Bose-Einstein condensation (BEC) has long been known to be at the basis of macroscopic quantum phenomena such as superfluidity and superconductivity, but has only rather recently been experimentally realized in a pure and unuestioned form in cold dilute gases of alkali-metal atoms [1]. Since then the field of quantum gases has provided a rich playground with many experimental and theoretical advances [2]. The formation of a Bose-Einstein condensate of molecules is generally expected as a further breakthrough, with the development of coherent matter waves consisting of molecules (the molecule laser) as a possible application. Also, the ultimate control over all degrees of freedom of molecules realized in a condensate would open the prospect of a new type of chemical reaction (superchemistry [3]), where the macroscopic occupation of a single molecular quantum state gives rise to the coherent stimulation of a chemical reaction (bosonic stimulation).

Alkali-metal atoms are ideal for applying laser cooling, the usual first step in the cooling process needed for BEC, since their relatively simple level structure provides for the requisite closed level system for successive photon absorption and emission cycles. Unfortunately, due to their additional rovibrational level structure, molecules do not offer such possibilities. Efforts are therefore underway to cool molecules by other methods [4]. Doyle’s group at Harvard University cools and traps molecules in a magnetic trap inside a helium refrigerator. Meijer’s group at Nijmegen uses time-varying inhomogeneous electric fields to slow and trap molecules. Three groups have produced cold molecules by photoassociation of pairs of colliding atoms followed by spontaneous emission.

In this Rapid Communication, we propose and analyze an approach that directly leads to a stable condensate of molecules: the efficient and coherent conversion of an atomic condensate into a diatomic molecular condensate via a stimulated Raman transition, enhanced by a time-dependent magnetic field that sweeps over a field-induced Feshbach resonance. For Na atoms the Raman transition probability is enhanced by seven orders of magnitude, leading to a conversion efficiency of up to 20%. The resulting condensate is expected to be as stable as the present atomic condensates. The approach shows promise as a more general process for Feshbach engineering molecular condensates from condensates of the constituent atoms/molecules.

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quasibound state during a collision. As illustrated in Fig. 1(b), this increases the penetration of the colliding atoms to the short distance range, thus greatly improving the overlap with the final molecular state.

Our approach to create a molecular condensate is closely related to a recent experiment by Ketterle’s group [10], showing a surprisingly strong decay of a Na condensate in a magnetic field that varied rapidly over a Feshbach resonance. The decay was explained via the above-mentioned different Zeeman dependence: a significant field increase during the brief existence of the quasibound state gives this state a surplus energy, which after dissociation provides for a very efficient heating mechanism leading to the destruction of most of the condensate [11,12]. The experiment we propose combines the transient generation of a condensate of quasibound diatoms by the field sweep method of Ref. [10] in an optical trap with a simultaneous coherent stimulated Raman pulse, inducing the further conversion to a permanent condensate of stable molecules. The irreversibility introduced by the time-dependent magnetic and Raman laser fields is a key element of our scheme, which helps to prevent back dissociation via the reverse bound-bound-free path.

We estimate the efficiency of this two-step approach by considering the atom pairs in their quasibound state as a molecular Bose-Einstein condensate, described by a coherent field $\phi_2(\mathbf{x},t)$ in addition to the field $\phi_1(\mathbf{x},t)$ describing the atomic condensate. Two further condensate components are considered: the molecules in the intermediate electronically excited state of the coherent Raman transition and the molecules in the final state, described by $\phi_3(\mathbf{x},t)$ and $\phi_4(\mathbf{x},t)$, respectively. The evolution of the mixed condensate system is described by a four-state model, governed by coupled field equations [13,3,11]:

$$ih \phi_1 = U_0 |\phi_1|^2 \phi_1 + 2 \alpha \phi_1^* \phi_2,$$

$$ih \phi_2 = \left( e_x - i \frac{\gamma_0}{2} \right) \phi_2 + \alpha \phi_2^* + \frac{i}{2} h \Omega_{L1} \phi_3,$$

$$ih \phi_3 = \left( e_x - i \frac{\gamma_{sp} - \hbar \omega_{L1}}{2} \right) \phi_3 + \frac{1}{2} h \Omega_{L1} \phi_2 + \frac{1}{2} h \Omega_{L2} \phi_4,$$

