $A_r=\sigma_r\phi$  becomes larger than  $A_f$ . In this case, increasing the laser intensity will cause no further increase in fluorescence intensity.

We have numerically calculated the quantum-mechanical dipole Franck-Condon overlap matrix elements in (4) and (5) needed to evaluate these expressions for sodium-atom photoassociation through both the  $X^1\Sigma_g\rightarrow A^1\Sigma_u$  and  $^3\Sigma_u\rightarrow^3\Sigma_g$  transitions for frequencies tuned to the red of the Na  $^2S$ - $^2P$  resonance line. Piece-

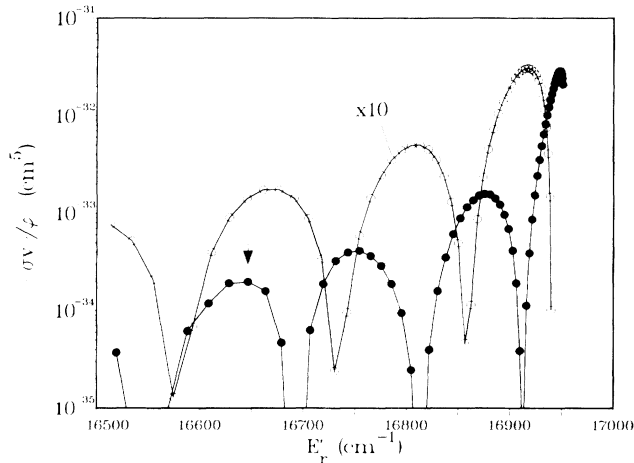


FIG. 1. Absorption coefficient per unit  $N^2$ ,  $\alpha_\lambda/N^2=(\sigma v)/\phi$ , for  $P(1)$  transitions,  $\epsilon_r''=0.01\text{ cm}^{-1}$ ,  $T=10\text{ mK}$ , as a function of excited-state vibrational energy  $E_r'=E_r''+h\nu_1$ : solid circles,  $^1\Sigma_g\rightarrow^1\Sigma_u$ ; open circles,  $^3\Sigma_g\rightarrow^3\Sigma_u$ . Arrow points to  $A^1\Sigma_u v'=107$ .

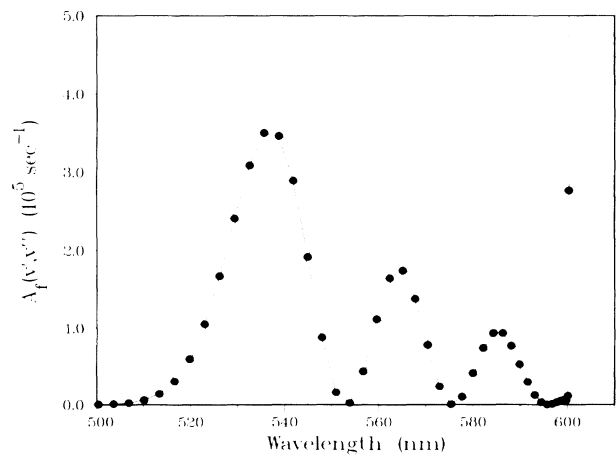


FIG. 2. Bound-bound  $^1\Sigma_u\rightarrow^1\Sigma_g$  emission spectrum from  $v'=107$ .

TABLE I. Upper-state total spontaneous-emission coefficient  $A_f(v')$  ( $10^8 \text{ sec}^{-1}$ ) and bound and free branching fractions, where  $f_b = A_f(\text{bb})/A_f$ .

$v'$	$^1\Sigma_u \rightarrow ^1\Sigma_g$			$v'$	$^3\Sigma_g \rightarrow ^3\Sigma_u$		
	$A_f$	$f_b$	$1-f_b$		$A_f$	$f_b$	$1-f_b$
107	1.09	0.183	0.817	79	1.20	0.110	0.890
115	1.13	0.114	0.886	91	1.25	0.074	0.926
130	1.17	0.070	0.930	111	1.30	0.001	0.999

wise analytic potential energy curves were obtained for the  $X^1\Sigma_g$  and  $A^1\Sigma_u$  states<sup>9-12</sup> and lowest  $^3\Sigma_u$  state<sup>9,11,13</sup> by combining experimental and *ab initio* data. The singlet and triplet dipole transition moments<sup>14,15</sup> and the first excited  $^3\Sigma_g$  potential<sup>9,11</sup> were taken from *ab initio* calculations.

