Optimal control of photoassociation of cold atoms and photodissociation of long-range molecules: Characteristic times for wave-packet propagation

M. Vatavse,
1,2 O. Dulieu,
1 R. Kosloff,
3 and F. Masnou-Seeuws
1

1Laboratoire Aimé Cotton, Bâtiment 505, Campus d’Orsay, 91405 Orsay Cedex, France
2Institute for Space Sciences, Bucharest-Magurele, Romania
3The Fritz Haber Research Center for Molecular Dynamics, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

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This paper aims at studying the time-dependent effects involved in the photoassociation reaction for a sample of cold alkali-metal atoms, within a two-channel model where the vibrational motion in the excited state is coupled by laser light to the continuum state describing two colliding atoms in the lowest triplet electronic state \((a^3 \Sigma_u^+)\). Both photodissociation and photoassociation processes are considered at a time scale shorter than the radiative lifetime, so that spontaneous emission does not have to be considered. The characteristic times are the vibrational period in the excited state, which for alkali-metal dimers can be estimated of the order of a few hundreds of picoseconds, and the Rabi period, depending upon the laser intensity. Numerical calculations using wave-packet propagation are performed for the coupling of the vibrational motion in the Cs₂ \(1\Sigma_g^+(6s + 6p_\Sigma^0)\) and \(a^3 \Sigma_u^+ (6s + 6s)\) channels by a cw laser slightly red detuned relative to the D₂ resonance line. The results show Rabi oscillations in the populations of the two channels during time intervals when the vibrational motion is stopped at the outer turning point. At intensities of \(\approx 250\ \text{kW cm}^{-2}\), a new characteristic time appears, a factor of 2 larger than the classical vibrational period, which corresponds to vibrational motion in the upper adiabatic potential created by the coupling. Such an effect modifies the scattering length for collisions in the lower state, and it clearly opens a possibility of control by tuning the laser intensity.

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I. INTRODUCTION

During the last 15 years, the physics of dilute gases has seen major advances in two fields: laser cooling of atomic samples and femtosecond chemistry. In both cases, a strong motivation is to use laser light in order to achieve a better control of the system by reducing the energy distribution of the various degrees of freedom. In this context, two fundamental processes, i.e., photoassociation and photodissociation, or in other words formation and breaking of the chemical bond, have motivated a lot of theoretical and experimental studies.

Among the many applications of cold atoms, the photoassociation reaction [1], where two atoms absorb a photon to create an excited molecule, has provided a wealth of accurate data on long-range molecular interactions, and the first experimental demonstration of the formation of ultracold molecules [2–4]. In contrast with thermal energies [5], photoassociation in the cold regime is a resonant process due to the extreme sharpness of the energy distribution of the initial continuum state [6]; this eliminates any contribution of continuum-continuum absorption and selects a well-defined rovibrational level as a final state. Photoassociation has been observed for all cold alkali-metal atoms [7], as well as for hydrogen [8] and helium [9]. Most of the experiments have been performed up to now with continuous laser light, and accordingly, theoretical investigations of the photoassociation process have been carried out mainly in the framework of a time-independent approach [6,10–12] using a perturbative treatment. In the framework of a Franck-Condon picture, photoassociation is modeled as a vertical transition at large interatomic distances between a continuum state of two colliding atoms and a rovibrational level of an excited molecule, with a wave function approximated by an Airy function at the outer turning point. At ultracold temperatures, only a few partial waves have to be considered, so that the photoassociated molecule is formed in a rotational level with small angular momentum \(J\). This picture is confirmed by experimental observation, where modulations in the photoassociation rate as a function of laser detuning faithfully reflect the nodal structure of the ground state wave function [13,14]. Under stationary conditions, a simple analytic expression for the number of photoassociated molecules has been derived [6], predicting, besides the modulation described above, a dependence on \(T^{J-n} n \Delta_l^{-\left(J^{2}+J+1\right) / 2}\), where \(T, n, I,\) and \(\Delta_l\) are, respectively, the temperature and density of the cold atomic sample, the intensity, and the red detuning of the photodissociating laser relative to the atomic resonance line. At low laser intensities, such a simple model is in satisfactory agreement with the experimental observation [15], quantitative agreement relying upon a numerical estimation of the wave function overlap.

In the thermal energy domain, the reverse process of photodissociation, i.e., photodissociation, has benefited from the development of ultrashort laser sources, allowing time-resolved studies of the transition state dynamics [16,17]. The photodissociation process is indeed well suited for such purpose, as the initial state (characterized by the molecular internal state) is well defined. For the theoretical interpretation, time-dependent calculations have been intensively developed [18]. In contrast with thermal energies, photodissociation of the cold excited molecules has not been studied, in particular, in case of stimulated photodissociation when the final state is a pair of ground state cold atoms. The bound-
free transition is then due to stimulated emission: this process will be simply called photodissociation in the following.

The aim of the present series of papers [19] is to take advantage of the above know-how to investigate the dynamics of both processes in the cold regime, in a time-dependent framework. Cold atomic collisions, or vibration of a photo-associated molecule, are characterized by two different time scales according to the range of internuclear distances: at short range \( R<50\,a_0 \), \( a_0=0.0529177 \) nm is the Bohr radius), strong interactions due to the chemical bond lead to fast \(<100\) fs) dynamics, while in the long-range domain weak interatomic interactions (multipole expansion, fine and hyperfine structure) produce slow motion. A time-dependent description offers the opportunity to study the interplay between these two regimes, to consider both continuous or pulsed laser light, and to overcome the restriction to weak laser intensities by going beyond the perturbative limit.

