

Coherent Transients in the Femtosecond Photoassociation of Ultracold Molecules

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We demonstrate the photoassociation of ultracold rubidium dimers using coherent femtosecond pulses. Starting from a cloud of ultracold rubidium atoms, electronically excited rubidium molecules are formed with shaped photoassociation pump pulses. The excited state molecules are projected with a time-delayed probe pulse onto molecular ion states which are detected in a mass spectrometer. Coherent transient oscillations of the excited state population are observed in the wings of the pump pulse, in agreement with the time-dependent solution of the Schrödinger equation of the excitation process.

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Recent years have witnessed dramatic developments in the production and control of molecular quantum gases [1–4]. Experimental and theoretical research is driven by the quest to create ultracold molecular gases in well-defined internal states [5,6] and to use quantum interferences to steer reactions at vanishing entropy [7]. An increasing number of theoretical proposals investigate new approaches on the photoassociation of ultracold molecules by tailored femto- and picosecond laser pulses [8–10]. This emerging field combines the physics of quantum gases at ultralow temperatures with the highly successful methods of coherent control using phase- and amplitude-shaped laser pulses [11]. The proposed advantages range from increased efficiency using chirped pulses [8] and utilizing molecular wave packet dynamics for transferring atomic pairs to close internuclear separations [9] to fully coherent formation and stabilization of strongly bound molecules in their electronic ground state [10,12]. These investigations are also of conceptual relevance in the context of coherent control of chemical reactions, as they involve pairs of colliding particles populating states in the continuum [13].

Despite the increasing interest, there are only a few experiments combining the regimes of the ultracold and the ultrafast. The interaction of ultracold molecules with femtosecond laser pulses is reported in Refs. [14,15]; Fatemi *et al.* [16] report the association of ultracold molecules by picosecond laser pulses. Here we present a feasibility study on the coherent formation of molecules from colliding pairs of ultracold atoms by shaped femtosecond laser pulses. In a pump-probe scheme indicated in Fig. 1, we find evidence for photoassociation of excited molecules by the ultrashort pump pulse and reveal the effect of the pulse shape on the ultracold molecule formation dynamics.

An ultracold gas of 10^8 ^{85}Rb atoms is stored in a background vapor loaded magneto-optical dark spontaneous-force optical trap (SPOT) [17] at a temperature of ≈ 100 μK . Densities of 10^{11} cm^{-3} are achieved with 90% of the atoms in the $F = 2$ ground hyperfine state.

Femtosecond pulses with a 100 kHz repetition rate and energies of 4 μJ are produced by a Coherent RegA 9050 Ti:sapphire laser. For the photoassociation pump pulses, a beam containing 10% of the output power is directed through a zero dispersion double grating pulse shaper, in which their spectral composition and phase are manipulated with a liquid crystal modulator (CRI, SLM-640). The pump pulse center frequency is tuned to $12\,500\text{ cm}^{-1}$ (800 nm), 79 cm^{-1} below the $5s + 5p_{1/2}$ dissociation limit. Because of its large bandwidth (390 cm^{-1} FWHM), the pulse spectrum reaches far to the blue of the potential asymptote. For optimal photoassociation efficiency, high spectral intensity proximately below the

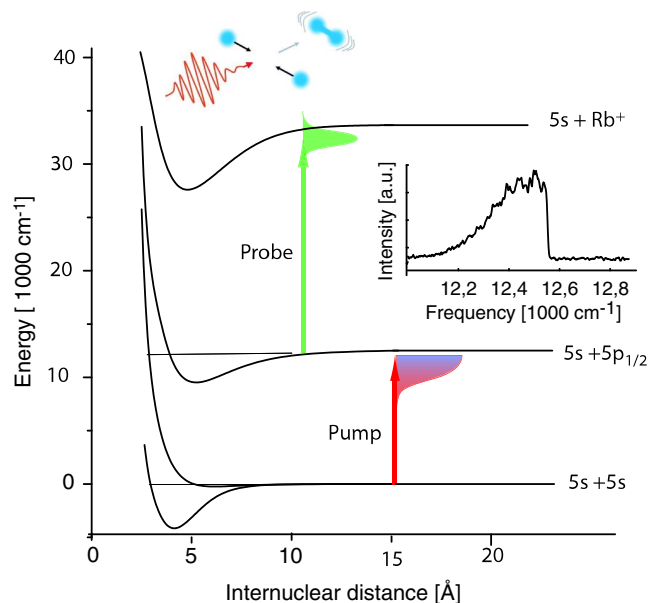


FIG. 1 (color online). Photoassociation and detection of ultracold molecules in a pump-probe scheme using ultrashort laser pulses. Pulse shaping restricts the femtosecond pump pulse spectrum to below the molecular potential asymptote (inset).

