

Correlation dynamics after short-pulse photoassociation

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Two atoms in an ultracold gas are correlated at short inter-atomic distances due to threshold effects where the potential energy of their interaction dominates the kinetic energy. The correlations manifest themselves in a distinct nodal structure of the thermal density matrix at short inter-atomic distances. We suggest pump-probe spectroscopy to probe these pair correlations: A suitably chosen, short photoassociation laser pulse excites part of the atomic pair density to an electronically excited state. This depletes the ground state pair density in the range of distances for which the resonance condition is fulfilled, creating a non-stationary wave packet in the electronic ground state. The dynamics of this non-stationary wave packet describing the two-body correlations is monitored by a time-delayed probe pulse. We discuss the choice of pulse parameters and experimental feasibility of this pump-probe spectroscopy of two-body correlations.

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I. INTRODUCTION

The simplest description of Bose-Einstein condensation (BEC) considers an ensemble of indistinguishable particles all in the same quantum state [1]. Such a picture leads to a mean-field representation of the many-body wave function as a direct product of the single-particle wave functions. This framework has been successful in describing many aspects of BEC physics. Mean-field approaches neglect two-body correlations which arise due to the long range interaction between two particles. In a microscopic theory, pair correlations can be incorporated explicitly by expanding the many-body wave function in cumulants [2] or correlation functions [3, 4]. Can one envision directly measurable consequences of these inter-atomic correlations? This question is the subject of the current study.

Photoassociation [5] combining two atoms to form a molecule with laser light, takes place at the same inter-atomic distances where correlations are significant. At ultralow temperatures, photoassociation spectroscopy with continuous-wave (cw) lasers is sensitive to the position of the nodes of the scattering wave function describing two colliding atoms [6]. The scattering wave function corresponds to the reduced pair wave function characterizing the two-body correlations up to a normalization factor [3]. The observed modulation in the spectroscopic features therefore serves as a probe of the static inter-atomic correlations. If one is to measure two-body correlations *dynamically*, the experiment has to generate a non-stationary initial state. This can be achieved by interaction with an external field which is fast relative to the ensuing dynamics. Here we suggest to employ the short-pulse photoassociation scenario [7, 8] to generate a non-stationary initial state by a pump pulse and to fol-

low its dynamics by a probe pulse. The idea is based on impulsive excitation where a selected part of the ground state probability density is suddenly removed to the excited potential energy surface [9], cf. Fig. 1. As a result the ground state phase space density is no longer stationary. The void in the ground state probability density is termed the dynamical 'hole'. The impulsive ex-

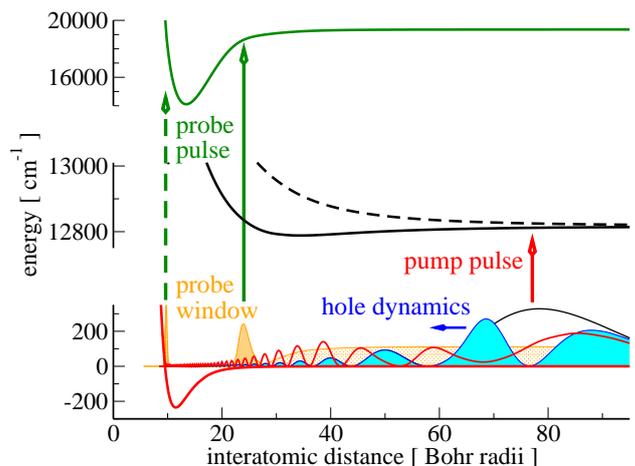


FIG. 1: (Color online) Pump-probe spectroscopy of the dynamical hole: A photoassociation pump pulse excites population from the ground state to the first excited state, leaving a hole in and transferring momentum to the ground state wave function. The wave functions are depicted before the pulse (black line), at $t_{max} + 24$ ps, i.e. just after the pulse (blue filled) and at $t_{max} + 126$ ps (red line). For red detuned pump pulses, the hole is accelerated toward shorter distances which leads to an enhancement of population at short R . A suitably time-delayed REMPI probe pulse can measure this population enhancement. The effect of the probe pulse is modelled by a window operator (shown in orange) where different shapes reflect different probe central frequencies. Another option (not shown) is to choose the same central frequencies for pump and probe, requiring an additional REMPI pulse.

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citation by the pump pulse also transfers momentum to the ground state wave function. The 'hole' dynamics are monitored by a suitably time-delayed probe pulse, detecting the enhancement of ground state density at a specific location by resonantly enhanced multi-photon ionization (REMPI), cf. Fig. 1.

As in any stroboscopic measurement, the pump and probe pulse are required to act on a timescale shorter than the observed dynamics [9, 10]. The correlations in ultracold atomic gases are due to threshold effects, where the kinetic energy of the colliding atoms is smaller or equal to the potential energy. The timescale of the correlations is related to the period of the last bound level, $T_{vib} \approx 2\pi\hbar \frac{\partial v}{\partial E}$, or to the scattering length a_S , $\tau \approx \mu a_S / \hbar k$ [7]. For the example of ^{87}Rb with a scattering length of $\approx 100 a_0$, the correlation timescale is typically of the order of 100 ps to 1000 ps. This timescale defines an upper limit to the pulse duration. A lower limit results from the broad spectral bandwidth of very short pulses. A broad-band excitation smears the dynamical 'hole' over a large range of distances, hampering precise control of the 'hole' location. The optimal photoassociation pulse is therefore a compromise between impulsive excitation and sharp spectroscopic features.