This paper is devoted to the time-dependent study of the evolution of a cold atom pair interacting with cw laser light, studied over duration in the nanosecond range, the influence of spontaneous emission being then negligible. The results will then provide insight for the evolution of the system interacting with a square-shaped nanosecond pulse (more realistic pulse shapes are beyond the scope of the present work). We shall see that in the cold regime \( T=E/k_B=1\) mK, where \( E \) is the relative kinetic energy and \( k_B \) the Boltzman constant) there is a competition between characteristic times associated with the relative motion of the atoms (vibrational period, collision time) and the electromagnetic coupling (Rabi period). The formalism is described in Sec. II. We limit ourselves to the simple picture of two molecular channels coupled by laser light: effects linked to rotation and hyperfine structure coupling will be neglected. In Sec. III, we give for all the alkali-metal dimers a classical estimation of the vibrational period, and of the Rabi period considering the range of internuclear distances: at long range \( a_0 \) dynamics, while in the long-range domain weak interatomic interactions (multipole expansion, fine and hyperfine structure) produce slow motion. A time-dependent description offers the opportunity to study the interplay between these two regimes, to consider both continuous or pulsed laser light, and to overcome the restriction to weak laser intensities by going beyond the perturbative limit. At longer time scales, corresponding to existing photoassociation experiments, a more elaborate treatment has to be implemented, and this will be the subject of further studies.

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and the functions $\chi_e$ and $\chi_i$ describe the relative radial motion of the atoms in these potentials.

The time-dependent Schrödinger equation is written, for the two component function $\Psi(t)$:

$$\hat{\mathbf{H}}\Psi(t) = [\hat{\mathbf{H}}_{\text{mol}} + \hat{\mathbf{W}}(t)]\Psi(t) = i\hbar \frac{\partial}{\partial t} \Psi(t). \quad (2)$$

The $\hat{\mathbf{H}}_{\text{mol}}$ operator is the usual molecular Hamiltonian involving kinetic energy operator $\hat{T}$ and electronic potential energy operator $\hat{U}_{el}$:

$$\hat{\mathbf{H}}_{\text{mol}} = \hat{T} + \hat{U}_{el}, \quad (3)$$

and the coupling term is written in the dipole approximation:

$$\hat{\mathbf{W}}(t) = -\hat{D} \cdot \hat{E}_L \varepsilon_0 \cos(\omega_L t). \quad (4)$$

involving the transition dipole moment of the dimer $\hat{D}$ and the electric field $\hat{E}$ with amplitude $\varepsilon_0$, polarization $\varepsilon_L$, and frequency $\omega_L/2\pi$:

$$\hat{E} = \varepsilon_0 \cos(\omega_L t) = \varepsilon_L \varepsilon_0 \cos(\omega_L t). \quad (5)$$

The explicit temporal dependence of $\hat{\mathbf{H}}$ is eliminated in the framework of the rotating wave approximation, and the transformation of the radial wave function of the nuclear motion:

$$\chi_g(R,t) = \tilde{\chi}_g(R,t) \exp(-i\Delta_L t/\hbar),$$

$$\chi_e(R,t) = \tilde{\chi}_e(R,t) \exp(-i\omega_0 t), \quad (6)$$

where $\Delta_L$ is the red detuning of the laser from the resonant atomic transition energy $\hbar \omega_0$. The coupled equations are now expressed as

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \tilde{\chi}_g(R,t) \\ \tilde{\chi}_e(R,t) \end{pmatrix} = \begin{pmatrix} \hat{T} + \hat{U}'_g(R) & \hbar \Omega \\ \hbar \Omega & \hat{T} + \hat{U}'_e(R) \end{pmatrix} \begin{pmatrix} \tilde{\chi}_g(R,t) \\ \tilde{\chi}_e(R,t) \end{pmatrix}, \quad (7)$$

where the potentials $\hat{U}'_g(R)$ and $\hat{U}'_e(R)$ are now referred to the $\Delta_L = 0$ origin, and dressed by the field (Fig. 2):

$$\hat{U}'_g(R) = \hat{U}_g(R) - \Delta_L, \quad \hat{U}'_e(R) = \hat{U}_e(R) - \hbar \omega_0, \quad (8)$$

The coupling term is expressed as a function of the Rabi frequency $\Omega(R)/2\pi$ of the system, related to the molecular transition dipole moment $\hat{D}_{ge}(R) = \langle \phi_g(R) | D(R) | \phi_e(R) \rangle$, in the field of a laser with intensity $I$, and polarization $\varepsilon_L$:

$$\hbar \Omega(R) = -\frac{\hat{D}_{ge}(R) \cdot \varepsilon_0}{2} = - \frac{1}{2} \sqrt{\frac{2I}{c \varepsilon_0}} \hat{D}_{ge}(R) \cdot \varepsilon_L = c \varepsilon_L \sqrt{\hat{D}_{ge}(R)^2}. \quad (9)$$

The time-dependent Schrödinger equation Eq. (2) is solved by propagating an initial wave function $\Psi_0$, using a Chebychev expansion of the evolution operator $\exp(-i\hat{\mathbf{H}}t/\hbar)$ [23]. The wave functions are introduced through their Fourier grid representation [24], defined on a grid of points with a constant stepsize $\delta R = \pi/k_{\text{max}}$ determined by the maximum momentum $k_{\text{max}}$ considered in the problem. The number of grid points is a power of 2, to benefit from standard powerful fast Fourier transform algorithms. In order to avoid prohibitive propagation time, outgoing boundary conditions for the wave functions are simply defined by transferring the outgoing portion of the wave function to another grid [25] with similar characteristics, where the propagation can be performed analytically. Use of an imaginary absorbing potential would have the same efficiency [26–28]. The transfer function $f_T(R)$ centered in $R_T$, defined on $N_T$ grid points and acting over the range $\Delta R_T = N_T \delta R$, is chosen as

$$f_T(R) = 1 + \frac{1}{2} \tanh(\alpha(R - R_T - \Delta R_T/2)). \quad (10)$$

All derivatives up to $N_T^{th}$ order are vanishing at the edge of the $\Delta R_T$ zone, ensuring that no reflection of the wave function will occur.

