

Ultracold-molecule production by laser-cooled atom photoassociation

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We propose a method for copiously producing ultracold ground electronic-state molecules by two-photon absorption to a Rydberg molecular level (that spontaneously radiates to the ground molecular state) during collisions of ultracold atoms in a laser trap. Using the Na_2 molecule as an example, the sequential two-photon absorption is via an intermediate high-lying vibrational level of the excited 1_g state and results in the formation of a given vibrational level of a $^1\Pi_u$ Rydberg molecular state. Realistic calculations demonstrating the validity of the method are presented.

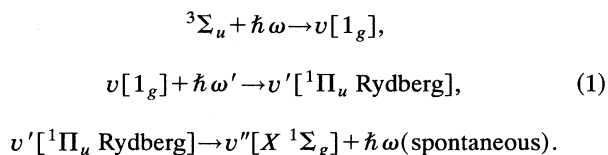
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Laser-cooling techniques [1–3] have enabled cooling of alkali-metal and noble-gas atoms from mK to μK temperatures. A magneto-optical trap (MOT) [4] or far off-resonance trap (FORT) [5,6] can confine these ultracold atoms. These techniques have led to prospects for improved atomic clocks, brighter atomic beams, and atomic beams with improved coherence for atom interferometers, as well as numerous studies on the novel aspects of ultracold collisions and high-precision spectroscopic measurements on the long-range excited states of alkali-metal dimer molecules. Atomic laser cooling methods cannot be applied to molecules, which lack a closed two-level energy level scheme for recycling population. If a method of producing ultracold molecules were available, it could lead to new spectroscopic studies of long-range molecular states, studies of ultracold molecule-molecule collisional relaxation processes, and possibly novel molecular beam sources. In this Rapid Communication we propose a method of assembling translationally cold molecules from cold trapped atoms using two-photon absorption during the collision of the atoms. Such cold molecules could be trapped in a FORT, which in principle could trap molecules as well as atoms. Although the basic concept is general, it will be illustrated by specific calculations using the Na_2 molecule. Sequential two-photon absorption of colliding $\text{Na}(^2S_{1/2}) + \text{Na}(^2S_{1/2})$ via an intermediate high-lying vibrational level of the excited 1_g state of Na_2 correlating asymptotically to $\text{Na}(^2S_{1/2}) + \text{Na}(^2P_{3/2})$ results in the formation of a $^1\Pi_u$ Rydberg molecular state in a vibrational level that selectively decays by spontaneous emission to only a few low-lying vibrational levels of the ground-state Na_2 molecule. We carry out realistic calculations demonstrating the validity of our scenario for ultracold-molecule formation.

Thorsheim *et al.* [7] proposed that photoassociation of cold trapped atoms could be used to produce molecules, which result from the spontaneous radiative decay of vibrational levels of an excited electronic state produced by free-bound laser excitation from the translational continuum states of the colliding ground-state atoms. Molecules made this way will be translationally cold, with a temperature comparable to that of the atomic from which they are assembled. Although the rate coefficient for such a process can

be fairly large, Thorsheim *et al.* showed that the Franck-Condon principle dictates that the molecules will be distributed over a large number of vibrational levels of the ground-state molecule, and that much of the reemitted light is to translationally hot continuum states instead of bound molecular states. By introducing a second step of optical control, it is possible to direct this process to produce bound ground-state molecules much more efficiently. A much larger number of ground-state molecules can be produced by using the dissipative process of spontaneous emission instead of stimulated emission. Using stimulated emission to form ground-state molecules from a Rydberg state would result in photodissociation of the ground states via the same path by which they are formed. Consequently the steady-state density would be very much lower than could be achieved by a spontaneous process.

