

Correlation dynamics after short-pulse photoassociation

Christiane P. Koch^{1,*} and Ronnie Kosloff²

¹*Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany*

²*Institute of Chemistry and The Fritz Haber Research Center, The Hebrew University, Jerusalem 91904, Israel*

(Received 3 March 2010; published 28 June 2010)

Two atoms in an ultracold gas are correlated at short interatomic distances due to threshold effects in which the potential energy of their interaction dominates the kinetic energy. The correlations manifest themselves in a distinct nodal structure of the density matrix at short interatomic distances. Pump-probe spectroscopy has recently been suggested [Phys. Rev. Lett. **103**, 260401 (2009)] to probe these pair correlations: A suitably chosen, short photoassociation laser pulse depletes the ground-state pair density within the photoassociation window, creating a nonstationary wave packet in the electronic ground state. The dynamics of this nonstationary wave packet is monitored by time-delayed probe and ionization pulses. Here we discuss how the choice of the pulse parameters affects the experimental feasibility of this pump-probe spectroscopy of two-body correlations.

DOI: 10.1103/PhysRevA.81.063426

PACS number(s): 32.80.Qk, 03.75.Kk, 82.53.Kp

I. INTRODUCTION

The simplest description of Bose-Einstein condensation (BEC) considers an ensemble of indistinguishable particles all in the same quantum state [1,2]. 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 correlation functions into cumulants [3,4]. Alternatively, one can also work directly with the correlation functions [5,6]. Can one envision directly measurable consequences of the pair correlations? We have recently answered this question in the affirmative [7], combining our previous work on short-pulse photoassociation [8–13] with a treatment of many-body pair correlations [3–6]. Here we discuss in detail how the choice of experimentally tunable parameters determines the feasibility of the proposed experiment.

Photoassociation assembles two atoms into a molecule with laser light [14]. Considerable experimental effort has already been devoted to photoassociation with short laser pulses. Early experiments were carried out at room temperature in mercury vapor [21]. 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 [22,23]. Recently, evidence of coherent formation of molecules in the electronically excited state was provided in a pump-probe experiment with chirped femtosecond laser pulses [24–28]. The proven experimental ability of pulsed photoassociation paves the way for developing a pump-probe spectroscopy to study ultracold two-atom correlation dynamics [7].

Photoassociation takes place at the same interatomic distances where pair correlations are significant. At ultralow temperatures, photoassociation spectroscopy with continuous-wave lasers is sensitive to the position of the nodes of the

scattering wave function describing two colliding atoms [15]. The two-atom scattering wave function is closely related to the reduced pair wave function characterizing two-body correlations [5,7]. The observed modulation in the spectroscopic features therefore serves as a probe of the static interatomic correlations. If one is to measure two-body correlations *dynamically*, a nonstationary initial state has to be generated. This can be achieved by interaction with an external field which is fast relative to the ensuing dynamics. Therefore the short-pulse photoassociation scenario [8,9] can be employed to generate a nonstationary initial state by a pump pulse and then follow its dynamics by a probe pulse [7]. The idea, sketched in Fig. 1, is based on impulsive excitation where a selected part of the ground-state probability density is suddenly removed to the excited potential energy surface [16]. 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” [7,17]. The impulsive excitation by the pump pulse also transfers momentum to the ground-state wave function. The hole dynamics can be monitored by a suitably time-delayed probe pulse, detecting the enhancement of ground-state density at a specific location by resonantly enhanced multiphoton ionization (REMPI) (cf. Fig. 1) or by a combination of probe and ionization pulse [7].

As in any stroboscopic measurement, the pump and probe pulses are required to act on a time scale shorter than that of the observed dynamics [16,18]. The correlations in ultracold atomic gases are due to threshold effects, where the kinetic energy of the colliding atoms is lower than or equal to the potential energy. The time scale of the correlations is related to the period of the last bound level, $T_{\text{vib}} \approx 2\pi\hbar \frac{\partial v}{\partial E}$, or to the scattering length a_S , $\tau \approx \mu a_S / \hbar k$ [8]. For the example of ⁸⁷Rb with a scattering length of $\approx 100a_0$, the correlation time scale is typically of the order of 100 to 1000 ps. This time scale defines an upper limit to the pulse duration. A more quantitative estimate of this limit is derived here by comparing the change in kinetic energy to the spectral bandwidth of the pulse. In contrast, the pulse duration cannot be too short since then the spectral bandwidth would be very broad. This would result in the dynamical hole being smeared over a large range of distances, hampering precise control of the hole location. Therefore the optimal pump pulse is a