dissociation limit is desirable, but spectral density at the atomic resonances has to be minimized as it strongly reduces pair density due to trap loss and radiation shielding. Therefore, an optical low-pass filter is applied to the pulse spectrum (see inset in Fig. 1), which is realized by a physical edge in the Fourier plane of the pulse shaper. This edge blocks all frequencies above an adjustable cutoff, which is set a few wave numbers below the $5s + 5p_{1/2}$ dissociation limit. The resulting frequency cutoff has a resolution of 1.5 cm^{-1} , and its spectral position is adjusted by moving the edge with a precision stage. Its absolute frequency is calibrated with respect to the atomic transition by measuring the trap fluorescence as a function of the cutoff frequency.

The pump pulse is followed by a probe pulse with a defined, variable delay of a few picoseconds to excite molecular pairs from the $5s + 5p_{1/2}$ state to just below the molecular ion dissociation limit at $33\,690 \text{ cm}^{-1}$. It is produced from the remainder of the RegA output power using a noncollinear optical parametric amplifier (NOPA) [18]. The probe pulse frequency is centered at $20\,160 \text{ cm}^{-1}$, with 1000 cm^{-1} FWHM bandwidth and an output power of 50 nJ per pulse. The probe beam passes an optical delay stage and is then collinearly overlapped with the photoassociation pump beam. Autocorrelation measurements of the pulses give 180 fs FWHM for the pump pulses and about 600 fs for the NOPA probe pulse. After passing a focusing lens, the pump and probe pulses have peak intensities of 2.5×10^4 and $1.4 \times 10^3 \text{ MW/cm}^2$, respectively, with waists of 100 and $120 \text{ }\mu\text{m}$.

Atomic and molecular ions produced in the trap are extracted from the trap by a constant electric field of 40 V/cm and mass selected by an rf quadrupole mass spectrometer before they are detected with single-ion detection efficiency. Excited state molecules created by the trapping laser fields (detuned from the $5s + 5p_{3/2}$ asymptote) are also ionized and detected with this technique and contribute a constant background at a molecular count rate of a few hundred hertz, which is independently measured and subtracted from the pump-probe signals.

Figure 2(a) shows pump-probe spectra of the molecular ion intensity as a function of the delay time between the pulses. They reveal characteristic behavior under variation of pulse delay and cutoff detuning from the $5s + 5p_{1/2}$ asymptote. When the probe precedes the pump pulse (negative delays), a constant signal of Rb_2^+ ions of typically $300\text{--}400 \text{ Hz}$ is detected. Near zero delay, when both pulses coincide in time, the molecular count rate increases swiftly, forming a peak of 0.5 ps width. When the pump is followed by the probe pulse (positive delays), an increased level of molecular ions is observed which is modulated by distinctive oscillations of a few picoseconds period. The frequency of the modulation perfectly matches the cutoff detuning from the potential asymptote if both are expressed in the same units [see inset in Fig. 2(a)]. With increasing detuning, the signal rapidly decreases