We illustrate the method for sodium molecule formation; similar schemes exist for the other alkali-metal atoms. A high-lying vibrational level v (in our calculations we take $v=48$) of the excited 1_g state [8,9], which correlates asymptotically to $\text{Na}(^2S_{1/2}) + \text{Na}(^2P_{3/2})$, is excited from the ground $^3\Sigma_u$ state, which correlates asymptotically to $\text{Na}(^2S_{1/2}) + \text{Na}(^2S_{1/2})$, during the collision of laser-cooled Na atoms. This excitation is caused by a laser whose frequency ω is tuned to excite the $v[1_g]$ level. Since the thermal kinetic-energy spread of optically trapped atoms is on the order of the natural linewidth of the cooling transition, most of the velocity distribution of the ground-state atoms is available for excitation, unlike normal temperature free-bound transitions. Another laser with frequency ω' is tuned to the transition from $v[1_g]$ to a v' level of the lowest $^1\Pi_u$ Rydberg state of Na_2 (in our calculations we take $v'=0$). This state then decays via spontaneous emission to the low-lying vibrational levels of the ground molecular electronic state. The method can be represented by the three step process,



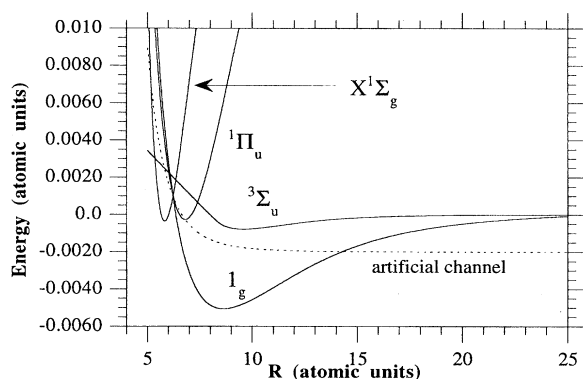


FIG. 1. Potential-energy curves vs internuclear distance R for the ${}^3\Sigma_u$ ground state, the dressed 1_g and ${}^1\Pi_u$ states, the $X^1\Sigma_g$ ground state shifted in energy such that the $v''=0[X^1\Sigma_g]$ level is at the same energy as the $v'=0[{}^1\Pi_u]$ Rydberg, and the artificial channel (dashed curve) that couples to the ${}^1\Pi_u$ Rydberg state. Energy and distance are expressed in atomic units, $4.359\,775 \times 10^{-18}$ J and $0.529\,177 \times 10^{-10}$ m, respectively.

Figure 1 shows the dressed molecular potential-energy curves involved in the process (the dashed curve will be explained below). The 1_g state has been lowered by energy $\hbar\omega$, the ${}^1\Pi_u$ Rydberg state by energy $\hbar(\omega + \omega')$, and the $X^1\Sigma_g$ state by energy $D_e - \hbar\omega_e/2$, where D_e and ω_e are its respective dissociation energy and vibrational frequency, measured from the bottom of the ground-state potential well. The laser frequency ω is chosen so as to populate a given vibrational level v of the 1_g state from a mK continuum state of ${}^3\Sigma_u$. The excited 1_g state is chosen because the given vibrational level v can be exclusively populated from the ${}^3\Sigma_u$ state, and population can be transferred from $v[1_g]$ exclusively to the $v'[{}^1\Pi_u]$, provided ω' is in resonance. The second laser frequency ω' is tuned to resonance with the $v[1_g] \rightarrow v'[{}^1\Pi_u]$ transition. The ${}^1\Pi_u$ Rydberg state [10] is chosen because low v' levels decay to the ground ${}^1\Sigma_g$ electronic state without substantial ionization or predissociation. Predissociation of the lowest few $v'[{}^1\Pi_u]$ levels is not expected because there is no predissociating state (doubly excited in the diabatic representation) that crosses the Rydberg state [11]. Because of the intrinsically small photoionization and photodissociation rates as expected laser powers, decay of the Rydberg state via either of these processes will be very much less than by radiative decay and therefore will not significantly limit the production of ultracold ground-state molecules. Choice of which v' vibrational level to use is dictated by two factors: the vibrational predissociation rates of the v' levels and the $v''[X^1\Sigma_g]$ levels that we wish to populate via the spontaneous decay. If many v' levels have negligible predissociation rates, then only the latter factor is of relevance. For the sake of definiteness we take $v'=0$. Since R_e of the ${}^1\Pi_u$ state lies outside that of the $X^1\Sigma_g$ ground state, the Franck-Condon principle results in a distribution of ground $v''[X^1\Sigma_g]$ levels, peaking near $v''=9$ with a half-width at half maximum of about $\Delta v=2$ from $v''=0$.

