Optimization of the Femtosecond Laser Impulse for Photoassociation and the Power-Law Decay for the Spin-Orbit Mediated Dissociation in the NaRb Dimer

J. Kozicki\textsuperscript{a,b,}\textsuperscript{1}, P. Jasik\textsuperscript{a,c}, T. Kilich\textsuperscript{b}, J. E. Sienkiewicz\textsuperscript{a,b}

\textsuperscript{a}Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, 80-233 Gdańsk, Poland
\textsuperscript{b}Advanced Materials Center, Gdańsk University of Technology, 80-233 Gdańsk, Poland
\textsuperscript{c}BioTechMed Center, Gdańsk University of Technology, 80-233 Gdańsk, Poland

Abstract

We use our newly-developed quantum dynamics code that allows us to study the dynamics of multiple coupled states under the influence of an arbitrary time-dependent external field, to investigate the femtosecond laser-driven process of association and the forbidden transition in the $^{23}$Na$^{87}$Rb dimer. In this process, the dimer is excited from the ground triplet state $1^3\Sigma^+$ to the $1^1\Pi$ state using the femtosecond laser pulse and next, the spin-orbit coupling between the $1^1\Pi$ and $2^3\Sigma^+$ states results in the singlet-triplet transition. The laser pulse parameters are optimised to obtain maximum yield in electronic levels correlating with the first excited atomic asymptote. We observe the detailed population statistics and power-law decay of these states. Finally, the analysis of the population oscillations allows for the determination of the optimal time delay for dumping molecule to its absolute ground state.

Keywords: quantum dynamics, field-molecule interaction, photoassociation, power-law decay, diatomic molecule, spin-orbit coupling, transition dipole moment

1. Introduction

Quantum dynamics is a growing discipline at the interface of chemistry, physics and materials science [1]. It allows to study the behavior of objects in a way, that emphasizes the quantum nature of their evolution in time. Quantum dynamics simulations are an indispensable tool for investigating processes such as chemical reactions [2], field-atoms interactions [3] and quantum computing [4, 5]. The particular emphasis is focused on investigating the photoinduced dynamics of breaking (dissociation) [6, 7, 8, 9, 10, 11] and creating (association) [12, 13, 14, 15, 16, 17] of the chemical bonds in the molecular systems. Photoassociation processes play a key role in the field of cold and ultracold physics and chemistry, allowing for the formation of molecules in the deeply bound ground states and investigation of their unique quantum properties [18, 19, 20, 21, 22]. On the other side, controlled photodissociation reactions enable for creation of atomic and molecular fragments in specific quantum states and use them for researching the selected properties of matter [23, 24, 25, 6, 26]. While the dissociation through the barrier of the potential (tunneling) is well described by exponential decay [27, 28, 29], the dissociation of the system of coupled excited electronic states should be rather described by other forms of decays. Several different models for these kinds of decays were investigated, such as product decay [30], dephasing [31], and the power-law decay [32, 33, 34].

The aim of our study is to show the time-dependent descriptions of the photoassociation and photodissociation processes in the polar alkali diatomic molecules and the quantum properties of these reactions in their characteristic time regimes. We propose the femtosecond laser impulse parameters’ optimization procedure providing the maximization of the population in the coupled complex of excited electronic states. Dynamics investigations of this system of molecular states allow us, in the case of an association, to establish the optimal time delays for the femtosecond train of laser pulses enabling the formation of molecules in the deeply bound ground state, as well as present the general modified power-law decay allowing for the proper description of dissociation process.

All our considerations are based on an exemplary polar alkaline dimer, which is the NaRb molecule. The sodium rubidium molecular system has been studied both experimentally [35, 36, 37, 38, 39] and theoretically [40, 41, 42, 43]. It is worth underlining that in a recent experiment [44, 45] Guo et al. reported successful production of an ultracold sample of the absolute ground state of $^{23}$Na$^{87}$Rb molecules.

In our study, we apply our newly-developed code to simulate the laser-driven dynamics of photoassociation of the NaRb...
dimer that takes the spin-orbit coupling into consideration. The dynamics on multiple coupled electronic levels are determined by solutions to the coupled time-dependent Schrödinger equations. In recent years, several numerical methods and their improvements have been introduced, including higher-order split operator methods, the expansion of the time evolution operator to Chebyshev polynomials [46, 47, 48, 49, 50], or the semi-global method [51]. The effective Hamiltonian for describing nuclear kinetics in coupled multiple adiabatic or diabatic electronic states plays a key role.

