Laser-Catalyzed Production of Ultracold Molecules: The ^{6}Li + ^{6}Li^{7}Li $\xrightarrow{\hbar\omega}$ ^{6}Li − ^{6}Li + ^{7}Li Reaction

Xuan Li* and Gregory A. Parker
Homer L. Dodge Department of Physics and Astronomy, University of Oklahoma, USA

Paul Brumer
Chemical Physics Theory Group, Department of Chemistry, University of Toronto, Canada

Ioannis Thanopulos[1] and Moshe Shapiro[1,2]
[1]*Department of Chemistry, The University of British Columbia, Vancouver, Canada*
[2]*Department of Chemical Physics, The Weizmann Institute, Rehovot, Israel*

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We show that by using laser catalysis, we can employ translationally cold ($T_r \approx 1.75$ K) collisions to produce *ultracold* (0.01 mK $< T_p <$ 1 mK) (homonuclear) molecules. We illustrate this approach by studying the laser catalysis of the ^{6}Li + ^{6}Li^{7}Li $\xrightarrow{\hbar\omega}$ $(^6\mathrm{Li}^6\mathrm{Li}^7\mathrm{Li})^*(1^4A'')$ $\xrightarrow{\hbar\omega}$ ^{6}Li^{6}Li + ^{7}Li reaction in the collinear approximation. Ultracold ^{6}Li^{6}Li product molecules are shown to be produced at an extraordinary yield of up to 99.97%, using moderate laser intensities of $I = 100\ \mathrm{kW/cm^2} - 10\ \mathrm{MW/cm^2}$.

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The existence of Bose-Einstein Condensates (BEC) of various atoms [1] and the possibility of the production of their molecular analogues [2–7] has spurred great interest in reactions between ultracold, bosonic, or fermionic (spin-aligned), molecules. For the lightest alkali, Li, isotopic mixtures of the fermionic ^{6}Li and the bosonic ^{7}Li are of great interest because they lead to the creation of either heteronuclear or homonuclear diatomic molecules [3,7–11].

In this Letter, we show that the involvement of pulsed lasers of moderate intensities in the reactions between *cold* reactants can lead to the production of *ultracold* diatomic molecules. We propose achieving this goal via the "laser catalysis" scenario [12–16], according to which, a laser assists a chemical reaction in a process involving no net absorption of photons. According to this scenario, the laser assists the $A + BC \rightarrow AB + C$ reaction by first forcing a (virtual) transition of the $A + BC$ reactants to the $(ABC)^*$ excited state complex (ESC). The ESC then undergoes a stimulated emission process to the $AB + C$ ground state products, releasing a photon identical to the photon just absorbed. Thus, no net photons are absorbed, justifying the name "laser catalysis." When the process is done coherently and the intensity of the laser is high enough, the prediction is that the system would transit smoothly from reactants to products, with the ESC "stepping stone" remaining unpopulated even in a transient way [12], thus rendering the ESC an authentic "virtual state."

As an illustration of this concept, we consider in detail the $A = {}^6\mathrm{Li}(^2S)$, $B = {}^6\mathrm{Li}(^2S)$, and $C = {}^6\mathrm{Li}(^2S)$ triatomic system. The diatomic molecules $AB = {}^6\mathrm{Li}_2(3\Sigma_u^+)$ and $BC = {}^7\mathrm{Li}^6\mathrm{Li}(^3\Sigma^+)$ are taken to be in their lowest spin-aligned electronic states. The triatomic states are the $1^4A'$ states for the reactants and products, and the $1^4A''$ states for the ESC $(ABC)^*$. The zero energy is chosen to be at the three-body break up limit $(^2S + {}^2S + {}^2S)$. There is no natural barrier in the reaction path between chemical arrangements of the quartet ^{6}Li^{6}Li^{7}Li system. We note, however, that the lowest vibrational energy of the triplet ^{6}Li^{7}Li state is calculated to be $E(q = 1, v = 0) = -300.51194\ \mathrm{cm}^{-1}$, while the lowest vibrational energy of the triplet ^{6}Li^{6}Li state is calculated to be slightly higher, at $E(q = 2, v = 0) = -299.29412\ \mathrm{cm}^{-1}$. Figure 1 shows the schematic energy levels of the current ^{6}Li^{6}Li^{7}Li in a laser catalysis scenario.

