Dynamical interferences to probe short-pulse photoassociation of Rb atoms and stabilization of Rb₂ dimers

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We analyze the formation of Rb₂ molecules with short photoassociation pulses applied to a cold 85Rb sample. A pump laser pulse couples a continuum level of the ground electronic state X$^1\Sigma^+_g$ with bound levels in the 0$^3_u(5S+5P_{1/2})$ and 0$^3_u(5S+5P_{3/2})$ vibrational series. The nonadiabatic coupling between the two excited channels induces time-dependent beatings in the populations. We propose to take advantage of these oscillations to design further laser pulses that probe the photoassociation process via photoionization or that optimize the stabilization in deep levels of the ground state.

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Making ultracold molecules in the lowest vibrational level $v = 0$ of the ground electronic state and creating stable molecular condensates is presently an important challenge since it opens the road toward ultracold chemistry [1][2]. Schemes based on photoassociation (PA) of ultracold atoms [3] with cw lasers, have been very successful to form molecules in an excited electronic state. The latter have been stabilized into excited vibrational levels of the ground electronic state [1][5], but not yet into $v = 0$ except for the case of RbCs [6]. The possibility of controlling PA by use of short laser pulses has been discussed in theoretical papers [7][8][9][10] and very recently attempted by two experimental groups [11][12], both in the rubidium case. Success in such experiments will create a bridge between the two domains of cold matter and coherent control, where femtosecond (fs) pulses are used to control chemical reactions [13]. Unfortunately, up to now, PA experiments with fs laser pulses have achieved destruction of the molecules already existing in the trap rather than creation of additional molecules [11][12].

Finding ways to avoid this destructive effect is therefore a crucial step in the development of experiments. A promising route is PA through the resonant coupling mechanism as realized, with cw lasers, in Cs₂ [14] and RbCs [15]. For the case of Rb₂, it populates the $0^3_u(5S+5P_{1/2})$ and $0^3_u(5S+5P_{3/2})$ coupled series. This is a textbook example of global mixing of two molecular vibrational series due to spin-orbit (SO) coupling and manifested by strong perturbations in the Rb₂ 0$^3_u$ fluorescence and cw photoassociation spectra (cf. Refs. [16][17]). The aim of the present paper is to draw attention to the coherent character of the time evolution in the coupled excited states after the PA pulse, and to the possibility or taking advantage of the subsequent dynamical interferences to optimize stabilization and avoid the destruction of the molecules. We consider a simple model with pulses in the picosecond range which populate a limited number of bound vibrational levels, and we analyze characteristic time-dependent oscillations that should appear in experimental signals.

Time-dependent fluorescence signals manifesting the coupling between deeply bound levels of the two series have been previously observed by pump-probe spectroscopy [18]. In this experiment, a molecular beam of Rb₂ was excited by a 120-fs laser pulse from the $v = 0$ level of X$^1\Sigma^+_g$ ≡ X to low (∼ 5600 cm⁻¹ below the 5S+5P asymptote) vibrational levels of the A$^1\Sigma^+_u$ ≡ A state, with a classical inner turning point $\sim 8a_0$. A delayed pulse, operating around the outer turning point of the b$^3\Pi_u$ ≡ b potential (12a₀), probes the population transferred to this state. It presents an oscillatory behavior with several characteristic periods of the order of 1 ps. This is explained in terms of interferences between several paths for the motion of the wavepacket in the excited state due to the crossing, at $R_{short} \approx 9.3a_0$, of the potential energy curves (hereafter referred to as $V_A$ and $V_b$), corresponding to the two Hund’s case a A and b states.

This crossing can be seen in Fig. 1(a), where we plot $V_A$ and $V_b$ as determined in Ref. [19]. We also show the ground-state potential obtained by matching ab initio calculations [20] to the long-range dispersion potential $-\sum n C_n/R^n$ [21], and adjusting the repulsive barrier to reproduce the large value of the scattering length [22].

