

**Coherent control with shaped femtosecond laser pulses applied to ultracold molecules**

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We report on coherent control of excitation processes of translationally ultracold rubidium dimers in a magneto-optical trap by using shaped femtosecond laser pulses. Evolution strategies are applied in a feedback loop in order to optimize the photoexcitation of the  $\text{Rb}_2$  molecules, which subsequently undergo ionization or fragmentation. A superior performance of the resulting pulses compared to unshaped pulses of the same pulse energy is obtained by distributing the energy among specific spectral components. The demonstration of coherent control to ultracold ensembles opens a path to actively influence fundamental photoinduced processes in molecular quantum gases.

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**I. INTRODUCTION**

The interest to study interactions in ultracold molecular gases [1] is propelling various research programs to produce and trap dense ultracold molecular ensembles [2–7]. The goals and perspectives in this field range from quantum computation [8] and quantum scattering [9] to ultrahigh precision spectroscopy [10] and coherent ultracold chemistry [11]. The manipulation of molecular wave packet dynamics with shaped femtosecond (fs) pulses may open exciting possibilities to this field. In recent years, the control of molecular processes by shaped fs laser pulses through application of evolution strategies in a feedback loop has attained considerable success. Since it was proposed [12], coherent control with shaped femtosecond laser pulses has been applied to a large variety of experiments, i.e., selective fragmentation [13], population transfer [14], ionization [15], and high harmonic generation [16]. By using an iterative process, the method enables the discovery of an optimal laser pulse shape which drives the system towards a desired target state. It even became possible to decipher the molecular dynamics underlying the laser-molecule interaction by analyzing the optimal pulse shapes [15,17].

Theoretical work on photoassociation with pulsed lasers has started several years ago [18] and experiments with thermal mercury atoms in a gas cell [19] and with sodium atoms in a magneto-optical trap [20] have been performed. More recently, optimal control calculations were done proposing efficient ultracold molecule formation [21] and vibrational cooling [22] by appropriately shaped laser pulses. However, up to now there are no experimental results on the application of feedback-controlled optimization to photoassociation or manipulation of ultracold molecules. In this paper we

present experimental steps towards this goal by investigating the interaction of femtosecond laser pulses with ultracold ground state molecules in view of a pulsed photoassociation experiment. The low temperature of the atomic and molecular sample, while not directly influencing the interaction with the femtosecond pulses, leads to molecules in very high lying vibrational levels and allows us to study molecules under the same conditions of typical photoassociation experiments. In this work we demonstrate, in particular, the enhancement of the electronic excitation and subsequent fragmentation of ultracold molecules from a magneto-optical trap using shaped femtosecond laser pulses, which were adaptively optimized by an evolutionary algorithm.

**II. EXPERIMENTAL SETUP**

In our experiment, schematically depicted in Fig. 1, about  $10^7$   $^{85}\text{Rb}$  atoms are captured in a magneto-optical trap (MOT) at a density of  $10^{10}$  atoms/cm<sup>3</sup> and a temperature of 100  $\mu\text{K}$ . Diatomic rubidium molecules continuously form in the magneto-optical trap due to either three body collisions or light assisted two-body collisions of trapped Rb atoms. They populate predominantly the highest vibrational states below the dissociation limit in the triplet electronic ground state [23,24]. These  $\text{Rb}_2$  molecules, which are not trapped by the trap magnetic field, are detected in this experiment via resonant two photon ionization and time-of-flight mass analysis. The ionization laser is a 15 Hz Nd:yttrium-aluminum-garnet (YAG) pumped dye laser at wavelengths between 600 and 610 nm, a spectral width of 0.5  $\text{cm}^{-1}$ , and a pulse energy of 20 mJ. In the steady state of molecule formation and loss a maximum count rate of 0.5  $\text{Rb}_2^+$  molecular ions per laser pulse is observed, measured at a wavelength of 602.5 nm.