Figure 1 shows the calculated normalized absorption coefficient,  $a_\lambda/N^2 = \langle \sigma v \rangle / \phi$ , where  $a_\lambda$  is the Beer's-law absorption coefficient and  $N$  the Na number density. We show  $\langle \sigma v \rangle / \phi$  for the  $P(1)$  transition as a function of upper-state vibrational energy for a range of energies below the excited-state dissociation threshold. The temperature is 10 mK, and the photoassociation laser frequency is chosen so that  $\epsilon'' = 0.01 \text{ cm}^{-1}$ . Singlet and triplet Franck-Condon progressions are similar because both upper states have similar long-range attractive  $R^{-3}$  potentials. The stimulated-emission cross section for the  $v'=130, N'=0$   $A^1\Sigma_u$  level at the Franck-Condon peak near  $\lambda^{-1} = 16875 \text{ cm}^{-1}$  is  $9 \times 10^{-14} \text{ cm}^2$ . Photoassociation saturation ( $A_r \approx A_f$ ) occurs for this level when  $h\nu\phi > 400 \text{ W cm}^{-2}$ . The fluorescence production rate for photoassociation through  $v'=130$  with a 1-W-cm<sup>-2</sup> laser and a Na density of  $10^{11} \text{ cm}^{-3}$  is  $10^8$  photons  $\text{cm}^{-3} \text{ sec}^{-1}$ . Such fluorescence should be detectable by

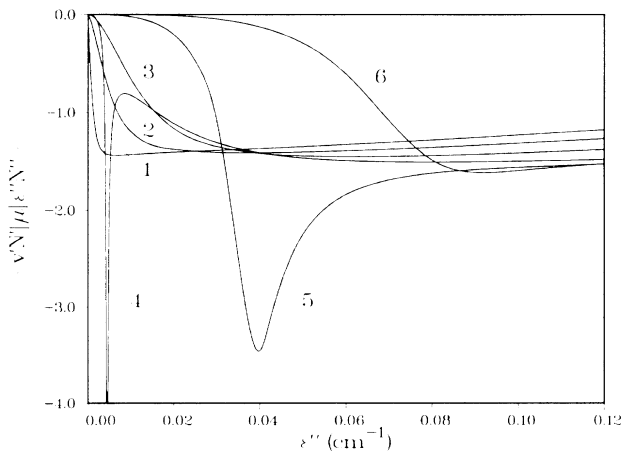


FIG. 3. Threshold behavior of  $^1\Sigma_g \rightarrow ^1\Sigma_u P(N'')$  photoassociation matrix elements for  $v'=130$  vs collision energy  $\epsilon''$ . The number by each curve shows the  $N''$  value.

standard techniques.

We have calculated the bound and free fluorescence spectra for the upper singlet and triplet levels. Table I shows the branching fractions  $f_b$  and  $1-f_b$  for the respective total bound and free fluorescence rates of selected upper levels. Both singlet and triplet emission from these levels is primarily to the continuum. Singlet emission differs from triplet emission in having a much larger fraction of bound emission. Figure 2 illustrates the bound-bound  $A^1\Sigma_u$  emission spectrum,  $A_f(v',v'')$ , for  $v'=107$ . A typical feature of such spectra is that the largest emission coefficients (off scale in the figure) are to the highest few  $v''$  levels, e.g., about 85% of  $v'=107$  bound-bound emission is to the last five levels. Note that the predominant free fluorescence results in hot atoms. This might limit the effective lifetime of an optical cold-atom trap, either by loss of fast atoms or collisional heating of the cold gas. For the conditions discussed in the previous paragraph, neither effect will be important on a 1-sec time scale for a trap with volume  $< 1 \text{ cm}^3$ . However, hot atom production could become a limiting factor for trap densities of  $10^{14} \text{ cm}^{-3}$  or larger.