In this paper, we consider PA at a detuning of $\approx 60$ cm⁻¹ below the D₁ line (1 cm⁻¹ $\approx 30$ GHz), exciting loosely bound vibrational levels of the coupled system in the vicinity of the up-to-now unexplored crossing at long range $R_{long} \approx 29.2a_0$ [Fig. 1(c)]. The $V_A$ curve crosses the $V_b$ potential curve shifted down from $V_b$ by $\Delta E_{b\nu}/3 = 79$ cm⁻¹ by the inclusion of the diagonal part of the spin-orbit effective Hamiltonian, $H_{SO}$ [19].

The diagonalization of $H_{SO}$ within the {A, b} sub-space, hereafter referred to as diabatic, renders two Hund’s case c $0^3_u(P_{1/2})$ and $0^3_u(P_{3/2})$ adiabatic curves, correlated with the 5S+5P_{1/2} and 5S+5P_{3/2} asymptotes, split by $\Delta E_{b\nu}$. The mixing angle $\theta(R)$ defines the transformation from the diabatic to the adiabatic basis at a given internuclear distance R:

$$|0^3_u(P_{1/2})\rangle = \cos(\theta(R))|A\rangle + \sin(\theta(R))|b\rangle,$$  \hspace{1cm}(1a)  

$$|0^3_u(P_{3/2})\rangle = -\sin(\theta(R))|A\rangle + \cos(\theta(R))|b\rangle.$$  \hspace{1cm}(1b)

In the adiabatic representation, the two excited channels are coupled by radial coupling, governed by the derivative $d\theta/dR$. We display in Fig. 1(b) the R-dependence of $\cos^2\theta$. There is a sharp variation, corresponding to a
singlet-triplet change of character, in the region of \( R_{\text{short}} \), where the two diabatic curves cross abruptly. In the range of distances from 10\( a_0 \) to 15\( a_0 \), the splitting between the diabatic curves \( V_A \) and \( V_b \) is very large compared to \( \Delta E_{\text{as}} \), and \( 0^1_a(P_{1/2}) \) has a pure singlet character. For \( R > 15a_0 \), \( \cos^2 \theta(R) \) decreases toward its asymptotic value 1/3, which, due to the very similar slopes of \( V_A \) and \( V_b \) at large \( R \) [cf. Fig. 1(c)], is reached only at distances far beyond 40\( a_0 \). In contrast with the crossing at \( R_{\text{short}} \) explored in Ref. [18], this long-range crossing is not localized.

We perform calculations for a system of \(^{85}\text{Rb}\) atoms at a temperature of 100 \( \mu \text{K} \) as in the usual photodissociation experiments [11, 12]. The \(^{85}\text{Rb}\) isotope is chosen since the manifestation of the resonant coupling between the two series is more remarkable [17]. Only s-wave scattering and \( J = 0 \) rotational levels are considered for simplicity, even though a full treatment of the rotational structure will be required to compare with experimental data when they become available. We consider a chirped pulse of duration \( \tau_C \), that delivers an energy \( E_{\text{pulse}} \) uniformly over an area \( \sigma \). It is centered at time \( t_P \) and has a frequency that varies linearly in time, \( \omega(t) = \omega_L + \chi \cdot (t - t_P) \), around the carrier frequency \( \omega_L \). The laser is red detuned from the atomic D\(_1\) line at \( \omega_{\text{DL}} \) by \( \Delta_L = h(\omega_{\text{DL}} - \omega_L) \); \( \chi \) is the linear chirp rate in the time domain. The instantaneous intensity \( I(t) \) of the pulse involves a Gaussian envelope with a full width at half maximum equal to \( \tau_C \). For this pulse, 98\% of the energy \( E_{\text{pulse}} \) is delivered in the time window \([t_P - \tau_C, t_P + \tau_C]\) [8], the instantaneous laser frequency being then resonant with all the excited levels with a binding energy in the range \( [\Delta_L - \hbar |\chi| \tau_C, \Delta_L + \hbar |\chi| \tau_C] \), which defines a PA window in energy [22], cf. Fig. 1(c).