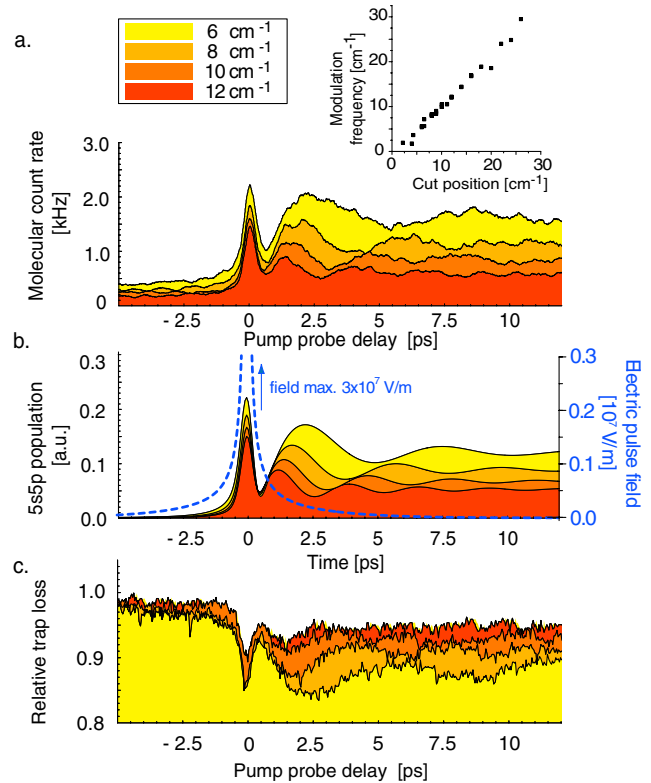


FIG. 2 (color online). (a) Experimental pump-probe signal of molecular ions for different cut positions below the $5s + 5p_{1/2}$ asymptote. Curves correspond to cutoff detunings from -6 (yellow) to -12 cm^{-1} (red) in steps of -2 cm^{-1} . A constant background of molecular ions at a rate of 310 Hz , which originates from the ionization of excited state molecules formed by the trap light, is subtracted from the data. The inset shows the variation of modulation frequencies in wave numbers versus the cutoff detuning. (b) $5s + 5p_{1/2}$ population from quantum dynamical simulation of the pump excitation with shaped femtosecond pulses. The dashed blue line shows the temporal envelope of the pump pulse electric field below $3 \times 10^6 \text{ V/m}$. (c) Fluorescence signal of the trapped Rb atoms as a function of the pump-probe delay. Signals are normalized to the trap fluorescence without femtosecond lasers.

for all delays, and the modulation oscillates with shorter periods.

Two competing mechanisms have to be considered that could potentially contribute to the molecular ion signal. One is the pump-probe ionization of molecules in the electronic ground state, formed by trapping light [19]. When changing the parameters of the dark SPOT, we find that the pump-probe signals follow the change of the atomic trap density on the $F = 3$ population and do not correlate with the variation of molecules formed by the trap light, which was measured using resonantly enhanced multiphoton ionization [19]. Another process that can result in the formation of molecular ions is the associative autoionization in collisions between rubidium atoms in ground and Rydberg states. A rate estimation for this indirect process, based on a capture model and experimen-

tal rate coefficients [20], limits its contribution to less than 20% of the observed rates. We conclude that the observed molecular ion signal at positive pump-probe delay times reflects predominantly the femtosecond photoassociation of atom pairs.

The delay-dependent modulations in the molecular count rate cannot be explained by wave packet motion in the excited state potentials as the time scales for such dynamics are a factor of 10 longer than the observed periods. To understand the observed signals, simulations of the pump-excitation step were performed by solving the time-dependent Schrödinger equation for a system of two diatomic interaction potentials [$^1\Sigma_g^-(5s + 5s)$ and $0_u^+(5s + 5p_{1/2})$], which are coupled by a time-dependent light field. The pump pulse electric field amplitude and phase were derived from the Fourier transform of a cut pulse spectrum matching the one used in the experiments. The Schrödinger equation was then solved numerically using a mapped Fourier grid Hamiltonian method [21], yielding the molecular dynamics on both electronic manifolds. The simulation results for the $5s + 5p_{1/2}$ population show good agreement with the experimental pump-probe data from $t = 0$ onwards, as depicted in Fig. 2(b). The peak at $t = 0$, the level increase, and the oscillations at positive delays are well reproduced.

The simulations indicate that the oscillatory modulation stems from the interaction of the molecular electronic dipole with the time-dependent light field of the pulse. Because of the spectral cut employed in the experiment, the pump pulse temporal profile strongly deviates from the transform-limited pulse shape. The temporal pulse envelope consists of a central maximum of 200 fs FWHM. The important modification of the temporal profile by the cutoff is the occurrence of long tails on the pulse envelope [see Fig. 2(b)], which reach out to a few picoseconds on both sides of the maximum. Within these tails, the light field oscillates with the frequency at the spectral cutoff. The simulations show that the molecular population in the $5s5p_{1/2}$ state occurs by nonlinear, off-resonant excitation into long range states that are strongly favored by high Franck-Condon factors and which lie closer than 0.01 cm^{-1} below the dissociation limit. The population of vibrational levels within the spectral window of the pulse, which would dominate in the perturbative limit, is negligible here. Therefore, the driven molecular dipole oscillates at a frequency very close to the atomic resonance frequency. The modulation on the photoassociation signal arises from the coherent energy exchange of the molecular dipole with the optical field in the tails of the pulse. The resulting beat frequency thus matches the cutoff detuning [inset in Fig. 2(a)].

These coherent molecular transients are closely related to the induced dipole dynamics observed for atoms by Monmayrant, Chatel, and Girard [22]. In fact, similar coherent transients in the atomic excitation are responsible for a reduction of the atomic fluorescence signal observed

in our experiments [see Fig. 2(c)]. The decrease in fluorescence reflects a delay-dependent loss rate of the trapped atoms induced by probe pulse, due to direct ionization or excitation and subsequent inelastic collisions. As the modulations in atom loss and molecular ion signal are highly correlated, one may thus interpret these signals as an indication of two closely linked processes in the interaction of a femtosecond laser pulse with an atomic vapor: The atoms coherently exchange energy with the laser field, resulting in atom loss induced by the probe pulse, while a small fraction of atom pairs at close distances is actually photoassociated to weakly bound states by the femtosecond pump pulse, resulting in the molecular ion signal.