Previous studies of pulsed photoassociation emphasized cold molecule formation [7, 8, 11–14]. Here we exploit the insight gained in these studies to construct a spectroscopic probe of the two-atom correlation dynamics. The choice of the pulse parameters controls the location and the momentum of the dynamical 'hole' [11, 15]. It can be analyzed by projecting onto the stationary energy eigenfunctions. From this viewpoint, the pump pulse redistributes the initial scattering state to bound molecular levels and other scattering wave functions. The 'hole' location is determined by the detuning from the atomic resonance [11]. The momentum of the 'hole' can be controlled by proper chirp parameters [15, 16] and by the choice of an attractive or repulsive potential of the electronically excited state [17].

Considerable experimental effort has already been devoted to photoassociation with short laser pulses. Early experiments were carried out at room temperature in mercury vapor [18]. In the ultracold regime, first experiments aimed at femtosecond photoassociation of rubidium dimers have led to dissociation of molecules created by the trap lasers rather than association [19, 20]. Recently, evidence of coherent formation of molecules in the electronically excited state was provided in a pump-probe experiment with chirped femtosecond laser pulses [21]. The proven experimental ability of pulsed photoassociation paves the way for constructing pump-probe spectroscopy to study ultracold two-atom correlation dynamics.

The paper is organized as follows. Section II introduces the theoretical description of the excitation by the pump pulse and 'hole' dynamics in a two-state picture as well as the model of the probe pulse absorption by a window operator. The effect of the pump pulse is studied

in Section III, and the observation of the 'hole' dynamics is detailed in Section IV. Section VI concludes.

II. MODEL

We consider two scattering atoms interacting via the electronic ground potential. The center of mass motion is integrated analytically and omitted from this description. For sufficiently low temperatures only *s*-wave encounters are considered. The ground surface supports both bound levels and scattering states. A stationary initial state is considered. For a BEC this state can be well approximated by a scattering state [3, 4] with momentum determined by the chemical potential. For a thermal state the initial state is a thermal mixture of scattering states [22]. In both cases the two body correlation decay at long interatomic distance. In a BEC the decay is caused by the emergence of other many body correlations. In the thermal ensemble thermal averaging leads to decay of the correlation. This means that for both cases the simulation can be based on an initial scattering state with a finite cutoff in internuclear distance. A photoassociation laser couples the electronic ground state to an electronically excited state where the potential can be either repulsive or attractive, cf. Fig. 1.

A. Excitation by a pump pulse and dynamics

The time-dependent Schrödinger equation is solved for two electronic states,

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{\mathbf{H}} |\psi(t)\rangle \quad \text{and} \quad \langle R | \psi(t) \rangle = \begin{pmatrix} \psi_g(R; t) \\ \psi_e(R; t) \end{pmatrix}$$

with the Chebychev propagator [23]. The Hamiltonian in the rotating-wave approximation reads

$$\hat{\mathbf{H}} = \begin{pmatrix} \hat{\mathbf{T}} + V_g(\hat{\mathbf{R}}) & \hat{\boldsymbol{\mu}} E_0 S(t) \\ \hat{\boldsymbol{\mu}} E_0 S^*(t) & \hat{\mathbf{T}} + V_{exc}(\hat{\mathbf{R}}) - \hbar\Delta_L \end{pmatrix}, \quad (1)$$

where $\hat{\mathbf{T}}$ denotes the kinetic energy, $V_{g/exc}$ the ground and excited state potential energy curve, and $\hat{\boldsymbol{\mu}}$ the transition dipole operator. Since the excitation occurs at long range, the *R*-dependence of $\hat{\boldsymbol{\mu}}$ can be neglected.

The pulse parameters appearing in Eq. (1) are E_0 corresponding to the maximum field amplitude, a slowly varying shape of the laser pulse $S(t)$, taken to be Gaussian, and the detuning Δ_L . The latter is given in terms of the atomic resonance line and the central laser frequency, $\Delta_L = \omega_{at} - \hbar\omega_L$. The pulse energy is calculated from the maximum field amplitude and transform-limited full-width half-maximum (FWHM) τ ,

$$\mathcal{E} = \epsilon_0 c \sqrt{\pi} \frac{r^2 E_0^2 \tau}{2 \ln 2}$$

with ϵ_0 the electric constant, c the speed of light and r the radius of the laser beam ($r = 100\mu\text{m}$ is assumed throughout this work).