We choose a nonperturbative description for the dynamics of the PA process and of the vibration of the molecules, and solve the time-dependent coupled Schrödinger equations [8, 9] to compute the wavepacket motion in the ground X and the excited A and B states. The X and A channels are coupled by \( \hbar \Omega(t) = -\sqrt{(t/t_P)}/(2e\epsilon_0)D(R) \), where \( c \) and \( \epsilon_0 \) are the speed of light and permittivity of vacuum, and \( D(R) \) is the molecular transition dipole moment; at large distances \( D(R) = 4.245e\alpha_0 \) (\( e \) = proton charge, \( \alpha_0 = \text{Bohr radius} \)). A radial grid up to \( 30000\alpha_0 \) has been built with the mapped grid method [24] to faithfully represent the initial state as a stationary scattering level in X, and the vibrational wavefunctions in the excited states. The time propagation was performed as in Ref. [8].

From now on, we concentrate on a short PA pulse, red-detuned by \( \approx 60 \text{ cm}^{-1} \) from the D\(_1\) line (corresponding to \( \lambda_{\text{hump}} = 798 \text{ nm} \)). The bandwidth is set to \( 15 \text{ cm}^{-1} \), large enough to resonantly couple the initial state \( |X, E = 98.85 \mu \text{K} \rangle \) with two levels of the \( 0^1_a(P_{3/2}) \) series and 13 levels of the \( 0^1_a(P_{1/2}) \) series, but small enough to avoid population of continuum levels in the excited state [cf. Fig. 1(c)]. The pulse is centered at \( t_P = 50 \text{ ps} \), with \( \tau_C = 10 \text{ ps} \), \( \chi = 4.41 \times 10^{-2} \text{ ps}^{-2} \), and \( E_{\text{pulse}} = 41 \text{ nJ} \) focused on \( \sigma = 2.8 \times 10^{-3} \text{ cm}^2 \). We choose \( \chi > 0 \) to maximize the population transfer [22].

We present in Fig. 2 the evolution of the population in the excited states, \(|\Psi_{\text{exc}}(R, t)^2| = |\Psi_A(R, t)^2| + |\Psi_B(R, t)^2|\), well after the PA pulse has finished. The PA probability for a single pair of atoms is \( 4.21 \times 10^{-6} \), and most excited population concentrates around two peaks at 22\( a_0 \) and 37\( a_0 \). The relative importance of these peaks changes in time. For example, the amplitude of the peak at 22\( a_0 \) oscillates with a period \( T^* \approx 8 \text{ ps} \).

This beating results from the interferences between the population of the stationary levels \( \nu' \) of the coupled system of excited states. Indeed, in the present case, the coupling is such that neither the diabatic nor the adiabatic stationary vibrational levels constitute a good basis for the analysis. Here, the coupled states \( |\phi_{\nu'}\rangle \), which have components on the two electronic channels, are labeled by \( \nu' \) according to their increasing energy \( E_{\nu'} \). In this basis, the decomposition of the two-component wavepacket reads \( \Psi_{\text{exc}}(R, t) = \sum_{\nu'} c_{\nu'} \phi_{\nu'}(R) \exp(-iE_{\nu'}t/\hbar) \), where each \( c_{\nu'} \) as well as the total excited population are constant after the pulse.

We show in Figs. 3(b) and 3(c) the radial density \( |\phi_{\nu'}(R)|^2 \) of two stationary states present in the ex-
cited wavepacket. The lower panel corresponds to a level 51 cm\(^{-1}\) below the 5S+5P\(_{1/2}\) limit. It turns out to be ascribable to a "0\(_{1}^+\) (P\(_{1/2}\)) level", as most of its probability density is accumulated close to the outer turning point \(R_{\text{ext},1/2} \approx 37a_0\), corresponding to this potential and this energy [black circle in Fig. 1(c)]. The state in Fig. 3(b), which corresponds to a level 54 cm\(^{-1}\) below D\(_1\), is a typical example of a "resonant 0\(_{3}^+\) (P\(_{3/2}\)) level" [17]; it has a 55\% weight in the adiabatic P\(_{3/2}\) channel, and features two maxima of probability, corresponding to the turning points \(R_{\text{ext},1/2}\) and \(R_{\text{ext},3/2} \approx 22a_0\) [red (gray) circle in Fig. 1(c)] in \(0\(_{3}^+\) (P\(_{1/2}\)) and \(0\(_{3}^+\) (P\(_{3/2}\)) respectively. As the instantaneous frequency of the chirped pulse is resonant with \(\sim 15\) levels in the coupled 0\(_{u}^+\) series, \(\Psi_{\text{exc}}\) will have components on stationary levels of both types, which explains the double-peak structure observed in Fig. 2.

