Pulse sequences in photoassociation via adiabatic passage

Xuan Li\textsuperscript{1,2,3}, William Dupre\textsuperscript{1} and Gregory A Parker\textsuperscript{1,3}

\textsuperscript{1} Homer L Dodge Department of Physics and Astronomy, University of Oklahoma, OK 73019-0225, USA
\textsuperscript{2} Department of Chemistry, The University of British Columbia, Vancouver, British Columbia V6T 1Z1, Canada
E-mail: li@nhn.ou.edu and parker@nhn.ou.edu

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\textbf{Abstract.} We perform a detailed study of pulse sequences in a photoassociation via adiabatic passage (PAP) process to transfer population from an ensemble of ultracold atomic clouds to a vibrationally cold molecular state. We show that an appreciable final population of ultracold NaCs molecules can be achieved with optimized pulses in \textit{either} the ‘counter-intuitive’ ($t_P > t_S$) \textit{or} ‘intuitive’ ($t_P < t_S$) PAP pulse sequences, with $t_P$ and $t_S$ denoting the temporal centers of the pump and Stokes pulses, respectively. By investigating the dependence of the reactive yield on pulse sequences, in a wide range of $t_P-t_S$, we show that there is not a fundamental preference to either pulse sequence in a PAP process. We explain this no-sequence-preference phenomenon by analyzing a multi-bound model so that an analogy can be drawn to the conventional stimulated Raman adiabatic passage.
In recent years, a number of schemes have been proposed to produce cold molecules via direct photoassociation of cold atoms [1–7]. Direct single-color photoassociation schemes [8] often result in incoherent formation of molecules in the ground states and require additional purification [9]. In other photoassociation schemes, in order to compete with incontrollable spontaneous emission loss from the excited electronic states, complex photoassociation schemes involving both continuous and pulsed laser fields are usually employed [10]. Alternatively, production of ultracold diatomic molecules by several exciting experiments were already realized by first creating the Feshbach molecules and then adopting the stimulated Raman adiabatic passage (STIRAP) technique [11–13]. However, such a method relies on a host of experimentally challenging techniques, including frequency combs, ultraslow lasers, and tuning of Feshbach resonances, which is only applicable to atomic species for which magnetooassocation is available. In addition, in order to connect the free spin polarized ground state atoms to the absolute ground spin singlets, this method depends heavily on strong spin–orbit couplings in the excited molecular state, which is not the case for all molecular systems of interest. In an alternative approach, Vardi et al [14] proposed using photoassociation via adiabatic passage (PAP), an idea recently explored by Shapiro et al [15] and Kuznetsova et al [16] which, in particular, utilizes Feshbach optimized photoassociation (FOPA) to enhance reactive yields. Such a PAP process is different from the method adopting the STIRAP technique in that it involves direct photoassociation from the continuum. It was shown that, with practical pulsed laser techniques in modern laboratories, one can use PAP to form ultracold diatomic molecules in the low-lying vibrational state with a production rate of $10^4$ molecules per second [15, 17]. Such an approach is advantageous because it requires a less complicated experimental set-up: a ‘parked’ (time-independent) scattering resonance, a result of either a shape resonance or a Feshbach resonance without magnetic sweeping through a pole.

In a PAP process two pulsed lasers, i.e. a pump laser and a Stokes laser, are used to transfer population from the initial continuum atomic states to a final bound diatomic state, by temporarily populating an intermediate state. However, there has been a misunderstanding in the past about the dependence of the reactive yield on the use of pulse sequences. With $t_p$ and $t_S$ denoting the temporal centers of the pump and Stokes pulses, respectively, it was argued in the past that a counter-intuitive scheme ($t_p > t_S$) is a ‘great improvement over’ the intuitive sequence ($t_p < t_S$), because the former scheme does not appreciably populate the intermediate state on an excited electronic potential energy surface and thus it minimizes the spontaneous emission loss [14]. This counter-intuitive pulse sequence was adopted by several follow-up
studies on such a PAP process [15, 16]. However, as we will demonstrate in this study, high reactive yields can be achieved with optimized pulses with any of the three possible sequences, the counter-intuitive, coincident \( t_P = t_S \), or intuitive PAP pulse sequences, without populating the intermediate state and, hence, the spontaneous emission loss is truly suppressed. We also show in detail that these optimized high yields are not rare for all three pulse sequences, and there is not a fundamental preference to a counter-intuitive sequence over the other two.