We believe that the only decay process competitive with ground-state formation involves the radiative decay of the $v'=0[{}^1\Pi_u]$ Rydberg level to the excited ${}^1\Sigma_g$ state correlat-

ing to $\text{Na}({}^2S_{1/2}) + \text{Na}({}^2P_{3/2})$. A simple estimate can be made of the relative decay rates γ_1 and γ_2 of the ${}^1\Pi_u$ Rydberg in the ground and excited ${}^1\Sigma_g$ states, respectively. An excellent approximation for these decay rates is given by the expectation value [12]

$$\gamma_i = \frac{4}{3\hbar c^3} \langle v'=0[{}^1\Pi_u] | \omega_i(R)^3 d_i(R)^2 | v'=0[{}^1\Pi_u] \rangle, \quad (2)$$

where $\hbar\omega_i(R) = V({}^1\Pi_u, R) - V_i(R)$ is the difference of the electronic potentials and $d_i(R)$ is the electronic transition dipole from the ${}^1\Pi_u$ state to the state i . On the basis of the ω_i^3 factors alone, we estimate $\gamma_1/\gamma_2 \approx 30$. This ratio is likely to be reduced since d_2 is likely to be larger than d_1 . However, even if $\gamma_1/\gamma_2 \approx 1$, our estimated molecular production rate would be decreased by only a factor of 2, and our estimate of the rate is no more reliable than this in any case.

We calculate the production rate of ultracold ground-state molecules using an artificial channel approach to simulate the decay of the $v'=0[{}^1\Pi_u]$ Rydberg state to the $X^1\Sigma_g$ state. Figure 1 shows the artificial channel as a dashed curve, the ${}^3\Sigma_u$ ground state, the dressed 1_g and ${}^1\Pi_u$ states, and the $X^1\Sigma_g$ ground state shifted in energy such that the $v''=0[X^1\Sigma_g]$ level is at the same energy as the $v'=0[{}^1\Pi_u]$ Rydberg (so all the potential curves can be conveniently plotted). The artificial channel couples to the $v'=0[{}^1\Pi_u]$ Rydberg state, and the flux that comes out on this channel simulates the decay of the Rydberg state to the ground state. The coupling strength to the artificial channel was chosen so that the width of the $v'=0[{}^1\Pi_u]$ resonance is about 2 MHz, the ${}^1\Pi_u \rightarrow X^1\Sigma_g$ spontaneous decay rate assumed by our calculation. The ${}^3\Sigma_u$ state is coupled to 1_g via the Rabi frequency Ω_1 , and 1_g is coupled to ${}^1\Pi_u$ via the Rabi frequency Ω_2 . A numerical close-coupling calculation is used to calculate the S -matrix element $S_{pg}(\varepsilon, l, \Delta_1, \Delta_2, \Omega_1, \Omega_2)$ for the process that makes the artificial channel product p , that is, the ground molecular product state, from the ground-state translational continuum with collision energy ε and relative angular momentum quantum number l . In this calculation a complex potential $V(R, 1_g) - i\hbar\gamma(v=48)/2$ is used for the intermediate state, where $\gamma(v=48) = 2\pi(0.07 \text{ MHz})$ is the radiative decay width of the intermediate $v=48$ level [9]. The rate coefficient for producing cold ground-state molecules is

$$K_p(T, \Delta_1, \Delta_2, \Omega_1, \Omega_2) = \left\langle \frac{\pi v}{k^2} \sum_{l=0}^{\infty} (2l+1) |S_{pg}(\varepsilon, l, \Delta_1, \Delta_2, \Omega_1, \Omega_2)|^2 \right\rangle, \quad (3)$$