For blue detuning ($\Delta_L > 0$) excitation into the uppermost repulsive potential correlating to the $5s + 5p_{3/2}$ asymptote, the $0_g^+(5s + 5p_{3/2})$ state, is assumed. For red detuning ($\Delta_L < 0$), V_{exc} is taken to be the $0_g^-(5s + 5p_{3/2})$ state, well-known for its purely long-range attractive well. In both cases, V_g corresponds to the lowest triplet well. In both cases, V_g corresponds to the lowest triplet state, $a^3\Sigma_u^+(5s + 5s)$. The potentials at short range are found in [24, 25]. They are connected to analytical long-range dispersion potentials ($C_3/\hat{R}^3 + C_6/\hat{R}^6 + C_8/\hat{R}^8$ with coefficients taken from [26, 27].

The Hamiltonian is represented on a Fourier grid with variable step size [28–30]. Our grid extends to about $R_{\text{max}} = 28000 a_0$. This ensures that no reflection of the wave packet at the outer boundary of the grid occurs: Within 10 ns, the fastest wave packet components occurring in our simulations reach about $R = 800 a_0$.

B. Modelling the absorption of the probe pulse by a window operator

In order to avoid a separate calculation for each pump-probe time delay, the total absorption is represented by a window operator $\hat{W}(\hat{R})$ [31, 32],

$$\Delta E = -\hbar\omega_L \Delta N_g \approx -\hbar\omega_L \langle \psi_g(t) | \hat{W}(\hat{R}) | \psi_g(t) \rangle,$$

with

$$\hat{W}(\hat{R}) = \pi(\tau_p E_{p,0})^2 e^{-2\hat{\Delta}^2(\hat{R})\tau_p^2} \cdot \hat{\mu}_p^2(\hat{R}). \quad (2)$$

The window operator contains the probe pulse parameters FWHM τ_p and maximum field amplitude $E_{p,0}$. The probe pulse central frequency determines the difference potential,

$$\hat{\Delta}(\hat{R}) = V_p(\hat{R}) - V_g(\hat{R}) - \hbar\omega_p$$

with $V_p(\hat{R})$ denoting the potential which is accessed by the probe. The R -dependence of the transition dipole moment $\hat{\mu}_p$ is neglected. The physical concept of the window operator is to collapse the observation process which is completed in a time proportional to the probe pulse duration τ_p to a single instant in time t_p . The finite width in time which corresponds to a finite width in frequency $\Delta\omega$ (the bandwidth of the pulse) transforms into a finite width in coordinate via the resonance condition given by the electronic potentials. This collapse of the measurement process assumes that the nuclear motion is frozen during the observation, i.e. the excitation is impulsive, and the window operator \hat{W} is independent of the state of the system [32].

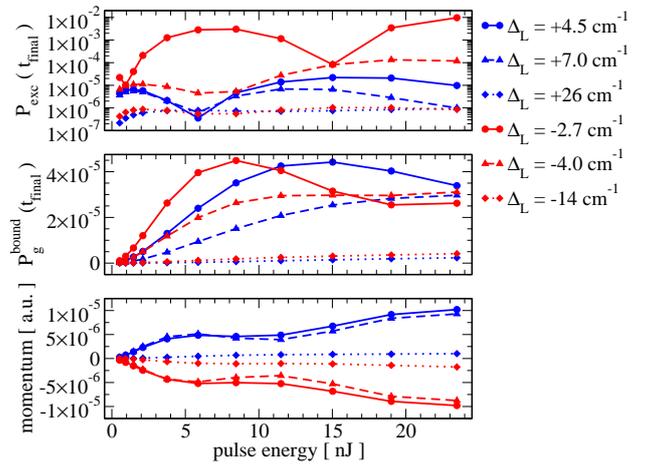


FIG. 2: (Color online) The effect of the pump pulse: Population transfer to the excited state (top), formation of ground state molecules (middle) and momentum kick (bottom). Shown are the excited state population (top), the population in bound levels of the electronic ground state (middle) and the ground state momentum (bottom) after the pump pulse is over as a function of the pulse energy. Different detunings are compared with corresponding Condon radii of $90 a_0$ (circles), $78 a_0$ (triangles), and $50 a_0$ (diamonds).

III. INDUCING THE CORRELATION DYNAMICS BY EXCITATION WITH THE PUMP PULSE

The photoassociation pump pulse transfers population to the electronically excited state, cf. upper panel of Fig. 2. For small and medium detuning, Rabi oscillations are observed in the population transfer to the excited state, $P_{\text{exc}}(t_{\text{final}})$. The difference between the data for $\Delta_L = -2.7 \text{ cm}^{-1}$ and all other curves is explained by excitation of the atomic resonance: the amplitude of a 10 ps pulse is still sufficiently large at zero detuning to excite population. The pump pulse does not only transfer population to the excited state, it has also an effect on the ground state wave function, creating the hole and transferring momentum, cf. lower panel of Fig. 2. The hole corresponds to population of both bound levels and higher energy scattering states, i.e. to the formation of ground state molecules and hot atom pairs. The population of bound levels is shown in the middle panel of Fig. 2. For small and medium detuning, molecules are formed mostly in the last bound level, $v = 40$ (between 90% and 99%). The small amount of initial population near the Condon radius is the limiting factor for the population of bound levels at large detuning. In that case, molecules in the last three levels are formed, with 55% to 65% in the level $v = 39$. These levels can be thought of as making up the hole, i.e. they determine the hole dynamics. The bound population decreases at large pulse energies for small detuning. This is due to power broadening, i.e. population residing at the 'right' distance is transferred to continuum states rather than to bound levels.