To investigate control schemes for the femtosecond photoassociation process, we have applied linear frequency chirps to the pump pulses. Figure 3 shows pump-probe traces for $\pm 25\,000 \text{ fs}^2$ at a cutoff detuning of 8 cm^{-1} and the corresponding trace for unchirped pulses. As indicated by the dashed lines, the applied chirp induces a phase shift of the transient oscillation without changing the oscillation period. In addition, the Rb_2^+ signal for large pump-probe delay times is similar in magnitude for both positive and negative chirps and smaller than in the zero chirp case. These findings are in good agreement with the time-dependent quantum calculations. The different chirps lead to a faster or slower phase change of the electric field of the pulse compared to the induced molecular dipole, which leads to the smaller population transfer compared to zero chirp. No enhancement of the population for chirped pulses is observed, in contrast to results obtained with

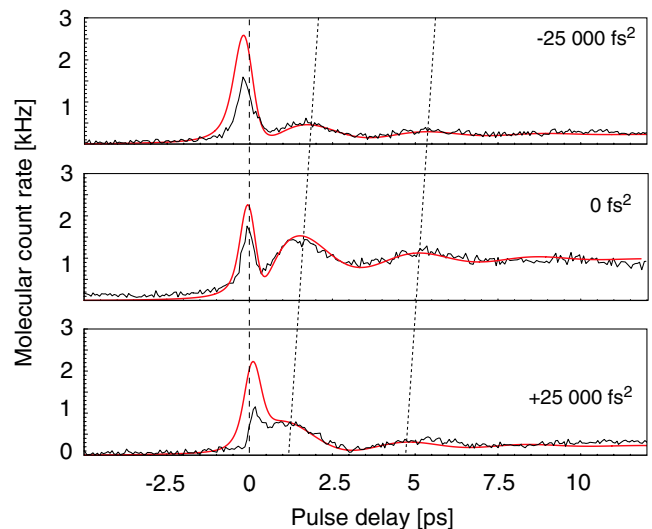


FIG. 3 (color online). Measured femtosecond pump-probe photoassociation traces (black curve) for three different chirp settings of the pump pulse. Chirp is found to shift the phase of the transient oscillation leading to a smaller population in the excited molecular state at large delay times. Good agreement is found with the solution of the time-dependent Schrödinger equation depicted as the gray (red) curve. As in Fig. 2, a background count rate of 350 Hz is subtracted from the data. The calculated curves are scaled to fit the experimental data.

chirped nanosecond pulses [23]. This difference is caused by the nonlinear, off-resonant excitation of a molecular wave packet near the dissociation limit in the present experiment, which does not move on the time scale of the pulse.

A clear deviation between simulations and experiments in Fig. 2 is found at negative delays, where a nonvanishing rate of molecular ions is detected. Photoassociation by the green pulse can be ruled out; the molecules therefore have to be formed by the red femtosecond pulse. Furthermore, the signal at negative delays is strictly correlated to the molecular count rate at positive delays (related to excited state molecules) at a ratio of 1:3, which is constant over a broad range of cutoff positions and pump pulse energies. This correlation suggests that the molecular ions detected at negative delays originate from ultracold molecules which are created by the preceding femtosecond pulse. As the experiment runs at a 100 kHz repetition rate, only cold molecules in the electronic ground state can be present in the interaction volume after the 10 μ s delay. These ground-state molecules are then near-resonantly ionized by a green-red pair of pulses via intermediate states below the $5s + 4d$ asymptote. As a possible explanation for the occurrence of ground-state molecules correlated to the femtosecond excitation of molecules from free atomic pairs, the simulation predicts a coherent population of ground-state molecules within the pump pulse by Raman processes. However, the formation rate is smaller than the excited state population rate by roughly 3 orders of magnitude. Therefore, it appears to be more realistic that the ground-state molecules are formed by spontaneous decay of the femtosecond excited molecules.