The initial state for the photodissociation process is defined as

$$\Psi_0 = \begin{pmatrix} 0 \\ \chi_e(r;0) \end{pmatrix}, \quad (11)$$

where $\chi_e(r;0) = \chi_e(R)$ is a well-characterized vibrational wave function with energy $E_v$ of the excited electronic state. We note that the choice of a representation for the photoassociation initial state in the present time-dependent approach is more complex; the usual representation of a continuum state by a Gaussian wave packet, under cold conditions, will have a tremendous extension, well beyond the interaction zone. Moreover, due to the small kinetic energy, there is a wide region where the potential is imposing the same nodal structure to the stationary wave functions at various energies, as observed in several photoassociation spectroscopy experiments [2,14,29]. The description of this nodal structure in a wave-packet formulation will be addressed in detail else-
TABLE I. Energy spacings $\Delta E_v$ and classical periods $T_{\text{VIB}}$ for vibrational levels in the $1_s(n_s + np_{3/2})$ potential of alkali-metal dimers, and Rabi times $T_{\text{Rabi}}$ for a linearly polarized laser with intensity $I = 1 \text{kW/cm}^2$ and $I = 32 \text{kW/cm}^2$. Dipole moments $D$ and $D_{ge}^{(3)}$ for the atomic/molecular transitions $(n_s \rightarrow np)/(a_{1g}) \rightarrow 1_s(n_s + np_{3/2})$ are also displayed. Long-range $C_3$ coefficients for the $1_g$ state are deduced from spin-orbit diagonalization involving long-range parameters of Ref. [34]. Values for Li$_2$ are in italics, to emphasize that Hund’s case c is not appropriate for this dimer.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$\Delta E_v$ (cm$^{-1}$)</th>
<th>$T_{\text{VIB}}$ (ps)</th>
<th>$T_{\text{Rabi}}$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^7$Li$_2$</td>
<td>0.28</td>
<td>118</td>
<td>367</td>
</tr>
<tr>
<td>$^{23}$Na$_2$</td>
<td>0.15</td>
<td>224</td>
<td>336</td>
</tr>
<tr>
<td>$^{39}$K$_2$</td>
<td>0.10</td>
<td>328</td>
<td>284</td>
</tr>
<tr>
<td>$^{85}$Rb$_2$</td>
<td>0.07</td>
<td>494</td>
<td>274</td>
</tr>
<tr>
<td>$^{133}$Cs$_2$</td>
<td>0.05</td>
<td>643</td>
<td>257</td>
</tr>
</tbody>
</table>

$\Psi_0 = \left( \begin{array}{c} \chi_g(R;0) \\ 0 \end{array} \right)$.

III. ESTIMATE THE CHARACTERISTIC TIMES

Prior to quantum wave-packet propagation, it is worthwhile to estimate the characteristic times governing the dynamics of the cold atom pair interacting with laser light. This will be relevant to gain insight into the best arrangement for maximum efficiency of the process.

Among the various attractive states varying as $R^{-3}$ at large distances, we focus on vibrational levels of the purely attractive $1_s(n_s + np_{3/2})$ Hund’s case c state of the alkali dimers, located within a few wave numbers below the lowest $(n_s + np_{3/2})$ dissociation limit. This state has been already observed by photoassociation with continuous lasers for Na$_2$, K$_2$, Rb$_2$, and Cs$_2$. Neglecting hyperfine structure of the atoms, it is connected at short distances to the lowest $1\Pi_g$ state of the alkali-metal dimer, and coupled at large distance through an electric dipole interaction to the lowest $a^1\Sigma_u^+(0_g^+, 1_u^a)$ state (see Fig. 1). The long-range $C_3/R^3$ behavior of the potential—where $C_3$ is the leading coefficient of the multipolar expansion of the atom-atom interaction including spin-orbit [30]—results in a very long classical period $T_{\text{VIB}}$ for the vibrational motion, as well as a high density of vibrational levels close to the dissociation limit. The classical period $T_{\text{VIB}}$ [31] is related to the slope of the energy dependence of the vibrational quantum number by

$$T_{\text{VIB}}(E_v) = \frac{2\pi}{\Delta E_v} \frac{\partial E_v}{\partial E_v}.$$

$T_{\text{VIB}}$ is the time necessary to go from outer turning point to inner and back. In the present problem, the levels are close enough so that linearization of the slope is possible, yielding

$$T_{\text{VIB}}(E_v) \approx \frac{2\pi h}{E_{v+1} - E_v} = \frac{2\pi h}{\delta E_v}. \quad (14)$$

The binding energy $(D - E_v)$ of an excited vibrational level lying in a potential with $C_3/R^3$ asymptotic behavior and dissociating at an energy $D$ can be estimated through the Leroy-Bernstein formula [32] as a function of the vibrational number $v$, the reduced mass $\mu$, and the asymptotic coefficient $C_3$. The energy difference $(E_{v+1} - E_v)$ is determined, leading to the approximate expression for $T_{\text{VIB}}$,

$$T_{\text{VIB}} \approx \frac{(C_3)^{1/3}}{3} \gamma(5/6) \left(\frac{2\mu \pi}{\gamma(4/3)} \frac{D - E_v}{\delta E_v}\right)^{-5/6},$$

where $\gamma(5/6)/\gamma(4/3) = 1.2678$ is a tabulated constant. Considering the resonance condition in a photoassociation experiment, $D - E_v = \Delta E$, the classical vibrational period of a dimer $A_2$ is calculated according to

$$T_{\text{VIB}}(ps) \approx [C_3(\text{a.u.)}]^{1/3} \sqrt{\frac{M_A}{40}} \Delta E \left(\text{cm}^{-1}\right)^{-5/6} \times 136 \text{ ps}.$$

where $M_A$ is the atomic mass of the atom $A$. The potassium atomic mass $M_K = 40$ is used as a reference scaling parameter. Assuming $C_3$ values around 10 a.u., the vibrational half-period has a magnitude of about 100 ps for a $1 \text{ cm}^{-1}$ detuning. Exact values involving the computed level spacing for the $1_g$ curve of alkali-metal dimers at 1 and 4.3 cm$^{-1}$ detunings are reported in Table I.
Another characteristic time, $T_{\text{Rabi}}$, is associated with the coupling $\hbar \Omega$ due to laser light with polarization $e_L$ [see Eq. (9)].