The fs laser pulses are generated in a Ti:sapphire oscillator (Tsunami; Spectra Physics) that provides pulses of 120 fs duration [full width at half maximum (FWHM)] at a rate of 80 MHz, a spectral width of  $\Delta\lambda = 10$  nm, and an energy of up

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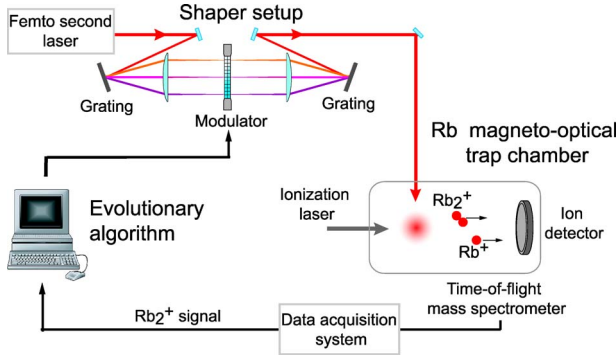


FIG. 1. (Color online) Experimental setup for iterative closed-loop maximization of ultracold  $\text{Rb}_2$  excitation from the ground electronic singlet or triplet states by shaped femtosecond laser pulses. The ultracold molecules are formed in a magneto-optically trapped gas of rubidium atoms. The laser pulse shapes represent individuals of an evolutionary algorithm. Their fitness is evaluated by the reduction of the  $\text{Rb}_2^+$  signal resulting from resonantly enhanced photoionization of the  $\text{Rb}_2$  molecules.

to 18 nJ/pulse. Low pulse energies ensure that the laser-molecule interaction is well described in a perturbative picture and no high intensity effects have to be considered. To modify the spectral components of the pulses we use a pulse shaper that allows independent phase and amplitude modulation [25]. It consists of a liquid crystal modulator (CRI; SLM-256) [26] with  $2 \times 128$  pixels, placed in the Fourier plane of a double grating zero dispersion compressor. A lens focuses the beam to a spot of  $150 \mu\text{m}$  diameter at the center of the trap, illuminating about 10% of the cloud volume. For the experiments the fs laser is tuned in the range between 780 and 820 nm.

### III. LASER-INDUCED LOSS

Transform-limited fs pulses with wavelengths near the Rb resonance lines and focused into the MOT are found to strongly interact with the trapped atoms, as observed through a significant decrease of MOT fluorescence. At small pulse energies, the trap loading rate outside the femtosecond beam can partly compensate for the losses in the focus, resulting in an area of reduced fluorescence predominantly where the beam is passing, whereas for high energies the trap is completely depleted. We attribute this to photon scattering from the femtosecond pulses, which causes an outward directed light force on the atoms, leading to trap loss. The effect is significantly stronger when the  $D2$  atomic resonance at 780 nm was part of the pulse spectrum than for the  $D1$  resonance at 795 nm, reflecting the higher transition dipole moment of the  $D2$  line. A narrow slit, representing a bandpass of 0.3 nm width, is scanned through the Fourier plane of the pulse shaper, which showed that only components resonant with the  $D1$  and  $D2$  atomic transitions are responsible for this effect. Singly charged rubidium ions have been detected when the central pulse frequency was resonant with one of the atomic transitions, indicating that resonant three-photon ionization contributes to the loss of atoms from the MOT. To study the laser pulse interaction with rubidium molecules,