We thus envision a collinear collision between counter-propagating ^{6}Li and ^{6}Li^{7}Li beams, having zero center of mass velocity, each prepared with translational tempera-

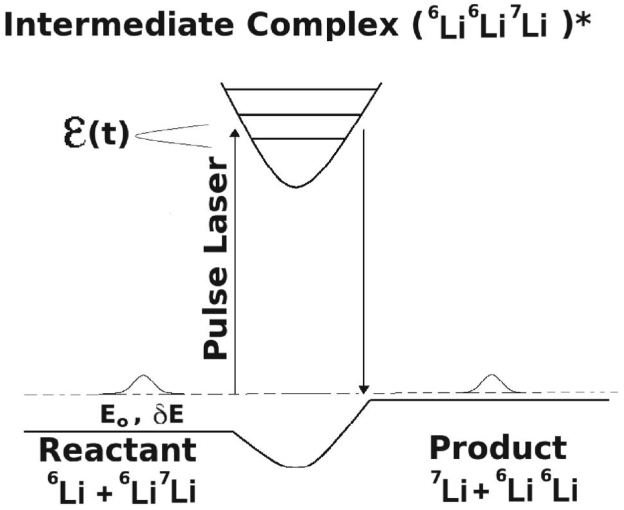

FIG. 1. Schematic energy levels of ^{6}Li^{6}Li^{7}Li system in the laser catalysis scheme.

tures of $T_r \approx 1.75$ K. By tuning the laser center frequency to be in exact resonance with a transition to one of the bound states of the ESC, we can make use of the energetic difference between the reactant and product diatoms to produce the $^6\text{Li}^6\text{Li}$ at *ultracold* temperatures. These temperatures range between $0.01 \text{ mK} < T_p < 1$ mK, depending on the bandwidth of the laser used. The intervention of the laser is necessary because at translational temperatures of 1.75 K, the nonradiative reaction probability is negligible ($< 1\%$).

We proceed now to outline the theoretical basis of our calculations. The total matter + radiation Hamiltonian is given in the dipole approximation as $H_{\text{tot}} = H - \vec{\mu} \cdot \vec{\varepsilon}(t)$, where H is the material Hamiltonian and $\vec{\varepsilon}(t) = \hat{\varepsilon}\varepsilon(t)$, with $\hat{\varepsilon}$ being the laser's polarization direction and $\varepsilon(t)$, its electric field strength. We expand the wave function, $\Psi(t)$, which solves the time-dependent Schrödinger equation, $i\hbar\partial\Psi/\partial t = H_{\text{tot}}\Psi$, in a complete basis composed of $|E_j\rangle$, the bound ESC, and $|E, q, n^-\rangle$, the ground-electronic or nuclear-continuum, eigenstates of H,

$$(E_j - H)|E_j\rangle = (E - i\epsilon - H)|E, q, n^-\rangle = 0. \quad q = 1, 2. \quad (1)$$

In the above, q denotes the asymptotic chemical arrangements and n, the internal quantum numbers associated with them, in the $t \rightarrow \infty$ limit. For narrow laser bandwidths it is usually sufficient to consider a single excited $|E_j\rangle$ bound state since in that case, the effect of other bound states is negligible [14,16]. Thus, the laser pulse creates a superposition of ground continuum states and one excited bound state of the form

$$|\Psi(t)\rangle = \sum_{q,n}\int dE b^-_{E,q,n}(t)|E, q, n^-\rangle \exp(-iEt/\hbar) + b_j(t)|E_j\rangle \exp(-iE_jt/\hbar). \quad (2)$$

We assume that initially there is no population in the ESC bound states, i.e., that $b_j(t = -\infty) = 0$. The system that starts in the $^6\text{Li} + {}^6\text{Li}^7\text{Li}$ reactants ($q_s = 1$) channel at the ground vibrational state ($n_s = 0$) is composed of a translational wave packet given as $\int dE b^+_{E,q_s,n_s}|E, q_s, n_s^+\rangle \exp(-iEt/\hbar)$ whose energetic dependence is determined by b^+_{E,q_s,n_s}. Using the connection between the $|E, q, n^-\rangle$ and the $|E, q_s, n_s^+\rangle$ states, we have that

$$b^-_{E,q,n}(t = -\infty) = S_{q,n;q_s,n_s}(E)b^+_{E,q_s,n_s},$$

where

$$S_{q,n;q_s,n_s}(E) \equiv \langle E', q, n^-|E, q_s, n_s^+\rangle\delta(E - E')$$

is the nonradiative scattering matrix element.