Here we use our newly-developed quantum dynamics code that allows us to study the dynamics of multiple coupled states under the influence of an arbitrary time-dependent external field, to investigate the femtosecond laser-driven process of association and the forbidden transition in the $^{23}$Na$^{87}$Rb dimer. In this process, the dimer is excited from the ground triplet state $1^3\Sigma^+$ to the $1^3\Pi$ state using the femtosecond laser pulse and next, the spin-orbit coupling between the $1^3\Pi$ and $2^3\Sigma^+$ states results in the singlet-triplet transition. We use the Born-Oppenheimer potential energy curves (PEC) which were presented in our previous work [42].

In the analysis, we use the lowest electronic states of the NaRb molecule, appropriate transition dipole moment functions (TDMF), and spin-orbit coupling (SOC) matrix elements. Additionally the femtosecond electromagnetic pulse parameters are optimized to obtain maximum yield in electronic levels correlating with the first excited atomic asymptote. We present a map of the optimization space of the pulse parameters and the detailed population statistics. Inspired by [32] we propose a modified power-law to describe the population decay. Finally, the analysis of the population oscillations allows for the determination of the optimal time delay for dumping molecule to its absolute ground state.

2. Computation method

The time propagation of a system of coupled time-dependent nuclear Schrödinger equations (TDSE) for multiple electronic levels and time-dependent Hamiltonian follows the semi-global method [51]. The couplings between the electronic levels are time-dependent. The TDSE has the following general form:

$$\frac{i\hbar}{\partial t} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{pmatrix} = \begin{pmatrix} \hat{H}_1(t) & \hat{V}_{12}(t) & \hat{V}_{13}(t) \\ \hat{V}_{21}(t) & \hat{H}_2(t) & \hat{V}_{23}(t) \\ \hat{V}_{31}(t) & \hat{V}_{32}(t) & \hat{H}_3(t) \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{pmatrix},$$

where $\hat{H}_{\mu}(t)$ corresponds to the Hamiltonian for the respective electronic level in the Born-Oppenheimer approximation and $\hat{V}_{\mu\nu}(t)$ are either: (1) the respective transition dipole moment functions $\mu$ multiplied by the laser impulse electric field $\varepsilon(t)$ or (2) the spin orbit potential $\xi$; depending on the nature of the coupling between the two electronic levels. The Hamiltonian for three electronic levels is summarized in Tab. 1.

Table 1: The schematic view of the Hamiltonian matrix of the system used in the calculations. The TDMFs between electronic levels $\mu$ multiplied by the electric field $\varepsilon(t)$ are marked with ‘$t$’. The lack of coupling between levels is marked with ‘$\circ$’. The spin-orbit coupling is marked with SOC. The PECs are on the matrix diagonal.

| $1^3\Sigma^+$ | $2^1\Sigma^+$ | $1^3\Pi$ |
|--------------|--------------|---------|
| $1^3\Sigma^+$ | PEC          | $\circ$ + |
| $2^1\Sigma^+$ | $\circ$      | PEC     |
| $1^3\Pi$     | +            | SOC     |

The gist of the semi-global method [51] is that the evolution operator is expanded, using $K$ terms, in the Krylov space into two parts: the time-dependent part of the Hamiltonian and the Hamiltonian in the middle of the timestep $t + \frac{\Delta t}{2}$, for which the time-dependent part serves as a correction calculated in the $M$ interior sub-steps. The calculation of solutions for $M$ interior sub-timesteps is iterated several times (usually two to five) within a single global timestep $\Delta t$ until the solution converges with the requested error tolerance $\epsilon$. Then the calculation moves on to the next timestep.