Two conclusions for the perspectives of forming ultracold molecules with shaped femtosecond laser pulses can be drawn from the experiments presented here. First, by appropriately shaping femtosecond laser pulses, and thus suppressing resonant components, atomic pairs can be coherently excited in a dilute ultracold gas leading to the formation of weakly bound molecules. Only a minor fraction of the frequency bandwidth of the ultrashort pulse is actually involved due to the unfavorable Franck-Condon overlap between the free atomic pair and the bound molecular state. As mainly states close to the dissociation threshold are excited, the coherent dynamics strongly resembles the dynamics recently observed for atoms [22]. Starting from magnetoassociated molecules will allow one to create wave packets involving vibrational states which are more deeply bound. Second, due to the femtosecond time scales of the pulses, the motion of the molecular wave packet has negligible influence on the observed dynamics, even for strongly chirped pulses. Therefore, shaped pulses at picosecond time scales need to be applied to implement coherent control schemes for photoassociation, which requires the development of shaping techniques for small-bandwidth laser pulses. Alternatively, the application of

coherent trains of femtosecond pulses represents a promising approach for the coherent control of ultracold molecule formation.

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- [1] E. A. Donley, N. R. Claussen, S. T. Thompson, and C. E. Wieman, *Nature (London)* **417**, 529 (2002).
- [2] S. Jochim, M. Bartenstein, A. Altmeyer, G. Hendl, S. Riedl, C. Chin, J. H. Denschlag, and R. Grimm, *Science* **302**, 2101 (2003).
- [3] M. Greiner, C. A. Regal, and D. S. Jin, *Nature (London)* **426**, 537 (2003).
- [4] M. W. Zwierlein, C. A. Stan, C. H. Schunck, S. M. F. Raupach, S. Gupta, Z. Hadzibabic, and W. Ketterle, *Phys. Rev. Lett.* **91**, 250401 (2003).
- [5] J. M. Sage, S. Sainis, T. Bergeman, and D. DeMille, *Phys. Rev. Lett.* **94**, 203001 (2005).
- [6] K. Winkler, F. Lang, G. Thalhammer, P. v. d. Straten, R. Grimm, and J. Hecker-Denschlag, *Phys. Rev. Lett.* **98**, 043201 (2007).
- [7] R. Krems, *Int. Rev. Phys. Chem.* **24**, 99 (2005).
- [8] J. Vala, O. Dulieu, F. Masnou-Seeuws, P. Pillet, and R. Kosloff, *Phys. Rev. A* **63**, 013412 (2000).
- [9] C. P. Koch, E. Luc-Koenig, and F. Masnou-Seeuws, *Phys. Rev. A* **73**, 033408 (2006).
- [10] A. Peer, E. A. Shapiro, M. C. Stowe, M. Shapiro, and J. Ye, *Phys. Rev. Lett.* **98**, 113004 (2007).
- [11] M. Shapiro and P. Brumer, *Principles of the Quantum Control of Molecular Processes* (Wiley, New York, 2003).
- [12] U. Poschinger, W. Salzmann, R. Wester, M. Weidemüller, C. Koch, and R. Kosloff, *J. Phys. B* **39**, S1001 (2006).
- [13] V. Zeman, M. Shapiro, and P. Brumer, *Phys. Rev. Lett.* **92**, 133204 (2004).
- [14] W. Salzmann, U. Poschinger, R. Wester, M. Weidemüller, A. Merli, S. M. Weber, F. Sauer, M. Plewicky, F. Weise, and A. M. Esparza *et al.*, *Phys. Rev. A* **73**, 023414 (2006).
- [15] B. L. Brown, A. J. Dicks, and I. A. Walmsley, *Phys. Rev. Lett.* **96**, 173002 (2006).
- [16] F. Fatemi, K. M. Jones, H. Wang, I. Walmsley, and P. D. Lett, *Phys. Rev. A* **64**, 033421 (2001).
- [17] C. G. Townsend, N. H. Edwards, K. P. Zetie, C. J. Cooper, J. Rink, and C. J. Foot, *Phys. Rev. A* **53**, 1702 (1996).
- [18] J. Piel and E. Riedle, *Opt. Lett.* **31**, 1289 (2006).
- [19] C. Gabbanini, A. Fioretti, A. Luchesini, S. Gozzini, and M. Mazzoni, *Phys. Rev. Lett.* **84**, 2814 (2000).
- [20] L. Barbier and M. Cheret, *J. Phys. B* **20**, 1229 (1987).
- [21] K. Willner, O. Dulieu, and F. Masnou, *J. Chem. Phys.* **120**, 548 (2004).
- [22] A. Monmayrant, B. Chatel, and B. Girard, *Phys. Rev. Lett.* **96**, 103002 (2006).
- [23] M. J. Wright, J. A. Pechkis, J. L. Carini, S. Kallush, R. Kosloff, and P. L. Gould, *Phys. Rev. A* **75**, 051401 (2007).