$$\frac{\hbar}{2} T_{\text{Rabi}}^{-1} = \hbar \Omega. \quad (17)$$

The value of transition dipole moment $D_{ge}^{(\pi)}$ can be deduced from the expression of the $1_g (ns + np_{3/2})$ state in terms of Hund’s case $a$ states,

$$|1_g (ns + np_{3/2})\rangle = \alpha_1(R) |^3\Sigma_g^+\rangle + \alpha_2(R) |^3\Pi_g\rangle + \alpha_3(R) |^1\Pi_g\rangle,$$  

where the coefficients $\alpha_1$, $\alpha_2$, $\alpha_3$ result from the diagonalization of the electronic Hamiltonian, including atomic spin-orbit interaction. Standard long-range calculations [33] show that the asymptotic values $\alpha_1^\infty = 0.765$, $\alpha_2^\infty = 0.135$, $\alpha_3^\infty = -0.629$ of these coefficients are relevant for the range of detunings investigated in the present work. The following values for $D_{ge}^{(\pi)}$ are then deduced, depending on the laser polarization:

$$D_{a^1\Sigma_g^+, 1_g}^{(\pi)} = \alpha_1^\infty \sqrt{2} D, \quad D_{a^3\Pi_g, 1_g}^{(\pi)} = \alpha_2^\infty 2D,$$  

where $D$ is the matrix element of the $z$-component of the atomic $s \rightarrow p$ transition dipole moment:

$$D = \langle p | ez | s \rangle.$$  

Table I displays values for $T_{\text{VIB}}$ and $T_{\text{Rabi}}$, for vibrational levels located at detunings 1 and 4.3 cm$^{-1}$, typical of the range explored in this work. For cesium dimer, the corresponding outer classical turning point is located at 150 a$_0$ and 90 a$_0$, respectively. The values of the coupling chosen in our examples to illustrate different experimental conditions are: $\hbar \Omega = 0.0584$, $\hbar \Omega = 0.367$, and $\hbar \Omega = 1$ cm$^{-1}$, obtained with linearly polarized lasers with intensities $I = 800$ W/cm$^2$, $I = 32$ kW/cm$^2$, and $I = 252$ kW/cm$^2$, respectively. The first value, $\hbar \Omega = 0.0584$ cm$^{-1}$, is typical for a photoassociation experiment with a cw laser.

It is clear from Table I that the present problem is unusual because of the large value of the vibrational period. Even at low intensity, the characteristic time for Rabi oscillations can become smaller than the vibrational time, so that the laser intensity is an important control parameter of the photoassociation process. Various experimental conditions are explored below, illustrating different values of the ratio of the characteristic times,

$$\frac{T_{\text{VIB}}}{T_{\text{Rabi}}} = \frac{2}{\hbar} \sqrt{c_{\text{vib}} \mu(C_2)} \sqrt[3]{\Delta L} \frac{(\Lambda E)}{c_{\text{Rabi}}} \sqrt{D_{ge}^{(\pi)}}.$$

We label the cases: $T_{\text{VIB}} \gg T_{\text{Rabi}}$ as the “strong coupling” case, $T_{\text{VIB}} \ll T_{\text{Rabi}}$ as the “weak coupling” case, and $T_{\text{VIB}} \approx T_{\text{Rabi}}$ the “intermediate coupling” case. We should note that the ratio in Eq. (21) is increasing when the intensity is increased or the detuning is decreased. The two factors are not independent, as larger detunings necessitate a larger laser intensity to keep the same efficiency in the photoassociation process. This will be discussed below in Sec. IV C. A resonance condition for photoassociation implies $D - E_c = \Delta L$, in Eq. (15). We will also refer to this definition, although less relevant, in our photodissociation study; it will then concern the relative energy of the outgoing atom pair. The influence of this condition will be also discussed.

Another characteristic time is linked to the radial motion in the ground state, and then to the definition of the initial state for photoassociation. As already mentioned, this aspect will only be briefly discussed here, as well as in Ref. [19].

IV. WAVE-PACKET PROPAGATION AND PHOTODISSOCIATION OF THE COLD EXCITED MOLECULES

The resolution of the time-dependent Schrödinger equation (2) is undertaken in the cesium case, for the $a^1\Sigma_u^+ \rightarrow 1_g (6s + 6p_{3/2})$ transition. The relevant potential curves are displayed in Figs. 1 and 2. The long-range domain is defined here by $R > 30 a_0$, leading to transition dipole moment values $D_{ge}^{(\pi)} = 1.08 D$ and $D_{ge}^{(\sigma)} = 0.27 D$, with $D = 3.24$ a.u. More than 320 vibrational levels are found in the $1_g$ potential. To illustrate, we shall consider the following initial vibrational levels, located in a region where the energy slope $dE_v / d\nu$ or the classical vibrational period $T_{\text{VIB}}$ matches two different regimes: (i) the level $v = 290$, with $E_v \approx -0.99$ cm$^{-1}$, $dE_v / d\nu \approx 0.05$ cm$^{-1}$ and $T_{\text{VIB}} \approx 600$ ps; and (ii) the level $v = 259$ with $E_v \approx -4.3$ cm$^{-1}$, $dE_v / d\nu \approx 0.17$ cm$^{-1}$ and $T_{\text{VIB}} \approx 200$ ps.

The corresponding vibrational wave functions $\chi_{290}$ and $\chi_{259}$ are computed with the Numerov integration method. Time propagation of a few nanoseconds, longer than the characteristic times but much smaller than the radiative lifetime ($\approx 30$ ns), is investigated, which could simulate the action of a square-shaped nanosecond laser pulse; the energy width of such a pulse is still smaller than the energy spacing between vibrational levels, and can be safely neglected for the present model where no rotation is included.