Now, it is easy to show that the population density at an internuclear distance \(R\) has a time dependence determined by all the beating frequencies \(\omega_{ij} = (E_i - E_j)/\hbar\), where \(E_i\) and \(E_j\) are the energies of those levels for which \(c_{ij} \neq 0\). The largest weights in the decomposition correspond to the levels of the coupled basis labeled by \(v' = 406\) and 408, two \("0\(_{1}^+\) (P\(_{1/2}\))\" levels separated by \(\Delta E \approx 4.24\) cm\(^{-1}\), which corresponds to a beating of \(T_{\text{beat}} \approx 7.85\) ps, in agreement with \(T^*\) observed in Fig. 2.

The observed oscillation in the population density close to \(R_{\text{ext},3/2}\) can be probed experimentally with a suitable laser pulse that ionizes the molecule and coherently populates several levels of the lowest \(\text{Rb}_2^+ (X^2\Sigma_g^+)\) potential [20] with classical turning point \(R_{\text{ext},+} \approx 22a_0\). The stationary wavefunction of one such level is plotted in Fig. 3(a). Assuming that the ionization process is a vertical transition, the population transfer to the ionic channel will concern the part of the wavepacket that is close to \(R_{\text{ext},+}\), i.e., the peak around \(R_{\text{ext},3/2}\). Indeed, we show in Fig. 3(a) the time evolution of the overlap \(\sum_{v''} |\langle \text{Rb}_2^+ (X^2\Sigma_g^+) | v'' \rangle \langle \Psi_{\text{exc}}(t) | v'' \rangle|^2\) for the levels \(v'' \in [185, 194]\) that have \(R_{\text{ext},+} \approx (21 - 23)a_0\) and can be populated using a laser with central wavelength \(\lambda_{\text{probe}} = 479.8\) nm and bandwidth \(\approx 30\) cm\(^{-1}\). The overlap is calculated with both A and b components of the excited wavepacket, as no selection rules apply to the ionizing transition.) The signal has a rich structure of peaks and troughs. In the Fourier transform (FT) of a long-duration signal [cf. Fig. 3(c)], one observes a characteristic time \(T_1 = 6.2\) ps (and its multiples), which is identified with the beating period between the levels \(v' = 407\) ["0\(_{1}^+\) (P\(_{1/2}\))\" level] and \(v' = 410\) ["resonant 0\(_{3}^+\) (P\(_{3/2}\))\" level, cf. Fig. 3(b)]. Thus, \(T_1\) is a characteristic time of the \(P_{1/2}\) \(P_{3/2}\) population transfer. Quite remarkably, a different ionizing pulse designed to probe the wavepacket close to \(37a_0\) (\(\lambda_{\text{probe}} = 408.3\) nm) would render a signal dominated by \(T_2 = 2T_{\text{beat}} = 15\) ps, the beating period between the two "0\(_{3}^+\) (P\(_{1/2}\))\" levels \(v' = 407, 408\) [cf. Fig. 3(b) and 3(c)] as the classical turning point of the 0\(_{3}^+\) (P\(_{3/2}\)) components is 22\(a_0\), where the \(\text{Rb}_2^+\) vibrational wavefunctions have no appreciable amplitude, almost no effect of the 0\(_{3}^+\) (P\(_{1/2}\)) - 0\(_{3}^+\) (P\(_{3/2}\)) coupling is expected to show up at this distance. Of course, some peaks are visible in Fig. 3(c) that correspond to other beating periods \(\omega_{v''}\). Nevertheless, \(T_1\) and \(T_2\) can be used as fingerprints of the two different ionization processes, as each of them appears only in one signal.