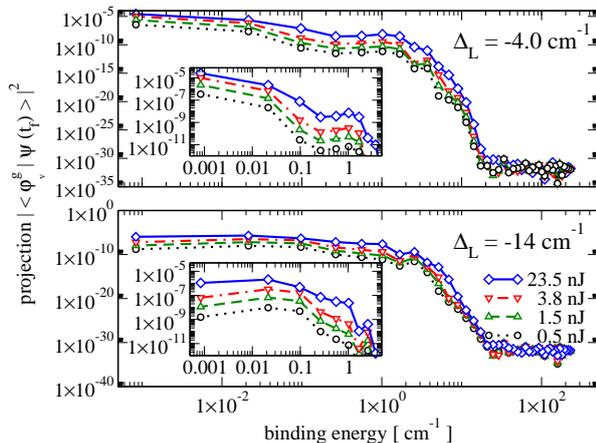


FIG. 3: (Color online) Formation of ground state molecules due to the pump pulse. Shown is the projection of the final-time wave packet onto the bound ground state vibrational levels for two red detunings.

The momentum expectation value of the ground state wave function after the pulse is shown in the bottom panel of Fig. 2. For blue detuning, the hole is accelerated toward larger distances, while for red detuning dynamics toward shorter distances occur (as indicated in Fig. 1). Population enhancement at short distance which is measured by the probe pulse can therefore only be expected for red detuning.

While some bound levels are populated, population transfer occurs also into continuum states, and the overall energy of the wave function is changed due to the interaction with the pump pulse. For red detuning, an increase in energy is always observed, while for blue detuning a decrease in energy occurs for medium and large detuning at large pulse energies. The projection of the wave packet onto the bound ground state vibrational levels after the pulse is shown in Fig. 3 for red detuning ($\Delta_L = -4 \text{ cm}^{-1}$). The vibrational distribution will be used to interpret the time-dependent signals for weak-field excitation. Dynamical signatures of the levels with binding energy of 1 cm^{-1} and less are expected. The corresponding vibrational periods are between 59 ps and 3 ns.

IV. OBSERVATION OF THE CORRELATION DYNAMICS BY THE PROBE PULSE

The probe pulse measures the two-atom amplitude at a certain range of distances. The dynamics are unraveled by varying the delay time between pump and probe pulse. Two-atom correlations may be detected by probing the molecular part of the ground state wave function. Detection of weakly bound ground state molecules has been developed in the context of photoassociation experiments using cw excitation [33]. It is based on resonantly enhanced multi-photon ionization. In the following, two

different detection schemes are explored.

(i) The dynamics of the hole can be probed when it arrives at short internuclear distance in the inner region of the potential. This implies the two-photon ionization scheme that has been utilized before in photoassociation experiments to detect molecules in the lowest triplet state [25]. The resonant enhancement is provided by the $^3\Sigma_g^-(5s + 4d)$ state, cf. Fig. 1, i.e. the probe pulse has a central frequency that is different from the pump pulse. Assuming ionization from the $^3\Sigma_g^-(5s + 4d)$ intermediate state to be saturated, the detection is determined solely by the Franck-Condon factors between the lowest triplet and the intermediate states. This is reflected by the corresponding difference potential that enters the window operator, Eq. (2).

(ii) Alternatively, the hole can be probed at the position of its creation. A possible REMPI scheme consists of overlapping a probe pulse that has the same central frequency as the pump pulse with another pulse ionizing from the $0_g^-(5s + 5p_{3/2})$ excited state. Such an ionization scheme has been utilized before in femtosecond photoassociation experiments to detect excited state molecules [21]. Assuming the detection to be determined by the probe pulse, the difference potential of the $0_g^-(5s + 5p_{3/2})$ and the lowest triplet states enters the window operator.

In the second detection scheme, one needs to ensure that the excited state wave packet that is created by the pump pulse does not interfere with the density that is excited by the probe pulse. This can be achieved by sending another ionization pulse simultaneously with the pump pulse such that any initial excited state density is immediately eliminated from the sample. The overall pump-probe scheme consists therefore of two time-delayed pulse pairs, pump + ionization pulse followed by probe + ionization pulse. Since all pulses just address wave packet density in a certain range of internuclear distances, no phase relation of the four pulses is required.

A. Probing the hole at short and intermediate distances

Since the excitation by the pump pulse leads to a redistribution of the ground state probability, the hole contains a part corresponding to bound molecules and a part corresponding to hot atoms. Overall, the hole is accelerated toward short distances for red detuning of the pump pulse. The signal is therefore expected to consist of two parts: At early times, a large peak reflects the arrival of both molecular and hot atomic density in the probe window. After the first reflection at the inner turning point of the potential, the hot atomic density leaves the short-range distances. Only the molecular part continues to move within the range of the potential. Small oscillations reflect the motion of the molecular part at later observation times.