Therefore, the current study of the pulse sequence in the PAP process is a direct investigation of the effect that different pulse sequences have on the dark states which contribute to the adiabatic passage at cold/ultracold temperatures. Such a dark state, among many other field-dressed virtual states, is defined to have a near-zero contribution from the excited intermediate state and to connect only the initial and final states (discrete or continuum). The merit of this dark state compared to that of other virtual states lies in the suppression of spontaneous emission loss and the enhancement of adiabatic population transfer to the target state. Note, this is different from the well-established and demonstrated dark state analysis in ultracold Bose–Einstein condensate (BEC) systems [18–20]. The fundamental distinction is whether the initial system can be appropriately represented by a sum of scattering/continuum states or simply by a single state. This leads to the finding that, in the latter case with BEC conditions, it still requires a counter-intuitive pulse sequence to ensure near complete population transfer. Also, the current study does not contradict previous experiments which aimed to study Autler–Townes splitting in a two-color photoassociation process from continuum [21, 22]. Although these studies verify the existence of a dark state, no pulse sequence dependence was studied.

In this study, we demonstrate the analysis for the PAP process in the example of forming NaCs diatomic molecules from ultracold atomic clouds. This paper is organized as follows. In section 2, we summarize relevant information about NaCs and the setup for this PAP process. In section 3, we present our results of simulations with different pulse sequences and further analysis. In section 4, we present a multi-bound model to explain this no-sequence-preference phenomenon.

2. System and the photoassociation via adiabatic passage process

Figure 1 shows a schematic of PAP. Initially, sodium and cesium atoms are held in a magnetic trap. A pair of laser pulses—a pump laser at a carrier frequency \( \omega_P \) and a Stokes laser at \( \omega_S \)—transfer a portion of the initial Na+Cs continuum-state population to a final low-lying vibrational state of the ground \( X^1 \Sigma^+ \) NaCs potential energy curve (PEC).

Figure 1 also shows the Born–Oppenheimer PECs of the \( X^1 \Sigma^+ \) and \( A^1 \Sigma^+ \) states used in our calculations; for details see [23–25]. We denote the ground \( X^1 \Sigma^+ \) PEC by X and the excited \( A^1 \Sigma^+ \) PEC by A. For the intermediate state in PAP we choose \( |A, v_A = 101, J_A = 1 \rangle \); for the final state we choose \( |X, v_X = 20, J_X = 0 \rangle \). The intermediate and final states are chosen so that the Rabi frequencies involved are reasonably large to minimize experimental effort. The pump (Stokes) laser is chosen to be resonant with transitions between the initial and intermediate states (the intermediate and final states) and it has a wavelength of 978 nm (752 nm). The transition dipole overlap between the initial \( (|X, E = 100 \mu K, J_X = 0 \rangle) \) and intermediate \( (|A, v_A = 101, J_A = 1 \rangle) \) states is 204 atomic unit = 518.5 Debye/\( \sqrt{3.16 \times 10^{11}} \mu K \); the transition dipole overlap between the intermediate
Figure 1. Schematic of PAP. $|E, X^+\rangle$ is the initial state in the $X^1\Sigma^+$ continuum, $|A, v_A = 101\rangle$ is the intermediate bound vibrational state in the $A^1\Sigma^+$ and $|X, v_X = 20\rangle$ is the final bound vibrational state. The carrier frequencies of the pulsed lasers are $\omega_p$ for the pump laser and $\omega_S$ for the Stokes laser.

$\langle A, v_A = 101, J_A = 1 | \mu_X A | A, v_A = 101, J_A = 1 \rangle$, is an energy-renormalized quantity: $\propto$ electric dipole/√energy. Such a large transition dipole overlap between the initial and intermediate states signals the presence of a resonance akin to that identified by [15] in Rb$_2$. In an independent scattering calculation we confirmed the existence of this resonance, which is caused by a quasi-bound state near zero energy on the ground PEC. Note, this current study builds on the concept of PAP [14–16]; scattering resonances (either shape resonances or Feshbach resonances) are naturally built into the theory such that our study is fully compatible with FOPA as discussed in [16] in which the Franck–Condon overlaps between the initial continuum states and the intermediate states are greatly enhanced by Feshbach resonances.