![FIG. 2: (color online) Evolution of the wavepacket in the excited channels \(\Psi_{\text{exc}}(R, t)\) after the PA pulse has finished.](image1)

![FIG. 3: (color online) Stationary wavefunctions of (a) the \(\text{Rb}_2^+ (X^2\Sigma_g^+)\) level bound by 264 cm\(^{-1}\); (b) the 0\(_{3}^+\) level 54 cm\(^{-1}\) below \(D_1\); and (c) the 0\(_{3}^+\) level 51 cm\(^{-1}\) below \(D_1\).](image2)

![FIG. 4: (color online) Evolution of the overlap of |\(\Psi_{\text{exc}}(t)\)| with (a) 10 \(\text{Rb}_2^+ (X^2\Sigma_g^+)\) levels with \(R_{\text{ext},+} \approx 22a_0\); (b) 16 \(\text{Rb}_2^+ (X^2\Sigma_g^+)\) levels with \(R_{\text{ext},+} \approx 37a_0\); (c) Fourier transform of signals in (a) [blue (black) line] and (b) [red (gray) line] in the time window \(t \in [70, 300]\) ps. The dashed vertical line stands for \(t_f = 50\) ps and arrows indicate the most relevant timescales.](image3)
We next analyze the dynamics after a dump pulse toward bound vibrational levels of Rb$_2$(X$^1\Sigma^+_g$). Note that due to selection rules, this transition is selecting the A$^1\Sigma^+_u$ component in the excited wavepacket. The results are shown in Fig. 4(a) for the vibrational levels with binding energy $E_{\text{bind}} \lesssim 24$ cm$^{-1}$, and in Fig. 4(b) for the levels with $1300$ cm$^{-1} \leq E_{\text{bind}} \leq 2500$ cm$^{-1}$, which have a reasonable Franck-Condon factor with $\Psi_{\text{exc}}$ and are reachable by a fs dump pulse ($\lambda_{\text{dump}} = 708$ nm). In both cases, $T_{\text{beat}}$ and the mean value of the vibrational period in the pure 0$^+_u$ (P$_{1/2}$) potential in this energy range, $T_0^u \approx 13$ ps, have an important role, and can be used to determine the best timing for the dump pulse.

In summary, we have studied the dynamics of Rb$_2$ 0$^+_u$ molecules created by a picosecond PA pulse from cold $^{85}$Rb atoms. The excited wavepacket spans $\sim 15$ vibrational levels in the coupled 0$^+_u$ basis and presents two maxima of probability at $R_{\text{ext,1/2}}$ and $R_{\text{ext,3/2}}$. The subsequent dynamics shows quantum interferences, with a beating of the population close to $R_{\text{ext,3/2}}$. This beating can be monitored by photoionizing the wavepacket with a laser with well-defined energy spectrum, which in practice defines a window of internuclear distances whose density probability is probed. The corresponding signal and its Fourier transform can serve as identification tool for ongoing PA experiments. We have also analyzed a pump-dump pair of pulses to form deeply-bound ground-state molecules. The resulting time dependence would allow, in an experiment with a sequence of pump-dump pairs at a high repetition rate, to choose the delay between consecutive pairs, so that a dump pulse would not dissociate the molecules created by the preceding dump pulse. Moreover, these molecules could be further transferred to even deeper levels by other pairs of pulses (see also Ref. 10). We studied here a pulse with a relatively large detuning to avoid coupling to the continuum levels in the excited channels. In the future, for a closer comparison with experiments, femtosecond PA pulses with smaller detunings and a mask to cut the blue part of the pulse spectrum that transfers populations to the continuum, will be analyzed. Also, we will further study the role of SO coupling in $^{87}$Rb and $^{133}$Cs samples.

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