Substituting Eq. (2) into the time-dependent Schrödinger equation, and using the rotating wave approximation (RWA) [17], we obtain a set of integro-differential equations for the expansion coefficients, $b_j(t)$ and $b^-_{E,q,n}(t)$,

$$\dot{b}_j = \frac{i\varepsilon(t)}{\hbar}\mu_j^s(t) + \sum_{q,n}\int dE b^-_{E,q,n}(t)\mu^-(E; j, q, n) \times e^{-i\omega_{E,j}t},$$

$$b^-_{E,q,n}(t) = b^-_{E,q,n}(-\infty) + \frac{i}{\hbar}\int_{-\infty}^{t} dt' b_j(t')\varepsilon^*(t')\langle E, q, n^-|\vec{\mu} \cdot \hat{\varepsilon}|E_j\rangle e^{i\omega_{E,j}t'}, \quad (3)$$

where $\mu_j^s(t)$ is the "source" term

$$\mu_j^s(t) \equiv \sum_{q,n}\int dE b^-_{E,q,n}(-\infty)\langle E_j|\vec{\mu} \cdot \hat{\varepsilon}|E, q, n^-\rangle e^{-i\omega_{E,j}t}. \quad (4)$$

Assuming the Markov-like "slowly varying continuum approximation" (SVCA) [4,18], which can be fully justified for this case [12], we obtain after some manipulations a simple differential equation for b_j,

$$\frac{d}{dt}b_j(t) = \frac{i\varepsilon(t)}{\hbar}\mu_j^s(t) - \frac{\pi}{\hbar}|\langle E_j|\vec{\mu} \cdot \hat{\varepsilon}|E_o, q, n^-\rangle\varepsilon(t)|^2 b_j(t) \quad (5)$$

where E_o is the energy center of the initial reactant wave packet.

The solution of Eq. (5) and its substitution into Eq. (3) yields the time-dependent probabilities to observe the intermediate state, the reactants, and the products. One can vary the experimentally controllable function $\varepsilon(t)$ and the initial wave packet, $\Psi(t = -\infty)$, to optimize the reactive scattering process, using, as the case may be, the constructive or destructive interferences between the nonradiative scattering route and the radiatively assisted route.

Computational results.— We have chosen the light pulse that induces transitions between the intermediate states and the reactant/product states to have a Gaussian envelope function,

$$\varepsilon(t) = 2R_e\varepsilon_0 \exp(-t^2/\Delta_t^2)\exp(-i\omega_0 t), \quad (6)$$

where ε_0 is the field strength, Δ_t (often = 431 ns) is the temporal pulse width, and ω_0 is the carrier frequency chosen to be in resonance with the $|E_{j=21}\rangle$ state. We have also chosen the initial reactant wave packet to have a Gaussian shape,

$$b^+_{E,q_s,n_s} = (\delta_E^2\pi)^{-1/4}\exp[-(E - E_o)^2/(2\delta_E^2)], \quad (7)$$

where δ_E is the energy bandwidth, determined by the initial temperature, and E_o is the center of the initial reactant wave packet. The energy-dependent dipole coupling terms, $\langle E_j|\vec{\mu} \cdot \hat{\varepsilon}|E, q, n^-\rangle$, are then calculated using the reactive version of the Artificial Channel Method [19].

In order to achieve the desired ultracold product temperature, we choose the detuning parameter defined as $\Delta \equiv \omega_0 - E_j + E_o$ to be equal to 0. In this way, a narrow (e.g., $\Delta_t = 431$ ns $- 43.1$ μs) transform-limited laser pulse carves out of the $T_r = 1.75$ K initial reactant distribution a narrow energetic component whose width is ~ 0.01 mK $-$ 1 mK and transforms it into products of roughly ~ 0.01 mK $-$ 1 mK. Therefore, the molecular reactants, ^{6}Li^{7}Li, can be prepared with a Maxwell-Boltzmann distribution at $T_r \approx 1.75$ K. With the typical experimental error in preparing the translational energies of the initial atomic species, the narrow energy bandwidth (δ_E) of the atomic species ^{6}Li and a narrow laser pulse will filter out the ultracold portion of the initial molecular beam of ^{6}Li^{7}Li reacting with ^{6}Li to form an ultracold cloud of ^{6}Li^{6}Li and ^{7}Li. Depending on the experimental error in beam preparation, the product cloud will then move uniformly in one direction with a known center of mass (c.m.) velocity which will be at least three to 4 times slower than the reactants and thus can be removed by a molecular optical lattice.