where $\varepsilon = \hbar k^2/2\mu = \mu v^2/2$, v is the relative velocity, and μ is the reduced mass. The brackets $\langle \rangle$ imply an average over the distribution of initial velocities v ; in our calculation, we take a single kinetic energy $\varepsilon/k_B = 1 \text{ mK}$. In general, S_{pg} will have a complex resonance structure, and the dependence on ε and l will be associated with the Wigner threshold law properties of the S matrix [9]. The upper bound for K for an

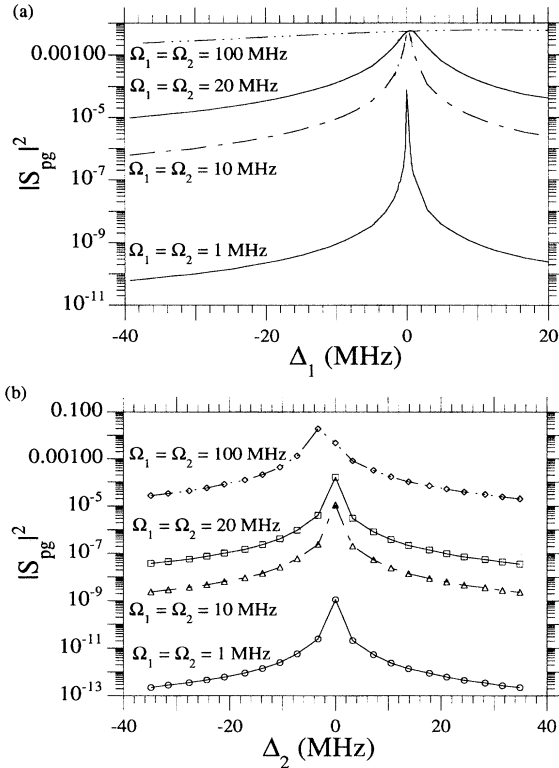


FIG. 2. (a) Calculated production probability $|S_{pg}|^2$ vs detuning Δ_1 of the laser with frequency ω_1 for four different sets of laser intensities. (b) Same as (a) but vs detuning Δ_2 of the laser with frequency ω_2 .

s wave ($l=0$) is $\pi v/k^2$, which has an order of magnitude of 10^{-10} cm³/s for trapped Na. The time required to convert all of the atoms in a trap with a density N to molecules is on the order of $(K_p N)^{-1}$. If the upper limit of K_p were reached, this time would be 0.1–1 s for typical trap densities. Fast conversion of trapped atoms to molecules requires that S_{pg} be as large as possible, preferably near its upper limit of unity.

Figure 2 shows the calculated production probability $|S_{pg}|^2$ versus detunings Δ_1 and Δ_2 of the two lasers for four different sets of laser intensities, and clearly shows the double resonance nature of this production probability. Detuning Δ_1 is defined to equal zero when ω is resonant with the transition to $v=48[1_g]$, and Δ_2 is defined to equal zero when ω' equals the difference of energy between $v'=0[1^1\Pi_u$ Rydberg] and $v'[1^1\Pi_u]$. The four sets of curves plotted in Fig. 2 correspond to the four sets of Rabi frequencies, $\Omega_1=\Omega_2=1, 10, 20,$ and 100 MHz. At low Rabi frequencies, the probability for producing cold ground-state molecules, $|S_{pg}|^2$, is proportional to $(\Omega_1\Omega_2)^2$. The probabilities are very sharply peaked about the resonance positions in both Δ_1 and Δ_2 , but at low power the width vs Δ_1 is much narrower than that vs Δ_2 , because the spontaneous decay rate of the $1^1\Pi_g$ intermediate level is much smaller than that of the $1^1\Pi_u$ level. With larger Rabi frequencies, the positions of the resonances shift, and the width of the resonances broaden considerably as a function of Δ_1 . The resonance vs Δ_1 shifts to $\Delta_1>0$, and the resonance vs Δ_2 shifts