$$ih \phi_4 = \left( e_x - \hbar \omega_{L1} + \hbar \omega_{L2} \right) \phi_4 + \frac{1}{2} h \Omega_{L2} \phi_3,$$

with uniform amplitudes $\phi_j = n_j \exp(i \theta_j)$ over the volume of the condensate. Here, in the notation of Ref. [11], $U_0 = 4 \pi \hbar^2 a_s / m$ is the off-resonant strength of the condensate self-energy with $a_s$ the background scattering length, the $\alpha$ terms describe the process that converts atoms into quasibound molecules, and $e_x - (i/2) \gamma_0 = [B(t) - B_0] \Delta \mu - (i/2) \gamma_0$ is the complex energy of the quasibound state including its short-range width $\gamma_0$ for decay inside the quantum reflection region [11]. Similarly, $e_x - (i/2) \gamma_{sp}$ is the complex excited-state energy with $\gamma_{sp}$ the spontaneous decay width and $\gamma_{sp}$ the energy of the final bound molecular state. The coupling between the $\phi_3$ and $\phi_4$ condensates is induced by laser L1, and that between $\phi_3$ and $\phi_4$ by laser L2 (laser frequencies $\omega_{L1}$, intensities $I_{L1}$, and Rabi frequencies $\Omega_{L1}$, with $i=1$ and 2). We take the laser fields to propagate in the same direction and to be in Raman resonance with the final state: $h(\omega_{L1} - \omega_{L2}) = \varepsilon_x$. In these circumstances the atomic recoil is negligible [7]. Furthermore, we choose equal linear laser polarizations perpendicular to the magnetic field.

As an example we focus on the situation of the experiment in Ref. [10] and consider a condensate of Na atoms in the lowest hyperfine state $|f,m_f\rangle = |1,1\rangle$. It is kept in an optical trap and subjected to a magnetic field varied over one of the Feshbach resonances at 853 G or 907 G in the direction of increasing field strength. The 853-G resonance is the most favorable choice, since its decay rate $\gamma_0 / \hbar$ is roughly a factor of 100 smaller [11]. We therefore continue with this choice. The Raman transition is taken to occur via the electronically excited bound state of $\Omega$ symmetry that connects asymptotically to the $S_{1/2} + S_{1/2}$ dissociation limit. We select the rovibrational ground state $\langle v, l \rangle = (0,0)$ of the final molecule in the Na+ Na triplet potential (combined electron spin $S = 1$), with spin structure $(S, M_S, L, M_L) = (1, 1, 3, +, 1)$, identical to that of the quasibound state [14]. Combining these two electronic ground states with a $(J, I, M_I) = (2, 3, +)$ excited state leads to a favorable combination of $\Omega_{L1}$ and $\Omega_{L2}$ Rabi frequencies.

We assume that the rovibrational relaxation of molecular states due to atom-molecule and molecule-molecule collisions has a relatively small effect compared to the $\gamma_0$ decay. We have verified that assumption for the collisions between atoms and quasibound molecules by adding a term $hG |\phi_1|^2$ to $\gamma_0$ with $G$ the rate coefficient. To very good approximation $G$ is equal to the value $4 \times 10^{-10}$ cm$^3$ s$^{-1}$ for the 907-G resonance, extracted from experiment [10] in Ref. [11]. Note that the molecular states 3 and 4 are not susceptible to rovibrational relaxation.

The $\alpha$ and $\Omega$ terms describe coherent intercondensate exchanges of atom pairs and play a role analogous to the coupling terms in the field equations for a coexisting mixed-condensate system of atomic $^{87}$Rb hyperfine components [15]. The values of the $\alpha$ and $\Omega$ parameters are obtained by a full quantum scattering calculation for static B and static laser intensities, taking into account the relevant subspaces of unbound ground-state atoms, and bound excited and ground states. All laser couplings between these subspaces are taken into account to arbitrary order, as well as a spontaneous emission decay width for the excited state. We emphasize that Eq. (1), with the appropriate values of the parameters, reproduces the results of the full quantum scattering calculation in the static case [16].