This behavior is indeed observed in the time-dependent expectation value of the window operator modelling the

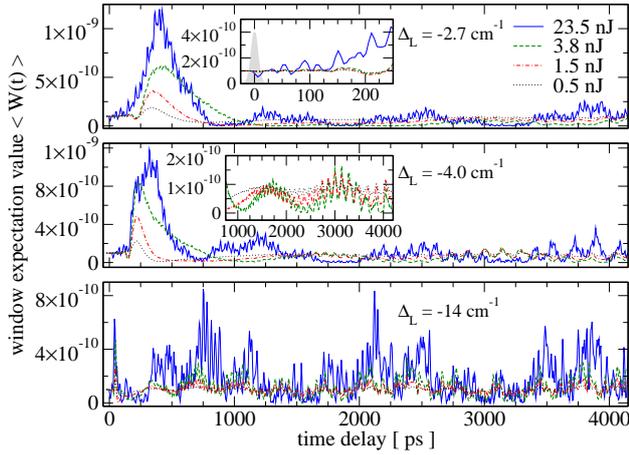


FIG. 4: (Color online) Probing the dynamical hole near the inner turning point: The time-dependent expectation value of the window operator is plotted for different energies and detunings of the pump pulse and a probe wavelength of 680 nm (window localized around $R = 10 a_0$).

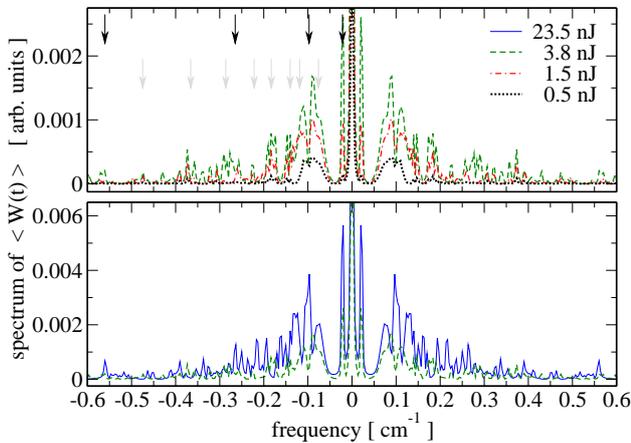


FIG. 5: (Color online) Spectrum of the time-dependent expectation value of the window operator (middle panel of Fig. 4, i.e. $\Delta_L = -4 \text{ cm}^{-1}$ and a probe window around $R = 10 a_0$). The black arrows indicate the position of ground state vibrational levels, the grey arrows some of the beat frequencies between different vibrational levels.

probe pulse absorption in Figs. 4 and 6. $\langle \hat{W}(t) \rangle$ is shown as a function of the pump-probe delay for probe wavelengths of 680 nm with 20 nm bandwidth and of 518.5 nm with 1 nm bandwidth, respectively. The spectra of these signals are obtained by filter-diagonalization [34, 35], a method allowing to accurately extract frequencies from just a few oscillation periods. The spectra of the probe signals of the middle panels of Figs. 4 and 6 are shown in Figs. 5 and 7.

For the probe measurement at $R = 10 a_0$ ($\omega_P = 680 \text{ nm}$), cf. Fig. 4, an enhancement of the signal by a factor up to 10 is observed at short delay times. The enhancement is larger for smaller pump pulse detuning since more population is excited creating a larger hole,

cf. Fig. 2. It is due to the accelerated population which contains both bound and continuum parts. At longer delay times, only the bound part of the wave packet returns to $R = 10 a_0$. This part of the dynamics is characterized by a large oscillation with overtones. It can be analyzed in terms of the vibrational periods of the molecular levels making up the bound part of the wave packet. The oscillation period corresponds to the vibrational period of the last, respectively last but one, level, cf. Fig. 3. The frequency of the long-term oscillations increases with pump pulse detuning. This may be rationalized in terms of the vibrational distributions, cf. Fig. 3.

The overtones represent a beating between the different vibrational levels making up the hole. This becomes evident in Fig. 5 where the spectrum of the probe signal is plotted for the detuning $\Delta_L = -4 \text{ cm}^{-1}$ and different energies of the pump pulse. The solid arrows indicate the spectral positions of the ground state vibrational levels, except for the last bound level which is too close to zero to be visible ($E_{\text{bind}}^{\text{last}} = 8.4 \times 10^{-4} \text{ cm}^{-1}$ or 25 MHz). Of the remaining levels, the second to last level at $E_{\text{bind}}^{\text{last-1}} = 2.1 \times 10^{-2} \text{ cm}^{-1}$ draws the highest peak for weak pump pulses in accordance with the vibrational distribution, cf. lower panel of Fig. 3. In the weak-field regime, upper panel of Fig. 5, the peaks in the spectrum appear at the same positions for different pump pulse energies. Increasing the pulse energy leads to more population in the lower lying vibrational levels and hence additional features, i.e. beat frequencies, appear in the spectrum. The strong-field and weak-field regime are compared in the lower panel of Fig. 5. At a pump pulse energy of 23.5 nJ, Rabi cycling occurs and significantly more momentum is transferred to the ground state wave packet than for 3.8 nJ, cf. lower panel of Fig. 2. This results in a shift of the spectral peak positions, cf. the solid blue and dashed green lines in the lower panel of Fig. 2: For strong field, so much energy is pumped into the system that the dynamics is not easily unraveled in terms of a decomposition into field-free vibrational periods.