The semi-global method is implemented in C++, thus allowing calculations faster than the original Matlab code [51] and extended with the ability to handle an arbitrary number of electronic levels (a feature not present in [51]) such as in Eq. 1. It is then used with the following parameters (which are discussed in detail in [51]): the timestep $\Delta t = 1$ a.u., the number of interior Chebyshev time points $M = 5$ and the number of expansion terms used for the computation of the function of a matrix $K = 7$. The error tolerance is set to $\epsilon = 10^{-10}$. The discretization grid has 6144 points and the absorbing boundary condition (the same as in [51]) is placed at the distance $R_{max} = 70 a_0$. Figure 1: (a) the electronic states of the NaRb molecule with the schematic arrow representing transition imposed by the impulse laser; (b) the transition dipole moment function $\mu$ and (c) the spin-orbit coupling $\xi$. See Tab. 1 for the schematic view of the Hamiltonian in which they are used.

1 Following Tannor [27] (page 396) we neglect the vector character of $\mu$. 
3. Results and discussion

Our previously calculated [42] PECs, TDMF $\mu_{1\Sigma^-→1\Pi}$ and SOC $\xi_{2\Sigma^-→1\Pi}$ along with the schematic photoassociation transitions are shown in Fig. 1.

As the initial condition, the $\nu = 20$ eigenfunction is placed on the $1\Sigma^+$ state, because it is one of the highest populated levels obtained in the experiment [44, 45]. Then the following laser impulse is used:

$$s(t) = I \text{sech}^2\left(\frac{t - t_p}{\tau_p}\right) \cos(\omega t),$$

where the frequency $\omega$ corresponds to a commercially available laser with the wavelength $\lambda = 1560$ nm, the impulse center $t_p = 111.26$ fs (4600 a.u., also marked in Fig. 3 with an arrow), while the intensity $I$ and the full width at half maximum (FWHM) are optimized to maximize population on the excited state (the FWHM of the impulse equals to 1.76$\tau_p$). The optimization is performed by scanning a range of these two parameters.

The scan of the sum of the population on two excited states $2\Sigma^+$ and $1\Pi$ is shown in Fig. 2. It is interesting to note the existence of three characteristic horizontal bands. The first band occurs for the intensity $I < 1.5 \times 10^{14}$ [W/cm$^2$]. Here the horizontal lines of the higher population indicate that the FWHM energy spread of the impulse does not affect the population and it mostly depends on the light intensity. The second band is in the middle range of $I$ between $1.5 \times 10^{14}$ and $2.5 \times 10^{14}$ [W/cm$^2$]. Here a semi-diagonal pattern emerges where the FWHM energy spread dependence plays a major role. Finally in the third range for $I > 2.5 \times 10^{14}$ [W/cm$^2$] a nonlinear behavior takes precedence and a chaotic pattern emerges. These findings indicate that there is possible an interplay between the intensity and the impulse duration with the eigenenergies and the vibration frequencies of the NaRb molecule occurring on the target electronic state $1\Pi$.

Next, using the optimal parameters $I$ and $t_p$ (marked with a cross in Fig. 2) corresponding to the maximum population, the time evolution of the population on the excited electronic levels is performed. Fig. 3 shows results for obtaining the maximum population found, which is $P_0 = 97.2\%$.

The effect of the spin-orbit coupling is visible in Fig. 3 as the population exchange between levels $2\Sigma^+$ and $1\Pi$. The period of the oscillation between the two levels is 296.35 fs. The first maximum on $2\Sigma^+$ occurs 172.49 fs after $t_p$ (see Eq. 2). In the figure the first 60 fs, when the laser impulse is weak and population is near zero, are not shown for brevity.

Due to the constant shift of the population between the two electronic levels caused by SOC the wavefunction is not fully representable by the eigenfunctions on the target PEC, hence some part of the wavefunction goes to the continuum and is responsible for dissociation. This causes a population decay over a larger timescale and only a fraction of the original population remains at the end, as shown in Fig. 4. As we show below, this is not an exponential decay as in the predissociation process [29]. It is instead a distribution of the power-law, as it happens by the coincidence of population exchange between two levels [32, 52, 53, 54].