*ckoch@physik.fu-berlin.de

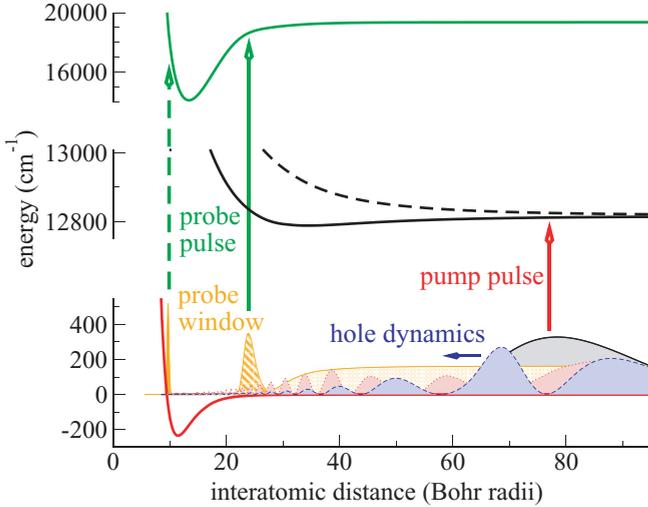


FIG. 1. (Color online) Pump-probe spectroscopy of the dynamical hole. A photoassociation pump pulse excites the population from the ground state to the first excited state, leaving a hole in the ground-state wave function and transferring momentum to it. The ground-state wave function (bottom) is depicted before the pulse [solid (black) line], at $t_{\max} + 24$ ps, i.e., just after the pulse [dashed (blue) line] and at $t_{\max} + 126$ ps [dotted (red) line]. For red detuned pump pulses, the hole is accelerated toward shorter distances, which leads to an enhancement of the population at short distances. A suitably time-delayed REMPI probe pulse can measure this population enhancement. The effect of the probe pulse is modeled by a window operator [shown by thin (orange) lines], where different fillings reflect different probe central frequencies. Another option is to choose the same central frequencies for pump and probe, requiring an additional REMPI pulse (see Fig. 1 in Ref. [7]).

compromise between impulsive excitation and sharp spectroscopic features.

The insight gained in photoassociation studies [8–13] can be used to determine the pulse parameters when constructing a spectroscopic probe of the two-atom correlation dynamics [7]. The choice of the pulse parameters controls the location and the momentum of the dynamical hole [7, 10, 19]. It can be analyzed by projection 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 [7, 10]. The momentum of the hole can be controlled by proper chirp parameters [17, 19] and by the choice of an attractive or repulsive potential of the electronically excited state [20], that is, by pulse detuning.

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 Sec. III, and the observation of the hole dynamics is detailed in Sec. IV. Section V 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 contribute. 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 [5, 6], with the momentum determined by the chemical potential. For a thermal state the initial state is a thermal mixture of scattering states [29]. In both cases the two-body correlation decays at a long interatomic distance due to the vanishing interaction. 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,

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

with the Chebychev propagator [30]. The Hamiltonian in the rotating-wave approximation reads

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

where $\hat{\mathbf{T}}$ denotes the kinetic energy, $V_{g/\text{exc}}$ the ground- and excited-state potential energy curves, 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, $\Delta_L = \omega_{\text{at}} - \hbar\omega_L$. The pulse energy is calculated from the maximum field amplitude and transform-limited full-width at half-maximum (FWHM) τ ,

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

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 with 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 state, $a^3\Sigma_u^+(5s + 5s)$. The potentials at short range are given in [31] and [32]. They are connected to analytical long-range dispersion potentials $C_3/\hat{\mathbf{R}}^3 + C_6/\hat{\mathbf{R}}^6 + C_8/\hat{\mathbf{R}}^8$ with coefficients taken from [33] and [34]. We restrict our model to this two-state description, considering only the lowest triplet state as the electronic ground state. In principle, a laser pulse excites scattering amplitude from both the lowest triplet state and the singlet ground state into all states correlating with the $5s + 5p_{3/2}$

asymptote. The resonance condition might differ for singlet and triplet, giving rise to different probe signals for the two. As pointed out in Ref. [7], this effect may be used to map out the pair correlation functions for the singlet and triplet components.

The Hamiltonian is represented on a Fourier grid with variable step size [35–37]. Our grid extends to about $R_{\max} = 28000a_0$. 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 $R = 800a_0$. A single scattering state with a scattering energy corresponding to $20\mu\text{K}$ is considered as the initial state in the calculations that follow. The effects of averaging over many thermally populated scattering states and the influence of temperature have been discussed in our previous work [7]. Here we focus on how the pulse parameters need to be chosen to realize a pump-probe spectroscopy that yields a sufficiently high signal to be experimentally feasible.

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

To avoid a separate calculation for each pump-probe time delay, the total absorption is represented by a window operator $\hat{\mathbf{W}}(\hat{\mathbf{R}})$ [38,39]:

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

with

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

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,

$$\hat{\Delta}(\hat{\mathbf{R}}) = V_p(\hat{\mathbf{R}}) - V_g(\hat{\mathbf{R}}) - \hbar\omega_p, \quad (3)$$

with $V_p(\hat{\mathbf{R}})$ 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 coordination 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, that is, the excitation is impulsive, and the window operator $\hat{\mathbf{W}}$ is independent of the state of the system [39].