The overall probe signal is much larger for a measurement at $R = 24 a_0$ ($\omega_P = 518.5 \text{ nm}$) than for one at $R = 10 a_0$ ($\omega_P = 680 \text{ nm}$). However, the *relative* enhancement is significantly smaller, cf. Fig. 6. Since the measurement occurs at larger distances, there is ground state amplitude initially within the probe window, cf. Fig. 1, leading to a strong background. The pump pulse cycles population which shows up as a dip in the probe signal around zero delay, cf. Fig. 6. Due to the shape of the potentials, the probe window is much broader for $\omega_P = 518.5 \text{ nm}$ than for $\omega_P = 680 \text{ nm}$ for the same probe spectral bandwidth. The oscillations and overtones at large delays are therefore less clearly resolved for $\omega_P = 518.5 \text{ nm}$. Similarly to Fig. 4, larger pump pulse detuning leads to faster oscillations and larger pump pulse energy to a stronger signal in Fig. 6.

The probe spectra for a measurement at $R = 24 a_0$ ($\omega_P = 518.5 \text{ nm}$) and a pump pulse detuning of $\Delta_L = -4 \text{ cm}^{-1}$ are analyzed in Fig. 7. The signal background

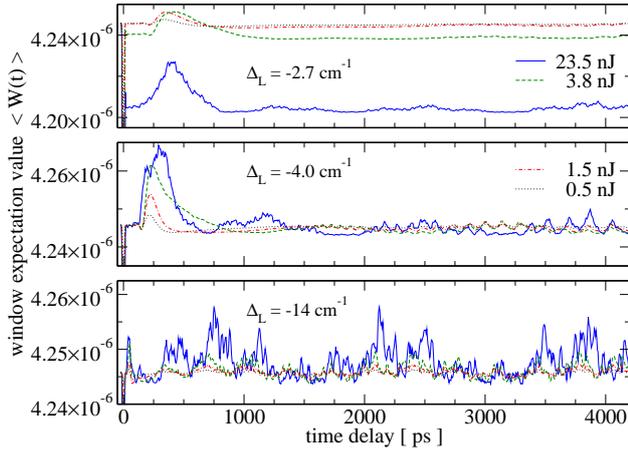


FIG. 6: (Color online) Probing the dynamical hole at intermediate distances: The time-dependent expectation value of the window operator is plotted for different energies and detunings of the pump pulse and a probe wavelength of 518.5 nm (window localized around $R = 24 a_0$).

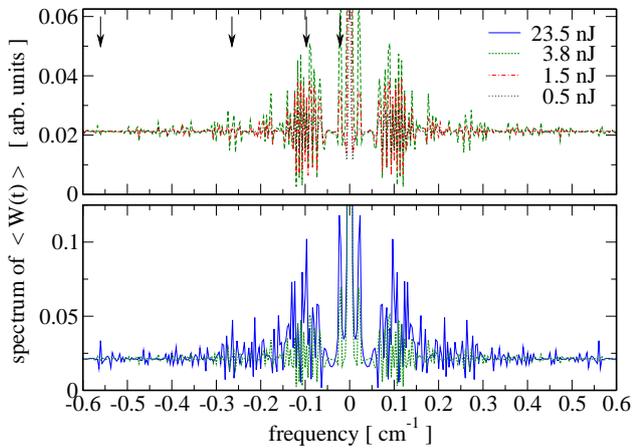


FIG. 7: (Color online) Spectrum of the time-dependent expectation value of the window operator (middle panel of Fig. 6, i.e. $\Delta_L = -4 \text{ cm}^{-1}$ and a probe window around $R = 24 a_0$). The solid arrows indicate the position of ground state vibrational levels.

leads to a non-zero offset of the spectral baseline. The positions of the peaks are again compared to those of the vibrational levels, indicated by black arrows. As expected they agree very well, with the beating between different vibrational levels leading to a splitting of the peaks. For a strong pump pulse, similarly to Fig. 5 a shift of the peak positions is observed compared to smaller pump pulse energies. The similarities in Figs. 5 and 7, i.e. peak positions and shifts, reflect the underlying wave packet dynamics which is completely determined by the (identical) pump pulse excitation. The differences such as the spectral baseline and specific peak shapes are attributed to the differing ways of measuring the dynamics.