Following [15, 17, 26], we write the total Hamiltonian as

$$H_{tot} = H - \mu \cdot \vec{E}(t),$$

where $H$ is the material (field-free) Hamiltonian, $\mu$ is the A–X electronic transition dipole moment, and $\vec{E}(t) = \epsilon \mathcal{E}(t)$ is the laser’s electric field, with the polarization direction $\epsilon$ and the (scalar) amplitude $\mathcal{E}(t)$. We expand the wave function of the system as

$$\Psi(t) = b_{v_X}(t)e^{-iE_{v_X}t} |X, v_X\rangle + b_{v_A}(t)e^{-iE_{v_A}t} |A, v_A\rangle + \int \text{d}E b_E(t)e^{-iEt} |X, E^+\rangle,$$

where $E_{v_X}$ and $E_{v_A}$ are the rovibrational energies of the final and intermediate states, respectively. We consider two lasers pulses (see figure 1): the pump pulse $\mathcal{E}_p(t)$ and the Stokes
pulse $\mathcal{E}_S(t)$. Both are assumed to be Gaussian: e.g. for the pump pulse,

$$\mathcal{E}_P(t) = 2\hbar \left\{ \mathcal{E}_P^0 \exp \left[ -\left( \frac{t - t_P}{\delta_P} \right)^2 \right] \exp(-i\omega_P t) \right\},$$

(3)

where $t_P$ is the temporal center of the pump pulse, $\delta_P$ is the pulse width, and $\mathcal{E}_P^0$ is the field strength. There is a similar expression for the Stokes pulse. For brevity we do not show the explicit derivation to solve the time-dependent Schrödinger equation which can be found in [14, 15, 17].

A Gaussian wave packet gives a classical description of two colliding atoms with the Heisenberg uncertainty relation between the energy bandwidth $\delta_E$ and the duration of the collision [14–16]. Also, in order to properly estimate the practical production rate at a later stage, a temporal center parameter $t_0$ (defined later on), which represents the arrival time of the wave packets at the interaction region, needs to be averaged since random collision events (at $t_0$) do not occur coincidentally with the applied laser pulses (at $t_P$ or $t_S$). Each calculation with a different $t_0$ needs to be taken with uncorrelated phases and thus the final averaged results are taken as a direct arithmetic mean, i.e. incoherent sum, of different $t_0$ calculations.

The averaging over the arrival time of the wave packets (at the interaction region) is one way, yet not the only way, of taking into account the lack of coherence of the initial conditions. Hence, the otherwise equivalent incoherent sum of energy-defined initial conditions is converted into an incoherent sum of collision time. Dalibard et al showed the equivalence between the more conventional ‘pre-averaging’ of the Liouville von Neumann equation for the density operator and a ‘post-averaging’ of the stochastic Schrödinger equation [27]. This is also equivalent to Koch’s approach in which a series of coherent Gaussian wave packets with random phases for initial distance $R_i$ are used and then one averages over results with these different phases [28]. The initial continuum state of the system, is then modeled as a coherent Gaussian wave packet defined by [15]

$$\mathcal{E}_E^0 = \frac{1}{(\delta_E^2 \pi)^{1/4}} \exp \left[ -\frac{(E - E_0)^2}{2\delta_E^2} + i\frac{(E - E_0)t_0}{\hbar} \right],$$

(4)

where the center energy of the wave packet is $E_0 = 100 \mu K$, the energy bandwidth is $\delta_E = 70 \mu K$, and the collision time is $t_0 = 500$ ns. The final $|X, v_X = 20, J_X = 0\rangle$ state is connected to the intermediate bound state by a $\sigma^-$-polarized Stokes pulse on resonance with $E_{v_X=101, J_X=1} - E_{v_X=20, J_X=0}$. The intermediate bound state is connected to the initial continuum state by a $\sigma^+$-polarized pump pulse, which is on resonance with $E_{v_A=101, J_A=1} - E_0$. The decay constant $\Gamma$ is taken as $1/\Gamma = 30$ ns, a typical lifetime for alkali metals. Given that the spontaneous emission is much faster than the slow pulse (a few $\mu$s in duration), pulse parameters must be carefully selected to populate only one of the virtual states, the dark state of this atom–molecule system, which serves to suppress the irreversible population loss from the electronically excited state in order to ensure a high reactive yield.

3. Results and analysis

We study the reactive yield for each particular pulse sequence by varying $t_P - t_S$. For each pulse sequence we vary all other experimental parameters of the two pulses, which include pulse durations characterized by full width at half maximum (FWHM) and the laser intensities, within a reasonable range (FWHM_{P,S} ∈ [100, 700] ns and $I_{P,S} ∈ [0, 10]$ kW cm$^{-2}$). The resultant

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reactive yields as a function of pulse sequences vary insignificantly over a broad range of $t_P - t_S$. First, the black solid curve in figure 2 depicts the relative yields when these parameters are optimized individually for each specific pulse sequence; we observe no dominating evidence for preference for any of the pulse sequences. In addition, even when these parameters are the same (optimized for the case of $t_P - t_S = -200$ ns), a double maxima structure is shown by the red dashed curve in figure 2 for reactive yields with all three pulse sequences; and still no clear preference is shown towards any particular sequences.