A. Photodissociation under typical experimental conditions with a cw laser: intermediate coupling case

We consider first the $v = 290$ level, bound by $D - E_v = 0.99$ cm$^{-1}$ and $\Delta L = 1$ cm$^{-1}$ (Fig. 5). The typical spacing between vibrational levels is 0.05 cm$^{-1}$ in this region. The radiative coupling is chosen equal to $\hbar \Omega = 0.0584$ cm$^{-1}$, yielding $T_{\text{Rabi}} = 286$ ps while $T_{\text{VIB}} = 643$ ps. Such a coupling (referred to as the “intermediate coupling” case above) corresponds to typical conditions of most of the photoassociation experiments; it requires a laser intensity of about 800 W/cm$^2$ in linear polarization. The spatial grid used for the propagation extends from 6 a$_0$ to 275 a$_0$, and supports 8192 points. The populations are smoothly varying in both channels. Figure 3 shows the progressive depletion of the population in the $1_g$ channel, which is visible in Fig. 4, too.
The weak modulations of the two populations can be attributed to a small effect of Rabi oscillations, which do not have enough time to take place, as the amplitude is moving fast towards the inner zone. This effect is, in fact, coupled to the vibrational motion, so that we observe modulations with a characteristic time $\sim 230$ ps slightly smaller than the Rabi period $T_{\text{Rabi}} = 286$ ps given by Eq. (17).

B. Photodissociation in the strong-coupling case

1. Small detuning, on-resonant laser

Such conditions are achieved for the $v = 290$ level and detuning $\Delta \omega = 1 \text{ cm}^{-1}$, when choosing the coupling $\hbar \Omega = 0.367 \text{ cm}^{-1} \approx 7 \delta E_v$; this yields $T_{\text{Rabi}} \approx 45$ ps, which is much smaller than the classical period $T_{\text{VIB}} \approx 643$ ps. The spatial grid used in this case is the same as before. The relevant dressed potential curves are presented in Fig. 5. All the effects mentioned in the previous paragraph are now magnified.

Figure 6 clearly demonstrates the existence of Rabi oscillations between the two levels. The temporal evolution of the wave packet during a time which is smaller than the vibrational period $T_{\text{VIB}}$ can be qualitatively understood within the intuitive Franck-Condon model, as the population is transferred from the main peak of the $1_g$ vibrational wave function to the continuum and backwards, creating a pair of atoms at $R_c \approx 150a_0$. One can differentiate the following.

(i) A regime of almost pure Rabi oscillations during a short-term evolution (0–150 ps) where the motion of the nuclei can be ignored in both channels (Fig. 7): the population remains located mainly around the crossing point $R_c \approx 150a_0$. However, the strong coupling induces a large transition region (about $50a_0$ in width), where the wave packet in the $\sigma^+ \Sigma_u^+$ channel does not vanish from the very beginning of the evolution [Fig. 7(a)], at $t = 6$ ps.

(ii) A longer term evolution (150–400 ps) (Fig. 8), during which the ground state wave packet starts moving both inwards and outwards. Population of the $1_g$ continuum becomes

![Figure 3](image3.png)

**FIG. 3.** Photodissociation (i.e., bound-to-free stimulated emission) of the cold excited Cs$_2$ molecule, under conditions typical from an experiment with cw light. The resonance condition is fulfilled here. The initial vibrational level of the $1_g$ state is $v = 290$ ($D - E_v = 0.99 \text{ cm}^{-1}$). Evolution of the populations on the $1_g$ (full line) and $\sigma^+ \Sigma_u^+$ (dashed line) channels for a coupling $\hbar \Omega = 0.058 \text{ cm}^{-1}$. The characteristic time of the smooth modulations, 230 ps, is slightly smaller than $T_{\text{Rabi}} \approx 286$ ps. Vertical dotted lines refer to the snapshots of Fig. 4.

The weak modulations of the two populations can be attributed to a small effect of Rabi oscillations, which do not have enough time to take place, as the amplitude is moving fast towards the inner zone. This effect is, in fact, coupled to the vibrational motion, so that we observe modulations with a characteristic time (230 ps) slightly smaller than the Rabi period $T_{\text{Rabi}} = 286$ ps given by Eq. (17).

![Figure 4](image4.png)

**FIG. 4.** Time evolution of the wave packets for the conditions of Fig. 3, showing population transfer from the bound vibrational state $1_g$ ($v = 290$ (left column), $D - E_v = 0.99 \text{ cm}^{-1}$, to the continuum of the $\Sigma_u^+$ state (right column). The absorption of the wave packet by the transfer function $f_T$ at the edge of the grid is also visible. Characteristic times are $T_{\text{VIB}} \approx 643$ ps and $T_{\text{Rabi}} \approx 286$ ps.

![Figure 5](image5.png)

**FIG. 5.** Photodissociation of the cold excited Cs$_2$ molecule, in the strong coupling case described in Sec. IV B: the field-dressed potential curves $1_g$ (full line) and $\sigma^+ \Sigma_u^+$ (dashed line) around their crossing point, for a detuning $\Delta \omega = 1 \text{ cm}^{-1}$ and the probability density of the initial level $v = 290$ of the $1_s(6s + 6p_{3/2})$ state, bound by $D - E_v = 0.99 \text{ cm}^{-1}$.
comes effective, so that outward motion is also visible in the excited channel. The efficiency of the population exchange between the channels is strongly reduced, washing out the Rabi oscillations. The velocity of the outgoing flux in the $a^3S_u^-$ channel can be estimated from Figs. 8(h)–8(j) to be about 10 ms$^{-1}$, although the resonance condition would tend to favor nearly zero kinetic energies. This represents a large increase of the kinetic energy distribution compared to the energies inferred by the resonance condition $D-E_v=\Delta L$, due to the nonlocalized character of the transition. Population of continuum levels with larger kinetic energy is then achieved, so that by absorption of a photon, a small fraction of the population is now transferred back to the $1_g$ continuum [Figs. 8(d) and 8(e)].