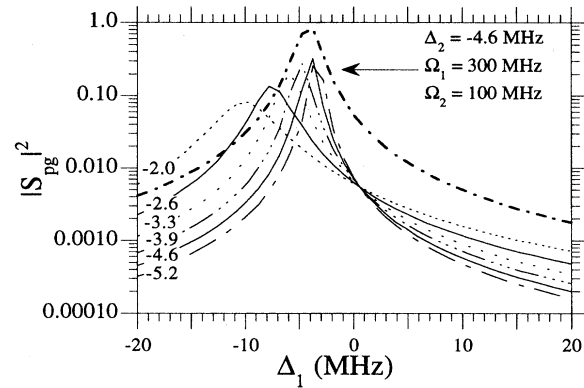


FIG. 3. Calculated production probability $|S_{pg}|^2$ vs detuning Δ_1 for five values of $\Delta_2=-2.0, -2.6, -3.3, -3.9,$ and -5.2 MHz, with $\Omega_1=\Omega_2=100$ MHz; and for $\Delta_2=-4.6$ MHz, with $\Omega_1=300$ MHz, $\Omega_2=100$ MHz.

to $\Delta_2<0$, indicating that the $v[1_g]$ state is pushed more by the interaction with the photons of frequency ω than the ω' photons. However, the resonance width vs Δ_2 does not broaden as much with increased Rabi frequencies as the resonance with Δ_1 . Further increase of the Rabi frequencies shifts the resonance to larger Δ_1 and broadens it still further, but does not increase the peak probability. The broadening with Δ_1 is necessary if a substantial part of the temperature distribution of the cold atoms is to be turned into cold molecules, i.e., a wide distribution of atoms with varying kinetic energies in the incoming state must be transferred to molecules for copious molecule production.

Optimization of the probability for cold-molecule production requires simultaneously varying $\omega_1, \omega_2, \Omega_1,$ and Ω_2 , since the resonance frequencies ω_1, ω_2 vary as Ω_1 and Ω_2 are increased due to power shifts. Such a four-parameter variation is difficult to carry out. However, we have carried out some calculations at large Rabi frequencies, $\Omega_1=\Omega_2=100$ MHz, with $\Delta_2=-2.0, -2.6, -3.3, -3.9, -4.6,$ and -5.2 MHz as a function of Δ_1 , and have obtained probabilities $|S_{pg}|^2$ close to unity, as shown in Fig. 3. Note that the optimal calculation will not have $\Omega_1=\Omega_2$. As shown in Fig. 3, using $\Omega_1=300$ MHz, $\Omega_2=100$ MHz, and $\Delta_2=-4.6$ MHz yields a higher probability.

In conclusion, our calculations indicate that a large fraction of the ultracold atoms in a laser-cooled atom trap can be converted into ultracold molecules via two-photon association by the mechanism of Eq. (1). Optimization of the production rate requires determination of the four optimum parameters for the two laser fields, $\omega_1, \Omega_1, \omega_2,$ and Ω_2 , since power shifts of the levels occur close to the optimum, but the regime of variation of the parameters is limited. Experimental variation of these parameters to obtain the optimum should be possible. The density of cold molecules that could be produced will depend also on the processes by which they would be lost from the region in which they are produced. Since the molecules would not be trapped in a MOT, they would rapidly move out of the region of the MOT. They could in principal remain confined in a FORT, since the dipole force acts on molecules as well as atoms and does not suffer the same limitation of requiring a two-state cycling

transition that a MOT does. However, vibrational or rotational relaxation due to atomic or molecular collisions could also heat the molecules and eject them from a FORT. Rotational relaxation would probably be fast, so only $J=0$ levels could be trapped. Vibrational relaxation might be slow enough to permit trapping. Such issues will have to be inves-

tigated in more detail to determine if a significant density of cold molecules could be confined in a FORT.

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