The third window operator shown in Fig. 1 that corresponds to a probe wavelength of 516.5 nm and to a probe

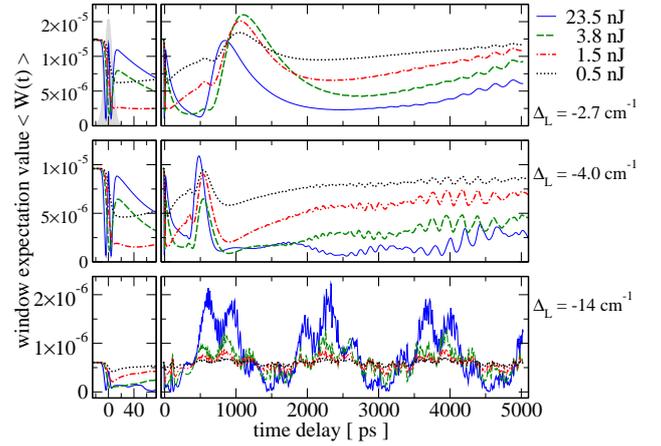


FIG. 8: (Color online) Probing the dynamical hole at the position of its creation: The time-dependent expectation value of the window operator is shown for different pump pulse energies and a probe wavelength of 780.5 nm (window localized around $R = 90 a_0$ for $\Delta_L = -2.7 \text{ cm}^{-1}$, $R = 78 a_0$ for $\Delta_L = -4.0 \text{ cm}^{-1}$, and $R = 49 a_0$ for $\Delta_L = -14 \text{ cm}^{-1}$).

bandwidth of 1 nm does not show any time-dependence (data not shown). The population over the broad range of distances covered by this window does not sufficiently vary.

In conclusion, probing the correlation dynamics by ionization via the $^3\Sigma_g(5s + 4d)$ state allows for identifying the positions of the last bound levels of the ground state potential, provided time delays of a few nanoseconds can be realized. Probing the dynamics at very short distance, $R = 10 a_0$, yields a signal that clearly oscillates as a function of the pump-probe time delay. The strength of the probe signal is, however, somewhat discouraging. While a larger signal can be achieved by probing the dynamics at intermediate distance, $R = 24 a_0$, the contrast of the oscillations is diminished due to the broader probe window.

B. Probing the hole at the position of its creation

A similar time-dependence of the probe signal is expected for probing the correlation dynamics at the position where the hole is created and at short internuclear distances, i.e. a large enhancement at short times due to both the hot atomic and the molecular components of the hole and smaller oscillations at longer times that can be attributed to the molecular components. Additionally, when probing at the position of the hole creation and with pump and probe pulses that overlap in time, around zero delay, a strong dip of the probe signal should indicate transient population transfer to the excited state. These expectations are confirmed by inspecting the probe signals shown in Fig. 8. Moreover, a large signal strength and a strong relative enhancement or, respectively, depletion are observed.

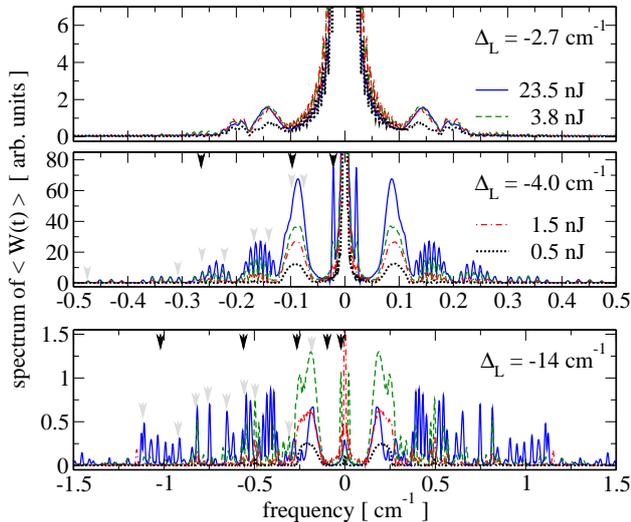


FIG. 9: (Color online) Spectrum of the time-dependent expectation value of the window operator for $\Delta_L = -2.7 \text{ cm}^{-1}$ and a probe window around $R = 90 a_0$, $\Delta_L = -4 \text{ cm}^{-1}$ and a probe window around $R = 78 a_0$ (upper panel) and for $\Delta_L = -14 \text{ cm}^{-1}$ and a probe window around $R = 49 a_0$ (lower panel). The black arrows indicate the position of ground state vibrational levels, the grey arrows some of the beat frequencies between different vibrational levels.

The motion of the ground state density toward the inner turning point followed by the refilling of the hole is reflected in the peak of the signal which occurs, depending on the pump pulse energy, between 840 ps and 1100 ps for $\Delta_L = -2.7 \text{ cm}^{-1}$, between 480 ps and 540 ps for $\Delta_L = -4.0 \text{ cm}^{-1}$, and between 100 ps and 110 ps for $\Delta_L = -14 \text{ cm}^{-1}$. The refilling of the hole corresponds to the 'recovery of the bleach' known from molecular pump-probe spectroscopy. Unlike those examples from gas-phase or condensed-phase dynamics, the signal in our case is not caused by vibronic motion of molecules but rather by the two-body correlations between atoms that are present in ultracold gases.

The highest pump pulse energy always yields the fastest refilling. This is attributed to the momentum transfer which increases with pulse energy, cf. Fig. 2. After the initial refilling, another depletion is observed followed by a slow recovery with small oscillatory modulations of the signal. As in Section IV A, a larger detuning of the pump pulse leads to a higher frequency of these oscillations. The amplitudes of the oscillations can be enhanced by increasing the pump pulse energy, in particular for large detunings.