Following the idea in [32] that the population decay in the case of two coupled levels should follow a power-law decay, we
analyze the population decay on the two excited levels $2\Sigma^+$ and $1\Pi$. The calculated population from Fig. 4 is fitted respectively to the modified power-law decay formula:

$$P(t) = P_0 \left( 1 - P_{f,\text{pow}} \right) \left( 1 + \frac{\tau_{\text{pow}}}{1 + \tau_{\text{pow}} - t_0} \right) + P_{f,\text{pow}},$$

(3)

and to the exponential decay formula:

$$P(t) = P_0 \left( 1 - P_{f,\exp} \right) \exp \left( \frac{t - t_0}{\tau_{\exp}} \right) + P_{f,\exp},$$

(4)

where $P_0 = 97.2\%$ is the initial population on both levels, $t_0 = 10$ ps is the start of the decay, $\tau_{\text{pow}}$, $\tau_{\exp}$ are the fitting decay parameters, and $P_{f,\text{pow}}$ and $P_{f,\exp}$ are the fitting parameters describing the final non-zero population. The $\sqrt{3}$ part of Eq. 3 was modified with respect to [32] with an extra $\tau_{\text{pow}}$ in the denominator in order to shift the function to the left so that the initial population is not infinite when $t = t_0$ (as is the case in [32]), but instead equals $P_0$. Also in both equations for decay we used a modification of type: $\left(1 - P_f\right) \cdot + P_f$ to allow extra fitting parameters $P_{f,\text{pow}}$ and $P_{f,\exp}$ for the final non-zero population. It shall be noted that compared to [32] the situation here is also different: both potentials $2\Sigma^+$ and $1\Pi$ are bonding potentials and neither of them is dissociative (see Fig. 1). Therefore, it is worth seeing how the modified power-law decay fits our numerical results.

The fit results in Fig. 4 are as follows: $\tau_{\text{pow}} = 196.03 \pm 0.04$ ps, $P_{f,\text{pow}} = 0.1801 \pm 0.0001$ and $\tau_{\exp} = 459.7 \pm 0.3$ ps, $P_{f,\exp} = 0.4246 \pm 0.0001$. The asymptotic standard error percentage of the fit [55] for the power-law is 0.02% and for the exponential law is 0.06%. The best fit for exponential law produces a nonphysical result, because the fitted final population $P_{f,\exp}$ (Fig. 4e) has value greater than the steadily decreasing population (a) or (c). The fit for the power-law (Fig. 4b) is significantly better, since it almost overlaps the numerical result (Fig. 4a), with error 0.02%. The final population (Fig. 4d) is $P_{f,\text{pow}} = 18\%$. Overall the modified power-law is a better description of the decay occurring in this situation.

4. Conclusions

In our study, we show the time evolution of three coupled potential energy curves of an exemplary diatomic NaRb system. The necessary potential energy curves and dipole transient moments were taken from our earlier ab initio calculations and supplemented with a newly calculated spin-orbital coupling between the upper singlet and triplet states. In our approach, the spin-orbit coupling is a function depending on the distance between the nuclei. The considered system is driven by a femtosecond laser pulse. The two parameters describing the femtosecond laser pulse, i.e. intensity and half-width, are independently optimized. The aim of optimization is to obtain the largest possible population of molecular states correlated with the first excited atomic asymptote. We also identify the period of population oscillation between the two excited levels $2\Sigma^+$ and $1\Pi$. This allows us to design the optimal sequence of electromagnetic pulses to dump the molecule to the ground state. The optimal time delay after a pump pulse to dump the molecule to the ground state is 172.49 fs using a pulse train of 296.35 fs. We are also examining the combined population decay from these two levels. We fit this to a modified power law and show that this fit is better than that of an ordinary exponential decay. We emphasize that these results can be important for a thorough insight into quantum processes where time plays a key role. Our approach is possible to apply to even more complex systems where only one soft bond (e.g. between two fragments in a molecule as in [6]) is most important to describe a time-dependent process. We confirm the finding in [6] that laser control can be applied to the spin-orbit coupled states.

All dynamic results are obtained from our new computer code which uses a semi-global method [51] to expand the time evolution operator. The method is improved to work with multiple electronic levels and time dependent couplings. It can be a valuable tool for scientists studying quantum dynamics and planning future experiments.

Author Information

Corresponding Author
* E-mail: jan.kozicki@pg.edu.pl

ORCID
Janek Kozicki: 0000-0002-8427-7263
Patryk Jasik: 0000-0002-6601-0506
Tymon Kilich: 0000-0001-6831-694X
Józef E. Sienkiewicz: 0000-0002-1149-3846

Conflicts of interest
There are no conflicts of interest to declare

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