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

Dynamical pair correlations are initiated by an impulsive photoassociation pulse. The resonance condition, $\hat{\Delta}(R_L) = \hat{\mathbf{V}}_{\text{exc}}(R_L) - \hat{\mathbf{V}}_g(R_L) - \hbar\omega_L = 0$, determines the central position of the dynamical “hole,” that is, the Condon radius R_L . The impulsive conditions on the pulse duration τ are determined by this point R_L . An estimate is based on the requirement that

the energy gain due to acceleration during the pulse, ΔE_{kin} , is smaller than the energy bandwidth of the pulse, $\hbar\Delta\omega = \hbar/\tau$. For a weak pulse such that excitation, but no Rabi cycling, occurs at R_L during the pulse, the energy gain is estimated by the acceleration due to the difference potential $\hat{\Delta}(R)$ at the point of resonance R_L . In a semiclassical picture, the gain in kinetic energy is estimated by integrating over the force,

$$\dot{P} = -\left. \frac{\partial \hat{\Delta}}{\partial R} \right|_{R=R_L},$$

which yields the change in momentum, $\Delta P = -\left. \frac{\partial \hat{\Delta}}{\partial R} \right|_{R=R_L} \tau$. Evaluating $\Delta E_{\text{kin}} < \hbar\Delta\omega$ leads to an estimate for the upper limit of the pulse duration τ :

$$\tau < \left(\frac{2\mu\hbar}{\left(\left. \frac{\partial \hat{\Delta}}{\partial R} \right|_{R_L} \right)^2} \right)^{1/3}. \quad (4)$$

For excitation in the asymptotic region where the difference potential can be approximated to leading order by $-C_3/R^3$, this becomes

$$\tau_{\text{asy}} < \left(\frac{2\mu\hbar R_L^8}{9C_3^2} \right)^{1/3}. \quad (5)$$

For the $0_g^-(P_{3/2})$ state of ^{87}Rb one obtains $\tau < 85, 300$, and 440 ps for $R_L = 50a_0, 78a_0$, and $90a_0$. A lower limit to the duration of the pulse τ can be estimated due to the requirement that the pulse does not excite the atomic transition; that is, only pairs are excited. This means that $\hbar\Delta\omega < |V_{\text{exc}}(R_L)| \approx |C_3/R_L^3|$ or

$$\tau_{\text{asy}} > \left| \frac{\hbar R_L^3}{C_3} \right|. \quad (6)$$

For the $0_g^-(P_{3/2})$ state of ^{87}Rb one obtains $\tau > 385$ fs, 1.3 ps, and 2 ps for $R_L = 50a_0, 78a_0$, and $90a_0$. The bounds on τ are plotted in Fig. 2.

They indicate how to determine the optimal transform-limited pulse duration of the photoassociation pulse as a compromise between impulsive excitation and sharp spectroscopic features. Note that the upper limit scales with $R_L^{2.67}$,

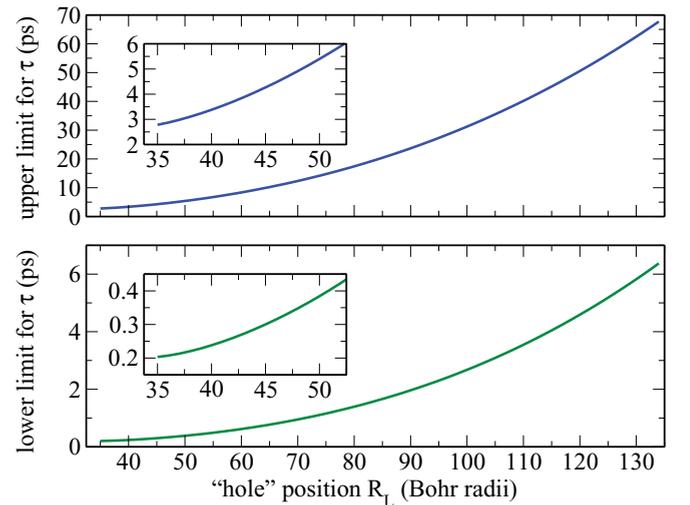


FIG. 2. (Color online) Upper and lower bounds on the transform-limited pulse duration τ according to Eqs. (5) and (6).

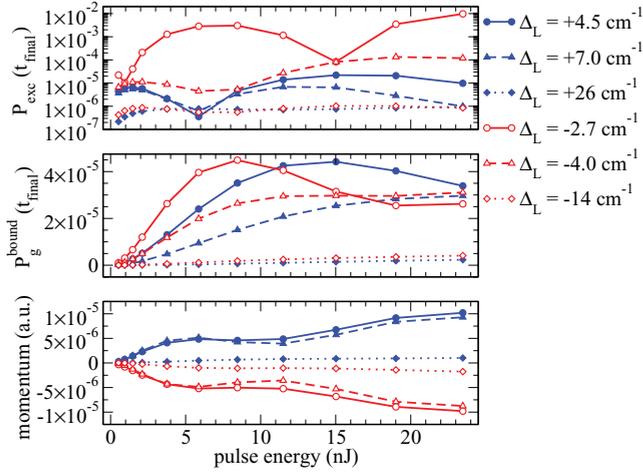


FIG. 3. (Color online) Effect of the pump pulse: population transfer to the excited state (top), formation of ground-state molecules (middle), and momentum kick (bottom). Plots show the excited-state population (top), the population in bound levels of the electronic ground state (middle), and the ground-state momentum (bottom) after the pump pulse is over as a function of the pulse energy. Different detunings are compared with corresponding Condon radii of $90a_0$ (circles), $78a_0$ (triangles), and $50a_0$ (diamonds).

while the lower limit scales with R_L^3 . The different scaling with R_L implies that there is a maximum radius R_L^* for which a hole can be drilled in the pair correlation function. However, this maximum radius amounts to $R_L^* \approx 160\,000a_0$ or $R_L^* \approx 8.5 \mu\text{m}$, with a corresponding τ of 10 ms, so it does not impose any practical limitations. The region of interest for R_L can be read from Fig. 1: The minimum R_L is due to the decrease in scattering amplitude with shorter internuclear distance. The maximum R_L is determined in terms of the pulses that can feasibly be produced in an experiment—larger R_L values require longer delay stages between pump and probe pulses and larger transform-limited pulse durations (cf. lower plot in Fig. 2) or smaller bandwidths, respectively. In the following calculations, we choose a transform-limited pulse duration of the photoassociation pulse of $\tau = 10$ ps, corresponding to an energy bandwidth of 1.5 cm^{-1} . The photoassociation pump pulse transfers the population to the electronically excited state (cf. upper plot in Fig. 3).