Figure 2 shows the time dependence of the probabilities in each state using a laser with an intensity of $I = 13.7$ MW/cm^2 with a $\Delta_t = 431$ ns. The reaction yield of the ultracold ($T_p = 1$ mK) product is shown to be 99.3% when the nonradiative reaction probability at this temperature is negligible ($<1\%$). The probability of the intermediate state $|E_{j=27}\rangle$ (dashed line in Fig. 2) remains very small compared to that of the reactant or product so that spontaneous emission is essentially nonexistent.

To illustrate the effect of the laser intensity, Fig. 3 shows the reaction yield as a function of the laser intensity with other parameters being fixed as they are in Fig. 2. Before reaching saturation at $I \sim 2$ MW/cm^2, the reaction yield increases monotonically with increasing laser intensity. However, in order to avoid spontaneous emission, losses from the population of the intermediate bound state necessitate a much higher intensity of $I \geq 10$ MW/cm^2. The intense laser pulse couples the material state with the field state to form two dress states that the population follows adiabatically from the reactants to the products on the ground dress state without populating the intermediate state significantly [12].

Total suppression of the reaction scattering process can also be achieved. For instance, if we use a detuning of $\Delta = 3 \times 10^{-3}$ cm^{-1} with the other parameters assuming the values of Fig. 2, total suppression, due to destructive interference with the nonradiative reactive process, results. The effect (not shown in detail here) is more significant in the cold regime ($T_p = 10$–100 K) where the nonradiative tunneling probability is non-negligible [16].

We also performed calculations for radiatively assisted reactions yielding other product temperatures, $T_p = 0.1$ and 0.01 mK. Here, we define a scaling variable, s, to describe the change of product temperatures as $T_p \rightarrow T_p/s$. And thus, for $T_p = 1$, 0.1, and 0.01 mK, we choose the following scaling relation for the experimental parameters

$$\Delta \rightarrow \Delta/s, \qquad \Delta_T \rightarrow \Delta_T \times s \tag{8}$$

and a laser intensity, I, large enough to saturate the reaction yield. These experimental parameters at $T_p = 0.1$, 0.01 mK with such scaling relation are suggested values to make sure the SVCA is still valid when the dipole moments vary faster for lower temperatures than they do for $T_p = 1$ mK. Though the SVCA is not necessary for the entire scheme to work, it requires more computations when the SVCA is not valid. The intermediate bound states are $E_{j=37}$ for $T_p = 0.1$ mK and $E_{j=32}$ for $T_p = 0.01$ mK to maximize the reaction yield.

For $T_p = 0.1$ mK, Δ_t and Δ are related to those in the $T_p = 1$ mK case by a scaling relation ($s = 10$) in Eq. (8), and the carrier frequency, ω_0, is changed to have a temperature of $T_p = 0.1$ mK. With $I = 1.37$ MW/cm^2, the reaction yield is saturated at 99.97%. For $T_p = 0.01$ mK, Δ_t and Δ are related to those in the $T_p = 1$ mK case by a

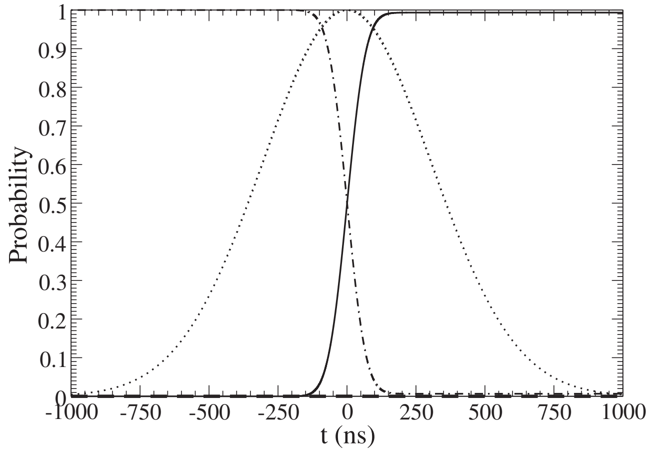

FIG. 2. Population of the reactant (dashed-dot line), product (solid line), and intermediate (dashed line of near zero value) states, and laser profile (dotted line) vs time; $T_p = 1$ mK.