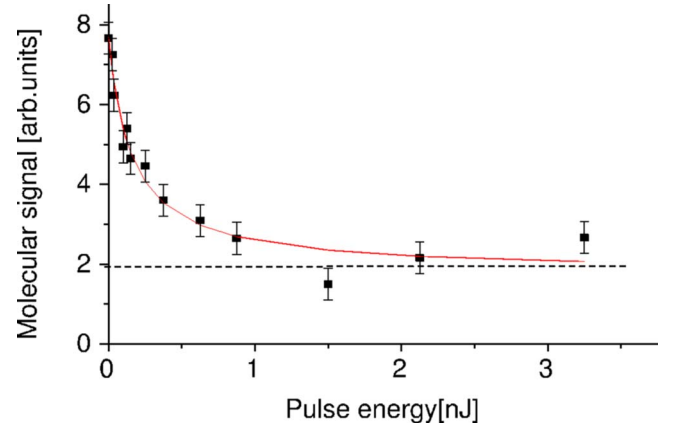


FIG. 2. (Color online) Reduction of the  $\text{Rb}_2^+$  molecular ion signal as a function of energy of transform limited femtosecond pulses. The pulses have a central wavelength of 800 and 10 nm FWHM. The  $D1$  atomic resonance at 795 nm is filtered out of the pulse. The ionization laser for REMPI is set to 602.5 nm. The solid curve represents a fit to a single photon excitation model as described in the text.

the atomic resonance components were removed from the pulse spectrum by a notch filter, realized by a physical block in the shaper's Fourier plane. In this way atomic losses from the MOT could be reduced below the detection threshold.

The rubidium dimers interact with the fs laser pulses over the entire accessible range of central wavelengths from 780 to 820 nm. As shown in Fig. 2, the molecular signal decreases rapidly at small pulse energies and levels off to 25% at a pulse energy of 0.6 nJ. As only molecules in the electronic ground state are detected, the signal reduction can be attributed to excitation by the fs pulses. The process can be modeled by a simple rate equation for the number of detected ground state molecules

$$\frac{dN_{\text{Mol}}}{dt} = R_{\text{form}} - (\Gamma_{\text{fs}} + \Gamma_{\text{loss}})N_{\text{Mol}}, \quad (1)$$

where  $R_{\text{form}}$  is the production rate of molecules from trapped atoms,  $\Gamma_{\text{fs}}$  is the rate of molecular loss induced by interaction with the femtosecond laser, and  $\Gamma_{\text{loss}}$  the molecular loss rate induced by other processes such as rest gas collisions or gravitation accelerating the molecules out of the detection volume. In the steady state  $dN_{\text{Mol}}/dt=0$  the number of molecules is given by

$$N_{\text{Mol}} = \frac{R_{\text{form}}}{\Gamma_{\text{loss}} + \Gamma_{\text{fs}}}. \quad (2)$$

The curve in Fig. 2 represents a fit to the data assuming a linear dependence of  $\Gamma_{\text{fs}}$  on the pulse energy of the laser, i.e.,  $\Gamma_{\text{fs}} \propto P_{\text{fs}}$ . The assumption of a quadratic or higher order dependence of the excitation rate on pulse energy does not fit the data. This indicates that, in the regime of pulse energies employed in the experiment, the interaction with the molecules has the character of an effective one-photon excitation [27].

According to Ref. [23], the molecules in the MOT initially populate the highest levels in the  $a^3\Sigma_u^+$  state. Due to

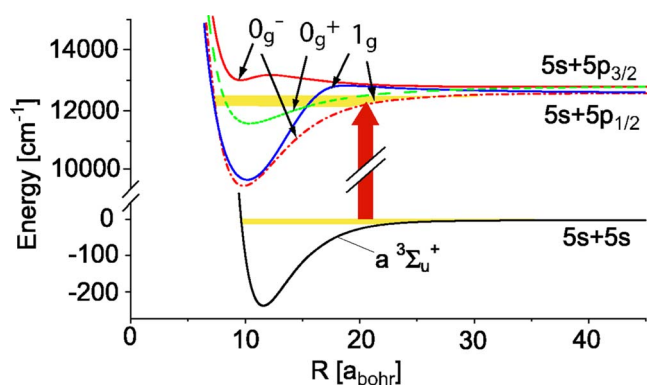


FIG. 3. (Color online) Potential curves of the rubidium dimer including spin-orbit interaction. Initially, the molecules are expected to populate the highest levels in the  $a^3\Sigma_u^+$  [23,24]. The molecular excitation by the femtosecond pulses is indicated by the arrow. The shaded areas show the initial and final distribution of molecular vibrational states.