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 the data for 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 the population. The pump pulse not only transfers the population to the excited state, but also has an effect on the ground-state wave function, creating the hole and transferring momentum (cf. lower plot in Fig. 3). The hole corresponds to populations of both bound levels and higher-energy scattering states, that is, to the formation of ground-state molecules and hot atom pairs. The population of bound levels is shown in the middle plot in Fig. 3. For small and medium detuning, molecules are formed mostly in the last bound level, $v = 40$ (between 90% and 99%). The small initial population near the

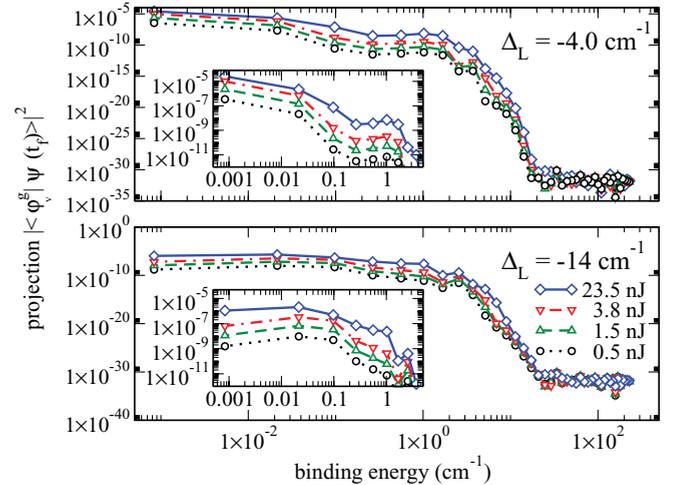


FIG. 4. (Color online) Formation of ground-state molecules due to the pump pulse. The projection of the final-time wave packet onto the bound ground-state vibrational levels for two red detunings is shown.

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; that is, they determine the hole dynamics. The bound population decreases at high pulse energies for small detuning. This is due to power broadening, that is, the population residing at the “right” distance is transferred to continuum states rather than to bound levels.

The momentum expectation value of the ground-state wave function after the pulse is shown in the bottom plot in Fig. 3. For blue detuning, the hole is accelerated toward larger distances, while for red detuning dynamics toward shorter distances occurs (as indicated in Fig. 1). Population enhancement at a short distance which is measured by the probe pulse can therefore be expected only for red detuning.

While some bound levels are populated, population transfer into continuum states occurs, 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 high pulse energies. The projection of the wave packet onto the bound ground-state vibrational levels after the pulse is shown in Fig. 4 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 energies of $\leq 1 \text{ cm}^{-1}$ 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 continuous-wave excitation [40]. It is based on resonantly enhanced multiphoton ionization. In the following, two 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 [32]. The resonant enhancement is provided by the $^3\Sigma_g^+(5s+4d)$ state (cf. Fig. 1; that is, 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 [24]. 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 therefore consists of two time-delayed pulse pairs: pump + ionization pulse followed by probe + ionization pulse. Since all pulses address the wave packet density only 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 modeling the probe pulse absorption in Figs. 5 and 7. $\langle \hat{W}(t) \rangle$ is shown as

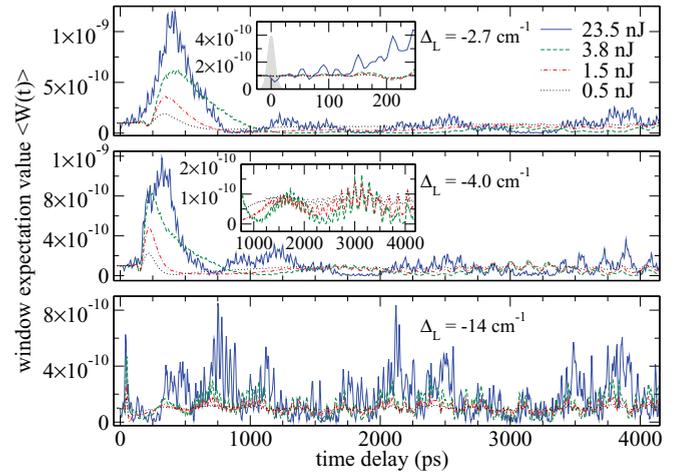


FIG. 5. (Color online) Probing the dynamical hole near the inner turning point. The time-dependent expectation value of the window operator is plotted for different energies and detunings of the pump pulse and a probe wavelength of 680 nm (window localized around $R = 10a_0$).

a function of the pump-probe delay for probe wavelengths of 680 nm with a 20-nm bandwidth and of 518.5 nm with a 1-nm bandwidth, respectively. The spectra of these signals are obtained by filter diagonalization [41,42], a method allowing accurate extraction of frequencies from just a few oscillation periods. The spectra of the probe signals in the middle plots in Figs. 5 and 7 are shown in Figs. 6 and 8.