We first determine the Rabi frequency $\Omega_{L1}$ of laser L1 by setting the second laser intensity to zero, performing effectively a one-color photoassociation (PA) experiment. In Fig. 2 we show the static photoassociation signal as a function of the excited-state energy $\varepsilon_x$. The coupled-channels calculation is done for two cases: one for a magnetic-field value close to resonance and the other off resonance. In agreement with the Franck-Condon principle, the maxima and minima correspond to the oscillations of the ground-state radial wave function squared. Clearly, the Feshbach resonance enhances the signal by seven orders of magnitude. Especially the
deeper $0^+_g$ states perform well since in a nonresonant case they have a poor Frank-Condon overlap. The PA signal can be described in a straightforward way by an analytical two-state model following from Feshbach’s resonance theory [5] for the quasibound state and the excited state. The inelastic transition probability is then given by

$$|S_{PA}|^2 = \frac{1}{4} \gamma_{sp} \gamma_{sb} \hbar^2 \Omega_{L1}^2 \left[ \lambda_2 \lambda_3 - \frac{1}{4} \hbar^2 \Omega_{L1}^2 \right]^2 + \frac{1}{4} \hbar^2 \gamma_{sp} \lambda_2^2,$$

with $\lambda_2 = \varepsilon_2 - E$, $\lambda_3 = \varepsilon_3 - E - \hbar \omega_{L1}$, and $\gamma_{sb}/\hbar$ the long-range decay rate of the quasibound state to outside the quantum reflection region [11], which decreases strongly with decreasing collision energy. A comparison with the coupled-channels result for $|S_{PA}|^2$ allows us to derive $\Omega_{L1}$.

As can be seen in Fig. 2, the PA signal and thus $\Omega_{L1}$ show a strong decrease for deeper excited-state levels, reflecting the fast radial oscillations of the quasibound state for small $r$. For similar reasons the Rabi frequency $\Omega_{L2}$, coupling the excited state with the $(\nu,l)=(0,0)$ ground state, shows an increase for the deeper $\varepsilon_3$ levels. This leads us to select the $J=2$ state at $\varepsilon_3 = -1346$ cm$^{-1}$ as a favorable compromise, with an associated outer turning point $r= 13.7 \alpha_0$. As Fig. 2 shows, the one-color PA signal is in a Franck-Condon maximum at this value of $\varepsilon_3$. We find $\Omega_{L1} = 1.07 \times 10^6$ s$^{-1} \sqrt{I_{L1} \text{(W/cm}^2\text{)}}$. This is a very satisfactory result taking into account the loss rate $\gamma_0/\hbar = 0.69 \times 10^6$ s$^{-1}$.

In a similar way, the second Rabi frequency is determined by setting $I_{L1}$ and $\gamma_0$ to zero. This isolates the bound-bound two-level system. We find $\Omega_{L2} = 1.12 \times 10^6$ s$^{-1} \sqrt{I_{L2} \text{(W/cm}^2\text{)}}$. Considering the spontaneous emission rate $\gamma_{sp}/\hbar = 6 \times 10^7$ s$^{-1}$, it should be possible to transfer a sizable fraction of the excited state into the ground state. Let us consider an experiment with equal Rabi frequencies $\Omega_{L1} = \Omega_{L2} = 34 \times 10^6$ s$^{-1}$ ($I_{L1} = 1000$ W/cm$^2$, $I_{L2} = 905$ W/cm$^2$), zero detunings, and a magnetic field ramp speed $\dot{B} = 0.31 \times 10^{-2}$ G/μs, for which a 60% transfer of atoms to the quasibound state occurs in the MIT experiment [10–12]. We consider a tailored time dependence of the laser intensities with a sequence of stimulated Raman adiabatic passage (STIRAP [17]) Raman laser pulses. With a sequence of seven pulses, a 3% conversion efficiency can be obtained. This result can be improved [11] by turning to a negative magnetic-field ramp $\dot{B} = -0.31 \times 10^{-2}$ G/μs, thus avoiding the $\gamma_0$ decay term in Eq. (1), since the $\varepsilon_3$ state is then below threshold. In Fig. 3 the solution of the coupled field equations (1) is shown for this case. We note that in this case the atom-molecule collisions remain as the only decay process for the $\phi_2$ state. A conversion of about 20% of the

FIG. 2. Probability $|S_{PA}|^2$ of the photoassociation transition for two Na atoms with collision energy of 1 nK, prepared in the $|f,m_f=1,+,1\rangle$ state. (a) Result close to the $B_0=853$ G resonance, calculated for $B-B_0=0.0004$ G. (b) Off-resonant result for $B=800$ G.