In order to demonstrate in detail that high reactive yields can be achieved with all three sequences, we show three examples in figures 3(a)–(c) with $t_P - t_S = -200$ ns, $t_P - t_S = 0$ ns, and $t_P - t_S = +200$ ns, respectively. We also plot the laser profiles for the pump and Stokes pulses for each pulse sequence. Note, neither the laser intensity nor the Rabi frequency is appropriate to be used for comparing the pump and dump processes, since a continuum state is involved in this three-state population transfer process. Figure 3 shows that, for all three sequences, the population in the intermediate bound (black dotted curves) state is kept minimized, which effectively avoids the spontaneous emission loss and thus increases the final reactive yield. Therefore, the physical process cannot be visualized as a simple pump–dump scenario, in which the intermediate state must be appreciably populated. Though the final reactive yield with the counter-intuitive sequence is slightly higher than those with the other two sequences, the difference is too small to indicate a practical discrimination against the intuitive or the coincident sequences.

4. Multi-bound model

Unlike the conventional STIRAP for three-bound-state systems [29], identification of a dark state in PAP, which only connects the initial continuum and final bound states, is nontrivial [14, 15]. The fundamental change is the replacement of the initial bound state with a set of continuum states. High reactive yields in quasi-three level systems with two continuum states and one bound state have been shown to be achievable with a coincident pulse sequence.
Figure 3. Populations of the initial $|X, E^+, J_X = 0\rangle$ (black dashed line), intermediate $|A, v_A = 101, J_A = 1\rangle$ (black dotted line), and final $|X, v_X = 20, J_X = 0\rangle$ (black solid line) states versus time for a continuum wave packet with center energy $E_0 = 100$ µK; laser profiles of the Stokes pulse (red dash-dot line) and the pump pulse (blue solid line) in (a) an intuitive sequence, with $I_S = 10$ kW cm$^{-2}$, $I_P = 10$ kW cm$^{-2}$, $t_S = 410$ ns, $t_P = 210$ ns, FWHM$_S = 210$ ns and FWHM$_P = 600$ ns; (b) a coincident sequence, with $I_S = 10$ kW cm$^{-2}$, $I_P = 7.2$ kW cm$^{-2}$, $t_S = t_P = 415$ ns, FWHM$_S = 230$ ns and FWHM$_P = 600$ ns; (c) a counter-intuitive sequence, with $I_S = 10$ kW cm$^{-2}$, $I_P = 10$ kW cm$^{-2}$, $t_S = 427$ ns, $t_P = 627$ ns, FWHM$_S = 245$ ns and FWHM$_P = 458$ ns.

[30, 31]. To transfer most of the population from the initial continuum state to the final bound state $|X, v_X\rangle$, one must optimize $\omega_P$ and $\omega_S$. To minimize loss through the spontaneous emission process, only a very small transient population should be transferred to the intermediate state $|A, v_A\rangle$.

In order to understand the fundamental mechanism, one can discretize the continuum states into series of bound states. In this study, we replace the continuum states in equation (2) by $2N + 1$ bound states,

$$\Psi(t) = b_{v_X}(t)e^{-iE_{x}\tau} |X, v_X\rangle + b_{v_A}(t)e^{-iE_{A}\tau} |A, v_A\rangle + \int dE b_{E}(t)e^{-iEt} |X, E^+\rangle$$

$$\approx b_{v_X}(t)e^{-iE_{x}\tau} |X, v_X\rangle + b_{v_A}(t)e^{-iE_{A}\tau} |A, v_A\rangle + \sum_{j=-N}^{N} b_{j}(t)e^{-iE_{j}\tau} |E_{j}\rangle .$$

(5)
Table 1. Comparison between the final probability in the $|X, v_X = 20\rangle$ state between calculations with continuum states and multi-bound states for the three typical pulse sequences; all laser configuration parameters are fixed according to their values in figure 3.

| $t_P - t_S$ (ns) | $P_{v_X=20}(t = \infty)$ (continuum) | $P_{v_X=20}(t = \infty)$ (multi-bound) |
|------------------|--------------------------------------|--------------------------------------|
| −200             | 80.6%                                | 79.6%                                |
| 0                | 84.6%                                | 83.6%                                |
| +200             | 87.7%                                | 87.2%                                |