For probe measurement at $R = 10a_0$ ($\omega_P = 680$ nm) (cf. Fig. 5), an enhancement of the signal by a factor of up to 10 is observed at short delay times. The enhancement is larger for smaller pump pulse detuning since more of the population is excited, creating a larger hole (cf. Fig. 3). This 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 $R = 10a_0$. This part of the

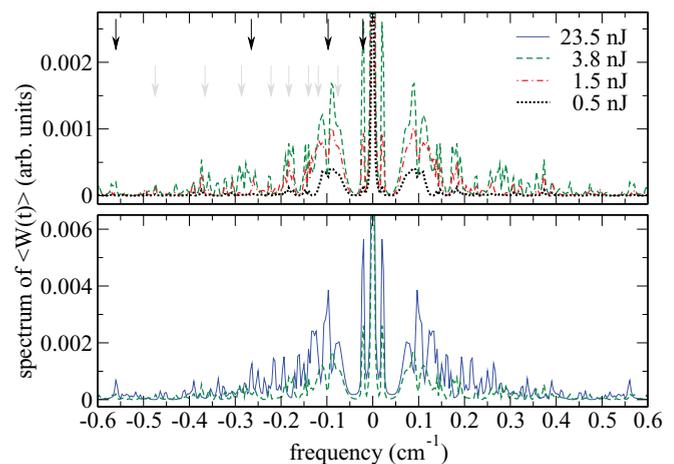


FIG. 6. (Color online) Spectrum of the time-dependent expectation value of the window operator (middle plot in Fig. 5, i.e., $\Delta_L = -4 \text{ cm}^{-1}$ and a probe window around $R = 10a_0$). Black arrows indicate the positions of ground-state vibrational levels; grey arrows, some of the beat frequencies between different vibrational levels.

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, with respect to the next-to-last, level (cf. Fig. 4). The frequency of the long-term oscillations increases with pump pulse detuning. This may be rationalized in terms of the vibrational distributions (cf. Fig. 4).

The overtones represent a beating between the different vibrational levels making up the hole. This is evident in Fig. 6, 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. Black arrows indicate the spectral positions of the ground-state vibrational levels, except for the last bound level, which is too close to 0 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 plot in Fig. 4). In the weak-field regime (top plot in Fig. 6), 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, that is, beat frequencies, appear in the spectrum. The strong-field and weak-field regimes are compared in the lower plot in Fig. 6. 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 plot in Fig. 3). This results in a shift of the spectral peak positions [cf. the solid (blue) and dashed (green) lines in the lower plot in Fig. 6]: For a 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 $R = 24a_0$ ($\omega_P = 518.5 \text{ nm}$) than for one at $R = 10a_0$ ($\omega_P = 680 \text{ nm}$). However, the *relative* enhancement is significantly smaller (cf. Fig. 7). Since the measurement occurs at larger

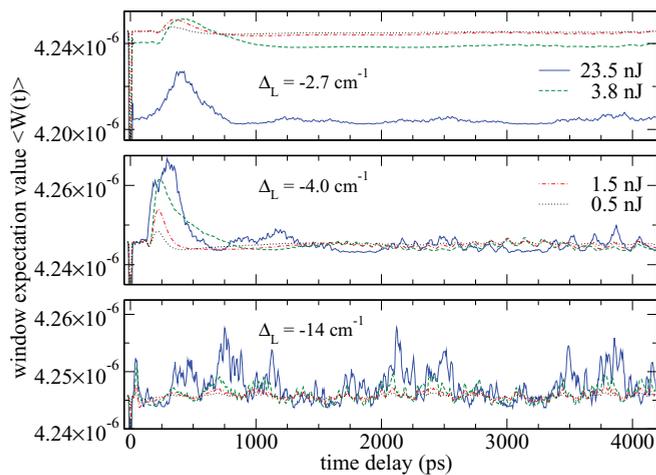


FIG. 7. (Color online) Probing the dynamical hole at intermediate distances. The time-dependent expectation value of the window operator is plotted for different energies and detunings of the pump pulse and a probe wavelength of 518.5 nm (window localized around $R = 24a_0$).

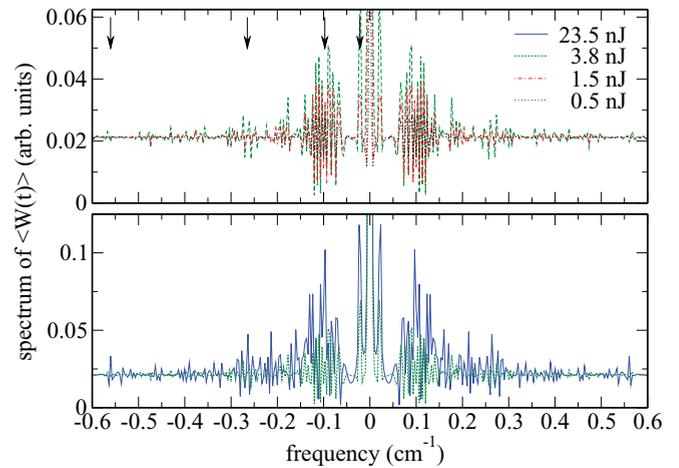


FIG. 8. (Color online) Spectrum of the time-dependent expectation value of the window operator (middle plot in Fig. 7, i.e., $\Delta_L = -4 \text{ cm}^{-1}$ and a probe window around $R = 24a_0$). Arrows indicate the position of ground-state vibrational levels.

distances, there is a ground-state amplitude initially within the probe window (cf. Fig. 1), leading to a strong background. The pump pulse cycles a population which shows up as a dip in the probe signal around 0 delay (cf. Fig. 7). 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. 5, larger pump pulse detuning leads to faster oscillations and a larger pump pulse energy to a stronger signal in Fig. 7.