2. Larger detuning, off-resonance laser

The outgoing flux in the $a^3S_u^-$ channel can be maximized by choosing a detuning $\Delta L$ larger than the binding energy of the initial level. From the point of view of the Franck–Condon principle, the kinetic energy is conserved. The mean kinetic energy of the initial $1_g$ vibrational level is about five times larger than its detuning (see, for instance, Fig. 7 of Ref.
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FIG. 9. Photodissociation of the cold excited Cs₂ molecule, in the strong coupling case described in Sec. IV B 2, showing the field-dressed potential curves $1_g$ (full line) and $a^3Σ_u^+$ (dashed line) around their crossing point at $R=R_c$, for a detuning $\Delta_{E_v}=5 \text{ cm}^{-1}$, and the probability density of the initial level $v=259$ of the $1_g(6s+6p_{5/2})$ state, bound by $D−E_v=4.3 \text{ cm}^{-1}$.

\[ \text{[6]; such a level will strongly interact with continuum states with kinetic energy much larger than zero. Moreover, it is worthwhile to investigate longer propagation time under conditions for which the width of the radiative coupling $h\Omega$ is not overlapping too many vibrational levels. Also, realistic experimental conditions imply a laser frequency far enough from the atomic transition, in order to avoid the destruction of the cold atom trap itself.} \]

The field-dressed potential curves are represented in Fig. 9. The initial $1_g$ vibrational level $v=259$ bound by $D−E_v=4.3 \text{ cm}^{-1}$ is coupled to the $a^3Σ_u^+$ channel through a laser detuned by $\Delta_{E_v}=5 \text{ cm}^{-1}$ (i.e., nonresonant condition) with a coupling parameter $h\Omega=1 \text{ cm}^{-1}$ efficient around $90\alpha_0$, in a region where $1_g$ vibrational levels are separated by about $0.17 \text{ cm}^{-1}$. For linear polarization, such coupling requires a laser intensity $I=252 \text{ kW/cm}^2$. The corresponding characteristic times are such that $T_{\text{VIB}}=186 \text{ ps}$ $> T_{\text{Rabi}}=16 \text{ ps}$. We mention that the spatial grid used for propagation extends from $6.3\alpha_0$ to $390\alpha_0$, and supports 8192 points.

The evolution of the population as a function of time is displayed in Fig. 10, while snapshots of the wave packets at various times are displayed in Fig. 11. The Rabi period and the vibrational period are clearly visible, and the reconstruction of the initial wave packet in the excited state, with a peak at the outer classical turning point, occurs at a time $T_{\text{R}}\approx 400 \text{ ps}$. This new characteristic time, a factor of 2 larger than the classical vibrational period, has to be interpreted. We have analyzed the results in terms of fractional revival, generalizing to the present motion of weakly bound vibrational levels the concepts developed for Rydberg wave packets [37]. This analysis shows that the explanation does not lie in that direction, the characteristic time $T_{\text{R}}$ being independent of the laser intensity over a wide range, and hence independent of the number of levels coupled by the electromagnetic field. In the spirit of several papers on light-induced phenomena (see Ref. [38], and references therein), we have studied the modification of the potential in the strong coupling regime. Considering the adiabatic potential obtained by diagonalizing the $2\times2$ potential matrix of Eq. (7), we obtain in the excited state a new adiabatic potential $U_{\text{ad}}^e$ with $R^{-3}$ behavior at distances larger that the crossing point $R_c$ and flat $R^{-6}$ behavior at distances $R<R_c$. The relevant potential curves $U_{\text{ad}}^e(R)$ and $U_{\text{ad}}^d(R)$ are displayed in Fig. 12. For the potential $U_{\text{ad}}^d(R)$, the motion is slower in the inner region than for the uncoupled potential $U_{\text{ad}}^e(R)$, so that the vibrational period is increased. Due to the presence of an avoided crossing, the level spacing is rapidly varying as a function of the vibrational number; considering the levels with spacing between 0.12 and 0.08 cm$^{-1}$, we find a classical vibrational period $T_{\text{ad}}$ between 285 and 432 ps. The period $T_{\text{R}}=400 \text{ ps}$, which is clearly visible in the evolution of the populations and of the correlation function in Fig. 10, has the correct order of magnitude to be identified with $T_{\text{ad}}$. Several stages are visible:

First, up to 200 ps, the population of the $1_g$ level decreases to populate the $3Σ_u^+$ channel, which takes up to 80% of the total population. At this point, the transfer stops as the maximum of the $1_g$ wave packet has been destroyed.

Between 200 and 300 ps, the $1_g$ packet is penetrating the inner zone, and the photodissociation process is stopped as there is little population in the region of the crossing. The amplitude of the Rabi oscillations becomes negligible. It is remarkable that we no longer see Rabi oscillations at a time $t>500 \text{ ps}$.
At $t = T_{\text{VIB}} \approx 186$ ps, which corresponds to the classical vibrational period in the unperturbed, excited potential.

At $t = T_{\text{R}} \approx 400$ ps, the initial wave packet is partly reconstructed, and strong Rabi oscillations are visible. The new vibration characteristic time then corresponds to the classical period for motion in the adiabatic potential.

Such effects are visible in the time evolution of the wave packets, where the reconstruction of the initial wave packet at the outer turning point $R_0 = 90a_0$ is manifested around 400 and 800 ps, corresponding to one and two periods $T_{\text{R}}$. On the lower $^3\Sigma_u^-$ channel, the outgoing wave packet spreads as a free wave packet, the motion in the potential $U_{g}^{\text{ad}}$ being accelerated in the inner region.