The strength of the probe signal without any pump pulse is given by the probability density amplitude at the Condon radius. For larger detuning, the Condon radius and hence the amplitude decrease, cf. Fig. 1. This determines the strength of the background signal from which the 'recovery of the bleach' is measured. It is decreased by an order of magnitude when increasing the pump pulse detuning from $\Delta_L = -4.0 \text{ cm}^{-1}$ to $\Delta_L = -14 \text{ cm}^{-1}$ (cf.

initial values in Fig. 8).

It might seem a little surprising at first sight, that an enhancement of the signal *above* its background value is observed for strong field and large detuning, cf. blue solid curve in the lowest panel of Fig. 8. This implies that, at certain times, corresponding to pump-probe delays of e.g. 610 ps or 2300 ps, more probability density resides within the probe window than is initially there. One would rather expect that, after the initial refilling of the hole, when the hot atomic component of the ground state wave packet has left the short internuclear distances of the probe window, the signal could not be completely recovered anymore. This picture holds, however, only for weak pump pulses. For a pump pulse energy of 23 nJ, Rabi cycling occurs, cf. upper panel of Fig. 2. It is accompanied by power broadening. A broadened pulse spectrum corresponds to addressing initial ground state density in a larger range of internuclear distances. Therefore the 23 nJ-pump pulse at a detuning of $\Delta_L = -14 \text{ cm}^{-1}$ excites not only the peak in the initial ground state wave function around $50 a_0$ but also part of the two neighbouring peaks, cf. Fig. 1. Since some of this population is cycled back to the ground state, it may contribute to the bound components of the hole and show up in the long-term oscillations of the probe signal.

The spectra of the probe signals are examined in Fig. 9. The highest peaks occur at the position of the last bound levels of the ground state potential that are indicated by the black arrows. The peak around zero is due to the last level which is not resolved on the shown frequency scales ($E_{\text{bind}}^{\text{last}} = 8.4 \times 10^{-4} \text{ cm}^{-1}$ or 25 MHz). It is off the top of the figure in the upper two panels for the smaller pump pulse detunings but reduced in the lower panel for the large pump pulse detuning. This is in accordance with Fig. 3 where for the larger detuning a smaller population of the last bound level is observed. The smaller peaks occurring at higher frequencies are attributed to beat frequencies between different vibrational levels, some of which are indicated by the grey arrows. Increasing the pump pulse energy leads to larger peaks and a finer resolution of the spectral features, in particular for the larger pump pulse detuning. A larger detuning of the pump pulse implies larger components in the ground state wave packet with binding energies above 0.1 cm^{-1} , cf. Fig. 3. This is reflected by peaks occurring at higher frequencies in the spectrum (note the different scales in the upper and lower panels of Fig. 9). For a very small pump pulse detuning, $\Delta_L = -2.7 \text{ cm}^{-1}$ and probing at fairly long range, $R = 90 a_0$, the dynamics are rather slow. An observation time of 5 ns is then not sufficient to resolve the spectral features of the probe signal.

V. CONCLUSIONS

A hole in the pair density of two atoms in their electronic ground state can be induced by a suitably chosen short pulse. Ideally, this pulse should be dark at the

atomic transition. In that case, only pair correlations are dynamically modified. The pulse has to be impulsive compared to the timescale of relative motion on the electronic ground state. For ultracold rubidium, the pulse duration should be a few picoseconds or, respectively, the spectral bandwidth a few wavenumbers. The same process could be applied to other species with the timescale modified to maintain the impulsive condition.

The hole represents a non-stationary superposition of many scattering states and a few of the last bound levels. The shape of the hole, i.e. its momentum and the position of its creation, are controlled by the pulse intensity and detuning from the atomic line. The timescale of the dynamics of the hole is related to the inverse of the energy difference of the last bound levels and the time delay associated with the scattering length [16]. Typically for rubidium this timescale is of the order of a few hundred picoseconds.

To monitor the dynamical evolution of the hole, a second weak pulse, delayed in time from the pump pulse, is applied as a probe. To enhance the sensitivity, a two-photon REMPI scheme is suggested. The probe pulse transfers amplitude to an intermediate state which then is ionized. We have modeled the absorption of the probe pulse by time-dependent perturbation theory applied to the first step. This assumes saturation of the second step in the REMPI scheme. The wavelength of the probe pulse determines the position of the measurement.

Probing the two-body correlation dynamics yields a signal with clear dynamical features. If one is able to provide for pump-probe delays of a few nanoseconds,

spectral features on a scale of less than 1 cm^{-1} can be resolved. Since pump and probe just address probability density at certain internuclear distances, no phase relation between the pulses is required, and long time delays between the pump and probe pulse can be realized by optical delay stages.

The full power of coherent control can be employed to modify the hole. The simplest modification makes use of chirped pulses. Chirping the pump pulse changes the shape of the hole, while chirping the probe pulse allows for measuring the momentum of the hole.

This pump-probe spectroscopy of the pair correlation dynamics can be combined with static external field control of the initial pair density. Specifically, tuning a magnetic field close to a Feshbach resonance may enhance the pair density at short and intermediate distances [36]. Obviously, this will lead to a larger probe signal strength. It remains an interesting open problem to study the effect of the Feshbach resonance on the dynamical properties.

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