The probe spectra for a measurement at $R = 24a_0$ ($\omega_P = 518.5 \text{ nm}$) and a pump pulse detuning of $\Delta_L = -4 \text{ cm}^{-1}$ are analyzed in Fig. 8. The signal background leads to a nonzero offset of the spectral baseline. The positions of the peaks are again compared to those of the vibrational levels, indicated by 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. 6, a shift of the peak positions is observed compared to lower pump pulse energies. The similarities in Figs. 6 and 8, 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, which corresponds to a probe wavelength of 516.5 nm and to a probe 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 vary sufficiently.

In conclusion, probing the correlation dynamics by ionization via the $^3\Sigma_g^+(5s + 4d)$ state allows identification of the positions of the last bound levels of the ground-state potential, provided that time delays of a few nanoseconds can be realized. Probing the dynamics at a very short distance, $R = 10a_0$, 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

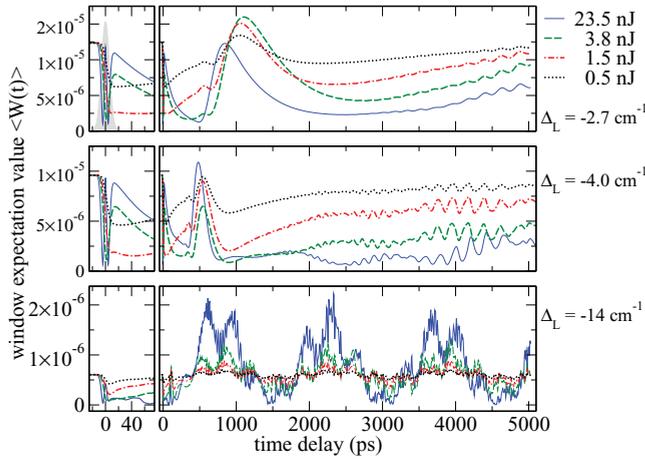


FIG. 9. (Color online) Probing the dynamical hole at the position of its creation. The time-dependent expectation value of the window operator is shown for different pump pulse energies and a probe wavelength of 780.5 nm (window localized around $R = 90a_0$ for $\Delta_L = -2.7 \text{ cm}^{-1}$, $R = 78a_0$ for $\Delta_L = -4.0 \text{ cm}^{-1}$, and $R = 49a_0$ for $\Delta_L = -14 \text{ cm}^{-1}$).

achieved by probing the dynamics at an intermediate distance, $R = 24a_0$, 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, that is, 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, which 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 0 delay, a strong dip in the probe signal should indicate transient population transfer to the excited state. These expectations are confirmed by inspecting the probe signals shown in Fig. 9. Moreover, a large signal strength and a strong relative enhancement or, respectively, depletion are observed.

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 and 1100 ps for $\Delta_L = -2.7 \text{ cm}^{-1}$, between 480 and 540 ps for $\Delta_L = -4.0 \text{ cm}^{-1}$, and between 100 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 the examples from gas-phase or condensed-phase dynamics, the signal in our case is caused not 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. 3). After the initial refilling, another depletion is observed, followed by a slow recovery with small oscillatory modulations of the signal. As

in Sec. 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. 9).

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. solid (blue) curve in the bottom plot in Fig. 9]. This implies that, at certain times, corresponding to pump-probe delays of, for example, 610 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 (see upper plot in Fig. 3). It is accompanied by power broadening. A broadened pulse spectrum corresponds to addressing the 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 $50a_0$ but also part of the two neighboring peaks (see 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. 10. The highest peaks occur at the position of the last bound levels of the ground-state potential, which are indicated by the black arrowheads. The peak around 0 is due to the last level, which is not resolved at the frequency scales shown ($E_{\text{bind}}^{\text{last}} = 8.4 \times 10^{-4} \text{ cm}^{-1}$ or 25 MHz). It is off the top of the figure in the upper two plots, for the smaller pump pulse detunings, but reduced in the lower plot, for the large pump pulse detuning. This is in accordance with Fig. 4, 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 gray 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} (see Fig. 4). This is reflected by peaks occurring at higher frequencies in the spectrum (note the different scales in the upper and lower plots in Fig. 10). For a very small pump pulse detuning, $\Delta_L = -2.7 \text{ cm}^{-1}$, and probing at a fairly long range, $R = 90a_0$, the dynamics are rather slow. An observation time of 5 ns is then not sufficient to resolve the spectral features of the probe signal.