FIG. 3. Solution of coupled condensate field equations (1) for sequence of seven Raman pulses separated by 2.5 μs and positioned around time instant $t=0$ at which $B$ crosses the resonant value $B_0$. (a) Field ramp. (b) Time-dependent Rabi frequencies of transition 1 and transition 2 (indistinguishable in figure). In each pulse the laser intensities have a Gaussian time dependence (FWHM=0.28 μs) with the L1 signal following the L2 signal after 0.04 μs. Maximum laser intensities: $I_{L1} = 1000$ W/cm$^2$, $I_{L2} = 905$ W/cm$^2$. Figures (c) to (f) show the time-dependent solutions for the density $n_1$ of the atomic condensate, and the densities $n_2$, $n_3$, $n_4$ of the molecular condensates. Initial atomic density $n_1=5.2 \times 10^{14}$ cm$^{-3}$ [10].
atomic condensate is achieved, including the (relatively small) reduction due to this decay.

Once a condensate of molecules is obtained, the remaining atoms can be removed by switching off the optical trap and replacing it by a magnetic trap. This will push out the strong-field seeking atoms and trap the molecules in their weak-field seeking \((S, M_s) = (1, +1)\) state. After the removal of the atoms, the remaining decay rate due to molecule-molecule collisions can be reduced by an expansion of the trap potential.

During the 16 years of struggle to realize a BEC of atoms, the main obstacle was the instability due to inelastic processes in collisions. In the case of molecules, stability will certainly also be a vital issue. With the molecules produced in the \(v = l = 0\) state we avoid rovibrational relaxation, the main decay channel for the weakly bound molecules (lifetime of the order of tens of microseconds). To avoid also the inelastic exchange channels, we propose to fully stretch the electronic and nuclear spins by a weak-field rf or Raman transition. What remain are the dipolar two-body decay and the three-body recombination with rates comparable to those for atomic condensates. Interestingly, an additional single-molecule decay channel is the radiative decay to the lower singlet \((S=0)\) states induced by the electronic spin-orbit coupling. We estimate the decay rate to be small: of order \(0.01\) s\(^{-1}\) for Rb\(_2\) and even slower for Na\(_2\). The formation of Na\(_2\) molecules will be an improbable process with a small overlap of initial and final states. Details of the stability problem will be described elsewhere [18]. We expect the final BEC of molecules to be as stable as the present atomic condensates.

The Bose-Einstein condensation of diatomic alkali-metal molecules will open a subject of intense theoretical and experimental study. Compared to the existing atomic condensates with their internal spin states, molecular condensates will add the feature of new internal degrees of freedom of a spatial type: the rotational and vibrational excitations. It will be possible to study their interplay with the spin degrees of freedom. In this connection we note that the Feshbach + Raman approach can be used to create (superpositions of) higher rovibrational states with comparable or even better conversion rates. This should allow a stable multicompont condensate system of a new type.

Another fascinating possibility would be to apply the above Feshbach + Raman technique to a degenerate gas of fermionic atoms in two different hyperfine components to allow \(s\)-wave collisions to take place. The freedom in the choice of experimental parameters within our scheme might enhance the formation of just the types of correlations that occur in a Bose condensate of Cooper pairs. Finally, Feshbach resonances in molecule-molecule scattering could be used also more generally in Feshbach catalyzing the binding of like and unlike molecules in a (multipspecies) condensate to engineer condensates of heavier molecules.

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[8] Even the population of a weakly bound state is rather inefficient due to the proximity of the laser frequencies to atomic resonance and the excitation of the atomic condensate by the second laser [D. Heinzen (private communication)].
[16] With the relatively slow microsecond Feshbach field sweep, the depletion of the correlation function in the atomic condensate at short range plays a minor role [M. Holland et al., e-print cond-mat/0005062 (2000), and private communication].