selection rules and Franck-Condon factors, they are preferably excited to the  $0_g^-$  and  $1_g$   $5s5p_{1/2}$  states (see Fig. 3). Emission back into the electronic ground state could only lead to signal reduction if the vibrational level population moves out of the excitation window of the ionization laser. However, scans of the detection laser with and without fs beam show reduced but qualitatively similar spectra which should not be the case for a vibrational redistribution. Instead it can be expected that excited molecules absorb further photons, so the whole process of molecular loss can be regarded as a resonance enhanced multiphoton excitation, followed by dissociation, predissociation, or ionization. This happens either within one pulse, or, as the laser repetition rate is comparable to the lifetime of the first excited state, it occurs in the subsequent pulse. At high energies all molecules in the laser focus are excited or dissociated and the residual signal in Fig. 2 is due to molecules which did not interact with the femtosecond laser, indicated by the dashed line. This shows that most of the molecules are produced within a small volume inside the MOT which is consistent with the picture that they form at the MOT center where the atom number density is at its maximum [28].

#### IV. APPLICATION OF COHERENT CONTROL

In order to demonstrate the practical applicability of coherent control concepts to ultracold molecules, the  $\text{Rb}_2^+$  signal acts as an input for a self-learning optimization algorithm which autonomously programs the pulse shaper in a closed loop experiment. The algorithm is based on evolution strategies and is described in detail in Ref. [29]. Because of the small molecular ion count rate and hence the low signal-to-noise ratio the signal is averaged over 128 dye laser pulses for each individual of the algorithm. To reduce the search space for the learning algorithm we chose a mixed scheme of parametric amplitude and free phase optimization where the algorithm tries to find the optimal pulse shape under the restriction that only a few sharp spectral peaks contribute to the pulse shape. During an optimization the parameters of

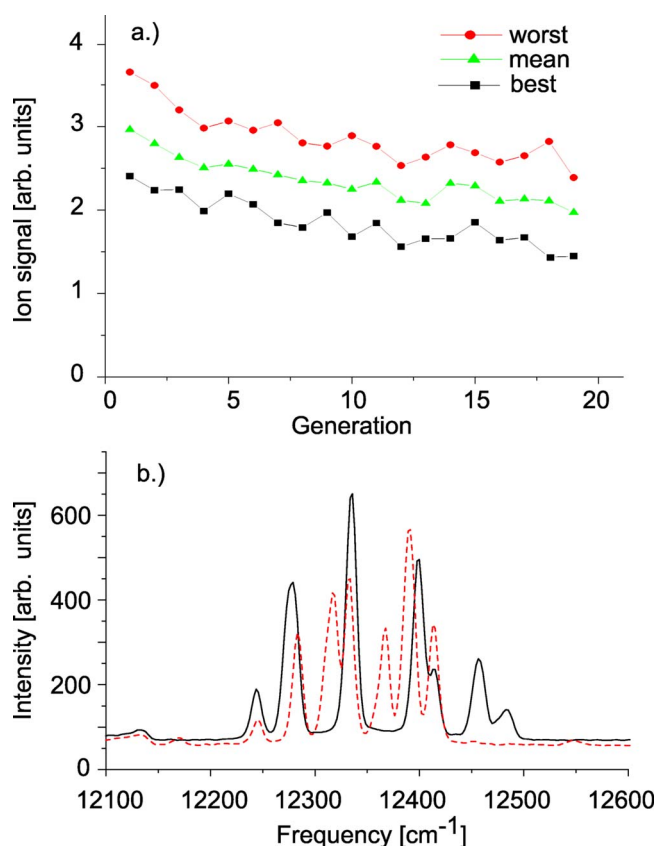


FIG. 4. (Color online) (a) Molecular ion signal resulting from the best, the worst, and the mean individual of the population for each generation during a closed loop experiment. (b) Femtosecond laser pulse spectrum of the final best individuals of two successive optimization runs under equal conditions with similar final optimization result.

these peaks, their spectral positions and amplitudes, are altered to find the most efficient excitation pulse. Moreover, the phase was optimized freely in order to allow a temporal modulation of the pulse. The evolutionary algorithm administers 31 individuals, each representing the pulse shaper parameters to produce pulses consisting of up to 11 Gaussian peaks of  $7 \text{ cm}^{-1}$  FWHM.