3. Larger detuning, on resonance laser

Looking at the same case, but relying on the resonance condition with detuning $\Delta L_3 = 4.3 \text{ cm}^{-1}$, the exchange of populations is reduced to $\approx 50\%$ (see Fig. 13). For propagation, we have used a spatial grid with 4096 points, extending from $6.3a_0$ to $200a_0$. The characteristic times are now a short time characteristic of Rabi oscillations $T_{\text{R}} \approx 16$ ps and an interplay between two longer times equivalent to the classical vibrational period $T_{\text{VIB}} \approx 186$ ps and the adiabatic period $T_{\text{ad}}$. The adiabatic potentials are slightly different from those of Fig. 12, as the laser detuning is reduced to $\Delta L_3$. The vibrational spacing of the levels is smaller, $\approx 0.07 \text{ cm}^{-1}$, yielding an adiabatic period $T_{\text{ad}} = 480$ ps. This new period is visible in Fig. 13. The time evolution of the wave packets is displayed in Fig. 14, showing a reconstruction of the wave packets in both diabatic channels around the transition point, in panels (d) and (i), at a time close to $T_{\text{ad}}$. This figure also shows that the outgoing wave packet in the lower channel is strongly reduced, since the available kinetic energy is much smaller.

C. Absence of population transfer in the intermediate and weak coupling cases at larger detunings

We have performed calculations at the same detuning $\Delta L_3$, reducing the laser intensity in order to increase the Rabi
consequence, we can study a representative initial Gaussian wave packet centered at the crossing between the two potential curves, with a most probable momentum $p_0 = 9.8 \times 10^{-3}$ a.u. (or a relative velocity $v_0 = 18 \text{ cm s}^{-1}$) corresponding to a Maxwellian distribution with the cesium Doppler temperature $T_D = 125 \mu \text{K}$. In order to confine the calculations on a reasonable spatial and time grid size, the spatial width of the wave packet is arbitrarily chosen equal to $\Delta p_0 = 0.1$ a.u., which corresponds to a temperature of 120 mK. Over a long propagation duration, such a wave packet will spread faster than its center moves.

The justification for such a procedure is the following: the initial state for the photoassociation is a mixed state. Even within a very small energy range there is a continuum of energy levels that cannot be distinguished experimentally. Since only relative motion of a pair of atoms is involved, the center of mass motion can be eliminated. Using relative coordinates, the state of the ensemble becomes $\rho = \exp(-\beta \mathbf{H})/Z$, where $\beta = 1/k_B T$, $\mathbf{H}$ is the internal Hamiltonian of the colliding pair, and $Z$ is the partition function. For low gas density, the density operator $\hat{\rho}$ can be evaluated using the energy eigenfunctions $\chi(\epsilon, J)$, where $\epsilon$ is the relative energy and $J$ the angular momentum:

$$\hat{\rho} = \frac{1}{Z} \sum_{J} \int_0^\infty d\epsilon (2J+1) e^{-\beta \epsilon} |\chi(\epsilon, J)\rangle \langle \chi(\epsilon, J)|. \quad (22)$$

The photoassociation yield is determined by coordinates in the vicinity of the resonance position. For large internuclear distances, the potential is flat and therefore, the Hamiltonian is dependent only on the kinetic energy. Using a random phase approximation, the density operator can be decomposed into a set of thermal Gaussian wave packets. For $s$ wave scattering, it becomes

$$\hat{\rho}_s(\beta) = C \int_{R_0}^{\infty} \Psi(\beta, r) \langle \Psi(\beta, r)|^2 dr, \quad (23)$$

where $C$ is a normalization constant and $\Psi(\beta, r)$ is a thermal wave packet defined as

$$\Psi(\beta, r) = \frac{1}{r} \psi(\beta, r) = \frac{1}{r} e^{-\frac{(r-R)^2}{2\sigma^2}}. \quad (24)$$

The width $\sigma$ is determined by the temperature $\sigma = \sqrt{\beta/4\mu}$. The validity of Eq. (23) and hence Eq. (24) depend on the temperature, and is limited to the region where the potential is negligible relative to the energy term, i.e., $V(R) \ll 1/\beta$. For very low temperatures (below $T \approx 1$ mK) the random phase approximation is not valid. The eigenfunctions in the continuum have a common stationary phase point in the outer region of the potential (around $9\hbar \omega_0$ for the present choice). This stationary point results in strong modulation in the initial density. In the present numerical application at higher temperature $T \approx 120$ mK, we may ignore this effect, which will be addressed in future work. At small internuclear distances when the potential energy becomes sig-

![FIG. 14. Same as Fig. 11, under resonance conditions ($\Delta_{L_1} = 4.3 \text{ cm}^{-1}$).](image)

V. WAVE-PACKET PROPAGATION FOR PHotoASSOCIATION: PROSPECTS

We have performed preliminary photoassociation calculations at a temperature for which the use of a Gaussian wave packet to describe the initial state is still valid. For sufficiently high temperatures, the thermal density operator $\hat{\rho}$ can be decomposed into a sum of Gaussian wave packets. As a consequence, we can study a representative initial Gaussian wave packet decomposed into a sum of Gaussian wave packets. As a model, showing the limit of the perturbative treatment. The present calculations are in contradiction with this simple prediction. An increasing efficiency in intermediate and weak coupling cases is predicted when the detuning is increased. The latter becomes close to the vibrational period, the coupling is too weak to yield any population transfer, in contrast with the situation described in Sec. IV A for detuning $\Delta_{L_1}$. This is linked to the marked decrease of the photoassociation or photodissociation efficiency. However, the perturbation theory of Refs. [6,14] predicts a variation of the photoassociation rate proportional to $1/\Delta_{L_1}^{-7/6}$, so that when the detuning is increased, the Rabi period should decrease as $\Delta_{L_1}^{-7/12}$ to keep the same efficiency. The classical vibration period has a more rapid decrease as $\Delta_{L_1}^{-5/6}$. Therefore, an increasing efficiency in intermediate and weak coupling cases is predicted when the detuning is increased. The present calculations are in contradiction with this simple model, showing the limit of the perturbative treatment.
significant relative to the kinetic energy term, again the approximation inherent in Eq. (23) is not valid and one has to use Eq. (24) instead.