The initial condition is chosen to match the initial condition in equation (4)

$$ (b_j^0)^2 = \int(U_j|b_j^0|^2)\text{d}E, $$

where the integration limits are $L_j = E_0 + (j - 0.5)\Delta E$ and $U_j = E_0 + (j + 0.5)\Delta E$, and $E_j = E_0 + j\Delta E$. The new bound-to-bound transition dipole overlap, $\mu_{v_A,j}$, is chosen to match $\mu_{v_A,E}$. The reaction dynamics can then be computed by solving $2N + 3$ coupled first-order differential equations without invoking any approximations. In this study, we choose $\delta_E/2$ and $N = 16$ so that convergence is reached. By using the same laser configurations as in figure 3, we show the results for this new multi-bound model in table 1 where the difference of dynamics between the continuum model and the multi-bound model is negligible; the time dependent population transfer dynamics are shown in figure 4. Therefore, investigating the dynamics of the multi-bound model enables understanding the physical process in figure 1. The Fourier transform of the initial bound state amplitude,

$$ f(t) \equiv \sum_j b_j^0 e^{-iE_j t}, $$

is plotted in figure 5(a). This clearly shows a time window with a width of 300 ns, which represents the dwell time for two colliding atomic wave packets in the interaction region with short internuclear distances. Obviously, an average over $t_0$ in equation (4) must be performed later on, which has been explained elsewhere [14, 15, 17]. Figures 5(b)–(d) shows the time dependent Rabi-frequencies, $\Omega_{v_A,v_X}(t)$ and $\Omega_{v_A,j}(t)$ for (a) $t_P - t_S = -200$ ns, (b) $t_P - t_S = 0$ ns and (c) $t_P - t_S = -200$ ns, where all laser configuration parameters are fixed according to their values in figure 3. In the conventional STIRAP for three-bound-state systems [29], a global ‘counter-intuitive sequence’ between the pump and Stokes pulses must be met to transfer all population from the initial state to the final state

$$ \Omega_S(t = -\infty) > \Omega_p(t = -\infty) $$

and

$$ \Omega_S(t = +\infty) < \Omega_p(t = +\infty); $$

in a multi-bound-level model, this counter-intuitive sequence in equations (8) and (9) is only required to be satisfied in this ‘collision/coherence time window’ (350–650 ns) defined by the initial condition, which is clearly shown in figures 5(b)–(d).
Figure 4. Populations of the initial $|E_j\rangle$ (red dashed line), intermediate $|A, v_A = 101\rangle$ (blue dashed line in the small inset) and final $|X, v_X = 20\rangle$ (black solid line) states versus time for the multi-bound model; laser profiles of the Stokes pulse and the pump pulse are the same as in figure 3.

Additionally, investigation in the reactive yield as a function of the arrival time of the initial wave packet, $t_0$ in equation (4), is performed to justify our finding that there is no natural preference in terms of pulse sequences. Figure 6 shows the dependence of the reactive yield on different $t_0$ values for three different pulse sequences: $t_P - t_S = -200$ ns, $t_P - t_S = 0$ ns, and $t_P - t_S = 200$ ns. Though the high yield region for the counter-intuitive sequence is slightly wider than that for the intuitive sequence, the relative advantage is not dominant. The reason lies in the ‘collision/coherence time window’, governed by the atomic thermal temperature described previously. Note, the current study of pulse sequences does not contradict any previous experimental findings in the conventional STIRAP process since the former process starts from continua and the latter process starts from a discrete level. More importantly, we hope such ‘counter-intuitive’ findings can stimulate the society’s interest, especially experimentalists, in putting effort in realizing this process as an alternative to produce ultracold diatoms.

5. Conclusions

In this paper, we show that an appreciable final population of ultracold NaCs molecules can be achieved with the optimal pulses in either the ‘counter-intuitive’ ($t_P > t_S$) or ‘intuitive’ ($t_P < t_S$) PAP pulse sequences. By investigating the dependence of the reactive yield on a wide range of
Figure 5. (a) Fourier transform of the initial bound state probabilities, $f(t)$, defined in equation (7); time dependent Rabi-frequencies, $\Omega_{\nu_A \nu_X}$, and $\Omega_{\nu_A \nu_j}$, for (b) $t_P - t_S = -200$ ns, (c) $t_P - t_S = 0$ ns, and (d) $t_P - t_S = 200$ ns where all laser configuration parameters are fixed according to their values in figure 3.

Figure 6. Reactive yield as a function of collisional time, $t_0$, for the three pulse sequences studied in figure 3.
pulse sequences we show that there is not a fundamental preference to either pulse sequence in a PAP process. By discretizing the initial continuum states into a sum of many bound levels and analyzing such a multi-bound model we provide an explanation for this no-sequence-preference phenomenon.

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