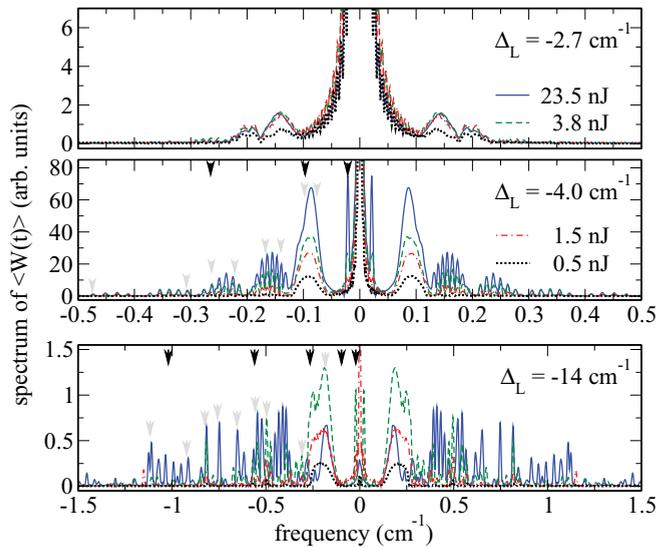


FIG. 10. (Color online) Spectrum of the time-dependent expectation value of the window operator for $\Delta_L = -2.7 \text{ cm}^{-1}$ and a probe window around $R = 90a_0$ (top), for $\Delta_L = -4 \text{ cm}^{-1}$ and a probe window around $R = 78a_0$ (middle), and for $\Delta_L = -14 \text{ cm}^{-1}$ and a probe window around $R = 49a_0$ (bottom). Black arrowheads indicate the position of ground-state vibrational levels; gray arrowheads, some of the beat frequencies between different vibrational levels.

V. CONCLUSIONS

A hole in the pair density of an ultracold gas is the consequence of sudden unitary population transfer from the ground to the excited electronic state. It represents a nonstationary state of the two-atom scattering whose evolution in time can be monitored by a suitably chosen probe pulse. Such pump-probe spectroscopy of pair correlations can be implemented by slight modification of existing experimental setups [24–28]. It can be applied to BECs as well as thermal ultracold gases. This corresponds to studying the dynamics of a pure state versus those of an incoherent ensemble for the time scales probed in such an experiment. The main effect of thermal averaging is the contribution of higher partial waves. This is particularly prominent in the presence of resonances [7]. If a resonance affects different scattering channels differently, such as shape resonances in either the singlet or the triplet channel of rubidium, pump-probe spectroscopy can be used to map out the coupled-channels pair wave function despite the finite lifetime of the resonance [7].

In the present work, we have studied the influence of the pulse parameters on the hole dynamics for a pure initial state. Creation of a hole can be induced by a short pulse that is faster than the time scale of the nuclear dynamics. A practical requirement is that this pulse must be transparent at the atomic transition. In that case, only pair correlations are dynamically modified. The pulse has to be impulsive compared to the time scale 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 wave numbers. The same process could be applied to other species with the time scale modified to maintain the impulsive condition.

The hole represents a nonstationary superposition of many scattering states and a few of the last bound levels. The shape of the hole in phase space, that is, its momentum, and the position are controlled by the pulse intensity, chirp, and detuning from the atomic line. As a result there is significant experimental flexibility in interrogating specific properties of the pair correlation. The time scale of the dynamics of the hole can be estimated by comparing the acceleration due to the difference potential and the energy associated with the bandwidth of the pulse. An upper bound of the transform-limited pulse duration is related to the gain in kinetic energy due to the gradient of the difference potential. A lower bound is imposed by the restriction not to excite the atomic resonance. For all “hole” positions of interest, this defines a window of possible transform-limited pulse durations which, for rubidium, are of the order of a few picoseconds to tens of 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. Typically the number of pairs is small, which means that a high sensitivity is required. In this study a two-photon REMPI scheme is suggested. The probe pulse transfers amplitude to an intermediate state, which is then ionized, leading to a high detection efficiency. 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 characteristics probe pulse duration, chirp, and central frequency determine the properties 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 cm^{-1} can be resolved. Since pump and probe address only the probability density at certain internuclear distances, no phase relation between the pulses is required, and long time delays between the pump and the 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 generates a measurement of position and momentum in phase space with accuracy limited by the uncertainty relation.

This pump-probe spectroscopy of 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 enhances the pair density at short and intermediate distances [43]. Obviously, this will lead to a larger probe signal strength. It remains an interesting open problem to study the effect of Feshbach resonance on the dynamical properties.

ACKNOWLEDGMENTS

We would like to thank Françoise Masnou-Seeuws and Pascal Naidon for many fruitful discussions. We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft. The Fritz Haber Center is supported by the Minerva Gesellschaft für die Forschung GmbH München, Germany.