Let us first consider the realistic experimental conditions of Sec. IV A. The time evolution of the channel populations is shown in Fig. 15, over more than 2 ns (the spatial grid used for propagation has 4096 points, extending from 6.3 \(a_0\) to 200 \(a_0\)). As the motion of the initial wave packet during the first 200 ps is almost unnoticeable, the initial Gaussian is completely depleted around the crossing point located at 150 \(a_0\); as \(T_{\text{Rabi}} \approx 286\) ps, single Rabi oscillation is observed, and the populations are nearly constant during the remaining propagation time. After one vibrational period \(T_{\text{vib}} \approx 600\) ps, a new Rabi oscillation is visible. The amplitude of such oscillations is very small after two vibrational periods and they reappear after three periods. The oscillation after 2 ns corresponds to the reconstruction of the initial wave packet, after reflection on the inner wall. As already mentioned, the present choice of the initial wave packet cannot provide a reliable representation of this feature. Indeed, the expected nodal structure of the initial wave packet should certainly affect the reconstruction.

Photoassociation under the strong coupling conditions of Fig. 10 also shows an interesting pattern, as illustrated by Figs. 16 and 17 (the spatial grid being the same as in the above paragraph). Rabi oscillations with large amplitude are present in the populations of the two channels during a time interval of 100 ps. Then the populations are constant during the next 200 ps, corresponding to motion of the two wave packets in the inner region. They reappear only at \(t = 300\) ps, the reconstruction occurring at \(t = 400\) ps. It is clear that the characteristic time corresponding to vibration in the adiabatic potential \(U_{\text{ad}}(R)\) is manifested in the results, demonstrating the field-modification of the potential; this result is particularly important as the motion in the lower state is also changed, due to the \(R^{-3}\) behavior of the adiabatic potential \(U_{\text{ad}}(R)\). This is visible in the time evolution of the wave packets, showing that the scattering properties in the ground state are accordingly modified. In the cold regime (\(T < 1\) mK) the same effect will lead to a field-induced modification of the scattering length.

VI. CONCLUSION

We have analyzed in the present work the different characteristic times involved in photodissociation of weakly bound excited cold molecules or photoassociation of two cold alkali atoms. The interplay between the classical vibra-
tional period, which is of the order a few hundreds of ps, and
the Rabi frequency have been discussed for various condi-
tions of laser intensity (1 kW cm\(^{-2}\), typical of present pho-
toassociation experiments, and 32 kW cm\(^{-2}\)), and detuning.
We have presented two-channel time-dependent calculations
for the vibrational motion in the Cs\(_2\) \(1_s^+\) excited attractive
potential, coupled by cw laser (or long pulse laser) to the
continuum of the lower \(a^2\Sigma_u^+\) state. Rabi oscillations are
visible when the vibrational motion is stopped at the outer
turning point, and disappear when the two atoms come
closer. This wave-packet analysis confirms the validity of a
Franck-Condon vertical transition model. Calculations were
performed for several values of the detuning; at \(\Delta \nu = 4.3\) cm\(^{-1}\)
the Rabi period has to be smaller than the vibra-
tional period, if one wants to see efficient population trans-
fer, which is not the case at small but significant detuning.
Under strong coupling conditions, when the Rabi period is
much smaller than the classical vibrational period, we have
observed a new characteristic time corresponding to vibra-
tion in the adiabatic potential obtained by diagonalizing the
matrix of the two potentials coupled by the laser field. This
effect accompanies a strong population transfer.
Calculations for photoassociation have been performed
under conditions corresponding to s wave scattering at a tem-
perature of 120 mK, to allow the description of the initial
state by a Gaussian wave packet with reasonable width. It is
remarkable that the adiabatic vibrational motion is clearly
visible in the strong coupling situation. The vibration motion
in the excited state is totally modified by the coupling, the
vibrational period increasing by a factor of 2. Therefore,
time-dependent pump-probe experiments should see this
modification as a signature of field induced effects. Accord-
ingly, the collision dynamics in the ground state are also
modified, due to increase of the kinetic energy in the inner
region.

The present work allows us to gain insight into the pos-
sible ways of controlling the photoassociation reaction in a
sample of cold atoms. We have shown that one possibility of
control is to tune the laser intensity to change the vibrational
period and the short range potential. This will be the subject
of further investigation, in the spirit of the collision suppres-
sion work developed by several authors [39–41]. In the cold
regime, this will result into a marked modification of the
scattering length [42,43]. The present work is proposing
time-dependent study of the vibration dynamics in the upper
state as a way of checking the modification of the ground
state scattering length. Another way of controlling by tuning
the laser frequency through use of chirped pulses has been
recently proposed by Vala et al. [19]. A comparison of the
efficiency and limitations of both techniques will be per-
formed in near future.

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[2] A. Fioretti, D. Comparat, A. Crubellier, O. Dulieu, F. Masnou-
Mourachko, and F. Masnou-Seeuws, J. Phys. B 30, 2801
(1997).
(1999).
Woestenenk, J.W. Thomsen, P. Van der Straten, and A.
[10] R. Napolitano, J. Weiner, C.J. Williams, and P.S. Julienne,
(1996).
[15] C. Drag, B. Laburthe Tolra, O. Dulieu, D. Comparat, M.
Vatasescu, S. Boussen, S. Guibal, A. Crubellier, and P. Pillet,
Chemical Bond (World Scientific, Singapore, 1994).
[18] R. Schinke, Photodissociation Dynamics (Cambridge Univer-
50, 5025 (1994).
[22] A. Vardi, D. Abrashkevich, E. Frishman, and M. Shapiro, J.
[24] R. Kosloff, in Dynamics of Molecules and Chemical Reac-
tions, edited by R.E. Wyatt and J.Z. Zhang (Marcel Dekker,
(1986).
[28] G. Balint-Kurti and A. Vibok, in Numerical Grid Methods and