The adaptive algorithm was applied to manipulate the excitation pulses with the aim to minimize the molecular signal from the MOT. For each iteration the ion signals corresponding to the best and worst individuals are protocoled together with the mean fitness of the whole generation. As depicted in Fig. 4(a), all three signals decrease during the particulate optimization to about 70% of the initial value after 20 iterations. The spectra of the final best individuals of two successive runs shown in Fig. 4(b) display several peaks which coincide in some but not all spectral positions. The frequency span of the fs pulse supports our assignment of excitation to the  $0_g^-$  and  $1_g$   $5s5p_{1/2}$  states (see Fig. 3). By comparing the excitation yield of the best individuals with transform-limited pulses of the same energy it is observed that the optimized pulse excites the molecules on average 25% more efficiently, which demonstrates the feasibility and potential of adaptive control.

We attribute the observed excitation enhancement to an increased spectral intensity at particular molecular resonances found by the evolutionary algorithm. Starting from a narrow band in the  $a^3\Sigma_u^+$  state [23,24], molecules are excited into bound states below the  $D1$  resonance. By shifting the peak positions, the algorithm finds transition frequencies from this band to certain vibrational states, thereby sharing the pulse energy more efficiently than a broad Gaussian pulse. The algorithm therefore has a large number of possible solutions to choose from and so the final pulse shapes after an optimization are not identical. In the spectral region between 12 000 and 12 500  $\text{cm}^{-1}$ , the vibrational level separation is about 10  $\text{cm}^{-1}$  in the  $0_g^-$  and  $1_g$   $5s5p_{1/2}$  states, respectively. The high density of states also explains the limited potential of the optimization because the optimization factor depends on the chosen peak width which is limited by the shaper resolution. The Franck-Condon factors may also be relevant for the excitation process since they differ for different vibronic transitions and favor particular frequencies which are enhanced in the experimentally acquired spectra. Yet, as the initial ground state population distribution in the vibrational states is not known accurately, no quantitative treatment or assignment can be made.

## V. CONCLUSIONS

In this paper we demonstrate the application of iterative adaptive control techniques to the manipulation of ultracold molecules. The minimization of molecular signal from a rubidium magneto-optical trap results in pulse shapes that significantly excite more  $\text{Rb}_2$  molecules than transform-limited pulses of the same energy. The resulting pulse spectra are not unambiguous because of the large number of possible opti-

mal solutions within the experimental accuracy. For future applications of shaped fs pulses in photoassociation experiments, the dissociative effect of the pulses has to be suppressed. On the one hand, photoassociated cold molecules may be dissociated by subsequent femtosecond pulses due to the high repetition rate of the femtosecond laser system. Therefore, photoassociated molecules have to be detected directly after their formation by increasing the repetition rate of the detection system, ideally matching the rate of the photoassociating beam. On the other hand, the excitation of ground state molecules may be coherently suppressed while enhancing the molecule formation through actively shaping the pulses. For this purpose, we currently theoretically investigate realistic scenarios for femtosecond photoassociation of cold molecules by numerically simulating the dynamical behavior of an atom pair interacting with an arbitrarily shaped electromagnetic field. It is also envisioned to use specifically shaped femtosecond laser pulses for the cooling of vibrational molecular excitations by pump-dump processes via an intermediate excited state. This approach could be applied to produce quantum-degenerate molecular gases in arbitrary vibrational states or superpositions of states.

*Note added in proof.* We recently became aware of similar studies in the group of I. Walmsley [30].

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