When the Hund's-case-(b) rotational quantum number  $N''$  for the lower state is nonzero, the presence of a small centrifugal barrier can lead to shape resonances. Figure 3 shows the  $\langle \epsilon'' N'' | \mu | v', N'' - 1 \rangle$  integrals as a function of  $\epsilon''$  near threshold for the  $p(N'')$  transitions to  $v'=130$ . For our  $X^1\Sigma_g$  potential the  $v''=65, N''=0, 1, 2,$  and  $3$  levels are bound, whereas the  $N''=4$  and  $5$  levels appear as quasibound levels, or shape resonances. A  $v''=65, N''=6$  resonance does not exist since it would lie above the centrifugal barrier for the  $N''=6$  potential.

Figure 4 shows the absorption spectrum which would be obtained in a small region of detuning near the threshold for  $v'=130$  excitation by collecting fluorescence as a function of excitation wavelength. Note the line shapes are very narrow because of the narrow

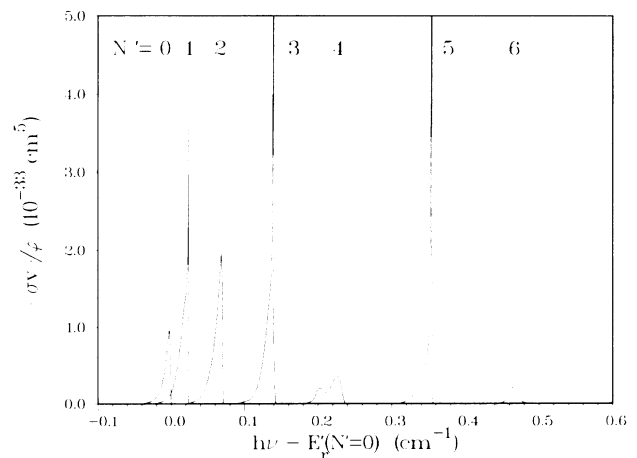


FIG. 4.  $^1\Sigma_g-^1\Sigma_u$  absorption spectrum  $\langle \sigma v \rangle / \phi$  at  $t=10 \text{ mK}$  for rotational levels near threshold for  $v'=130$  excitation.

kinetic-energy distribution at  $T=0.01$  K. The shading to the red is due to the thermal cutoff of absorption. The transition to  $N'=1$  has a sharp onset due to the threshold behavior of the  $s$ -wave integral for the  $R(0)$  transition. The transitions to  $N'=3$  and 5 show the effect of the sharp  $N''=4$  resonance. Transitions to higher- $N'$  levels become weak because of the small integrals for  $\epsilon'' \approx kT$  near threshold.

Our calculations show that signal strengths seem reasonable for doing experimental studies on photoassociation spectroscopy of ultracold Na atoms. Modification of our simple Breit-Wigner resonant-scattering theory will be necessary to describe photoassociation for  $T < 1$  mK. The ignored effects of molecular fine or hyperfine splitting will also certainly be important and observable. The  $\rho$ -tripling fine structure of the  $^3\Sigma-^3\Sigma$  transition and probably also the molecular hyperfine structure should be resolvable at Na temperatures which have already been achieved in the laboratory.<sup>1-4</sup> Theoretical predictions of relative intensities of such lines require developing line-strength expressions which take into account the change between an atomic angular momentum coupling scheme for the colliding atoms and a molecular coupling scheme for the excited molecule. A close-coupled scattering formulation of the near-threshold collision is necessary in order to take into account fine and hyperfine coupling, radiative coupling, and decay of the excited resonance. We therefore expect ultracold-atom photoassociation spectroscopy to be an exciting new tool, not only for spectroscopic studies, but also as a probe of the dynamics of near-threshold collisions.

Support for this work has been provided by the National Science Foundation (H.T. and J.W.) and the U.S. Air Force Office of Scientific Research (P.S.J.).

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