- [1] A. J. Leggett, *Rev. Mod. Phys.* **73**, 307 (2001).
- [2] C. J. Pethick and H. Smith, *Bose-Einstein Condensation in Dilute Gases* (Cambridge University Press, Cambridge, 2002).
- [3] T. Köhler, T. Gasenzer, and K. Burnett, *Phys. Rev. A* **67**, 013601 (2003).
- [4] T. Köhler and K. Burnett, *Phys. Rev. A* **65**, 033601 (2002).
- [5] P. Naidon and F. Masnou-Seeuws, *Phys. Rev. A* **68**, 033612 (2003).
- [6] P. Naidon and F. Masnou-Seeuws, *Phys. Rev. A* **73**, 043611 (2006).
- [7] C. P. Koch and R. Kosloff, *Phys. Rev. Lett.* **103**, 260401 (2009).
- [8] E. Luc-Koenig, R. Kosloff, F. Masnou-Seeuws, and M. Vatasescu, *Phys. Rev. A* **70**, 033414 (2004).
- [9] J. Vala, O. Dulieu, F. Masnou-Seeuws, P. Pillet, and R. Kosloff, *Phys. Rev. A* **63**, 013412 (2000).
- [10] C. P. Koch, R. Kosloff, and F. Masnou-Seeuws, *Phys. Rev. A* **73**, 043409 (2006).
- [11] C. P. Koch, E. Luc-Koenig, and F. Masnou-Seeuws, *Phys. Rev. A* **73**, 033408 (2006).
- [12] C. P. Koch, J. P. Palao, R. Kosloff, and F. Masnou-Seeuws, *Phys. Rev. A* **70**, 013402 (2004).
- [13] C. P. Koch and R. Moszyński, *Phys. Rev. A* **78**, 043417 (2008).
- [14] K. M. Jones, E. Tiesinga, P. D. Lett, and P. S. Julienne, *Rev. Mod. Phys.* **78**, 483 (2006).
- [15] F. Masnou-Seeuws and P. Pillet, *Adv. At. Mol. Opt. Phys.* **47**, 53 (2001).
- [16] G. Ashkenazi, U. Banin, A. Bartana, R. Kosloff, and S. Ruhman, *Adv. Chem. Phys.* **100**, 229 (1997).
- [17] E. Luc-Koenig, F. Masnou-Seeuws, and R. Kosloff, *Phys. Rev. A* **76**, 053415 (2007).
- [18] U. Banin, A. Bartana, S. Ruhman, and R. Kosloff, *J. Chem. Phys.* **101**, 8461 (1994).
- [19] S. Kallush and R. Kosloff, *Phys. Rev. A* **76**, 053408 (2007).
- [20] S. Kallush and R. Kosloff, *Phys. Rev. A* **77**, 023421 (2008).
- [21] U. Marvet and M. Dantus, *Chem. Phys. Lett.* **245**, 393 (1995).
- [22] W. Salzmann *et al.*, *Phys. Rev. A* **73**, 023414 (2006).
- [23] B. L. Brown, A. J. Dicks, and I. A. Walmsley, *Phys. Rev. Lett.* **96**, 173002 (2006).
- [24] W. Salzmann *et al.*, *Phys. Rev. Lett.* **100**, 233003 (2008).
- [25] F. Weise, A. Merli, F. Eimer, S. Birkner, F. Sauer, L. Wöste, A. Lindinger, W. Salzmann, T. Mullins, S. Götz *et al.*, *J. Phys. B* **42**, 215307 (2009).
- [26] T. Mullins *et al.*, *Phys. Rev. A* **80**, 063416 (2009).
- [27] A. Merli *et al.*, *Phys. Rev. A* **80**, 063417 (2009).
- [28] D. J. McCabe, D. G. England, H. E. L. Martay, M. E. Friedman, J. Petrovic, E. Dimova, B. Chatel, and I. A. Walmsley, *Phys. Rev. A* **80**, 033404 (2009).
- [29] C. P. Koch, R. Kosloff, E. Luc-Koenig, F. Masnou-Seeuws, and A. Crubellier, *J. Phys. B* **39**, S1017 (2006).
- [30] R. Kosloff, *J. Phys. Chem.* **92**, 2087 (1988).
- [31] M. Aymar and O. Dulieu, *J. Chem. Phys.* **122**, 204302 (2005).
- [32] J. Lozeille *et al.*, *Eur. Phys. J. D* **39**, 261 (2006).
- [33] A. Marte, T. Volz, J. Schuster, S. Dürr, G. Rempe, E. G. M. van Kempen, and B. J. Verhaar, *Phys. Rev. Lett.* **89**, 283202 (2002).
- [34] R. F. Gutterres, C. Amiot, A. Fioretti, C. Gabbanini, M. Mazzoni, and O. Dulieu, *Phys. Rev. A* **66**, 024502 (2002).
- [35] V. Kokouline, O. Dulieu, R. Kosloff, and F. Masnou-Seeuws, *J. Chem. Phys.* **110**, 9865 (1999).
- [36] K. Willner, O. Dulieu, and F. Masnou-Seeuws, *J. Chem. Phys.* **120**, 548 (2004).
- [37] S. Kallush and R. Kosloff, *Chem. Phys. Lett.* **433**, 221 (2006).
- [38] L. W. Ungar and J. A. Cina, *Adv. Chem. Phys.* **100**, 171 (1997).
- [39] E. Gershgoren, J. Vala, S. Ruhman, and R. Kosloff, *J. Phys. Chem. A* **105**, 5081 (2001).
- [40] A. Fioretti, D. Comparat, A. Crubellier, O. Dulieu, F. Masnou-Seeuws, and P. Pillet, *Phys. Rev. Lett.* **80**, 4402 (1998).
- [41] V. A. Mandelshtam and H. S. Taylor, *J. Chem. Phys.* **107**, 6756 (1997).
- [42] V. A. Mandelshtam and H. S. Taylor, *J. Chem. Phys.* **108**, 9970 (1998).
- [43] P. Pellegrini, M. Gacesa, and R. Côté, *Phys. Rev. Lett.* **101**, 053201 (2008).