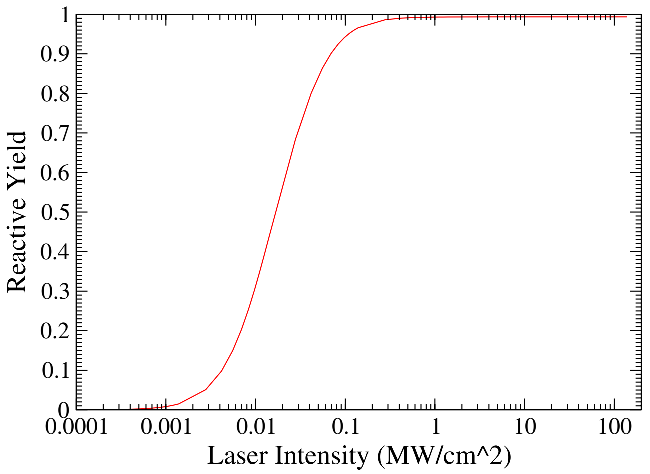

FIG. 3 (color online). Reaction yield vs laser intensity; $T_p = 1$ mK.

scaling relation ($s = 100$) in Eq. (8), the laser intensity is $I = 137\ \mathrm{kW/cm^2}$, and the reaction yield is 99.2%. For brevity, we do not show the plot of the $T_p = 0.1$ mK and $T_p = 0.01$ mK cases which is almost identical to Fig. 2 except for a scaling factor in Eq. (8).

The trap loss process in the above simulations is not appreciable. Since the product diatomic states are in the ground vibrational level and they correspond to nonrotational motion ($n = 0$), the inelastic collision in the reaction channel is zero. Though the reaction channel ^{7}Li + ^{6}Li^{6}Li is exoenergetic, the reactive scattering probability of the reaction channel is calculated to be small ($\approx 1\%$) at $T_p \sim 1$ mK. This does not conflict with the previous scattering calculations [11,20] on this system because Cvitaš *et al.* focused on the rotationally excited ^{7}Li + ^{6}Li^{6}Li ($v = 0$, $n = 1$) state. The production rate of the ultracold ^{6}Li^{6}Li diatoms, for the $T_p = 1$ mK case, is estimated to be $4 \times 10^5/\mathrm{s}$. This estimate is based on the temporal width of the pulse, the percentage of the carved portion of the broadly distributed initial molecular beam, and a typical molecular beam density of $10^{12}\ \mathrm{cm^{-3}}$.

The electronic potential energy surface (PES) used in this calculation is based on a full configuration interaction *ab initio* computation. Though a better PES with inclusion of future experimental spectra can be constructed, we see no reason why this should alter the qualitative features of this scheme. This is because laser catalysis only requires that the intermediate state is properly chosen so that the population transfer from the intermediate state to the reactants and the products are balanced [16]. Thus, one can tune the laser intensity and the laser detuning, respectively, to compensate the quantitative difference in Franck-Condon overlap and the transition energies. The same argument applies when one wishes to move to the three-dimension (3D) case. This simulation uses a collinear approximation which specifies all the rotational motions are absent, and in a 3D calculation only an additional ^{6}Li + ^{6}Li^{7}Li($v = 0, n = 1$) level would be opened on the ground-electronic PES. As long as the intermediate state is properly chosen to have a small Franck-Condon overlap with this additional state, the final reaction yield would remain optimum. One needs to perform a careful scattering calculation to make sure the reverse reactive scattering process is suppressed at the desired product temperature.

In summary, we have pointed out the possibility of producing mK ^{6}Li^{6}Li molecules, which according to our calculation may be performed at a yield as high as 99.97%, as a result of a laser-catalyzed reaction between counter-propagating 1.75 K cold ^{6}Li and ^{6}Li^{7}Li beams. This scheme is not restricted to the production of homonuclear molecules, and we can also apply this scenario to heteronuclear molecules which is of interest for applications like quantum computations.

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*li@nhn.ou.edu

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