Pulsed adiabatic photoassociation via scattering resonances

Alex C Han¹, Evgeny A Shapiro² and Moshe Shapiro¹,²

¹ Department of Physics, The University of British Columbia, 6224 Agricultural Road, Vancouver, BC V6T 1Z1, Canada
² Departments of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, BC V6T 1Z1, Canada
E-mail: alexhan@chem.ubc.ca

Received 3 April 2011, in final form 18 June 2011
Published 25 July 2011
Online at stacks.iop.org/JPhysB/44/154018

Abstract
We develop the theory for the adiabatic Raman photoassociation (ARPA) of ultracold atoms to form ultracold molecules in the presence of scattering resonances. Based on a computational method in which we replace the continuum with a discrete set of ‘effective modes’, we show that the existence of resonances greatly aids in the formation of deeply bound molecular states. We illustrate our general theory by computationally studying the formation of ⁸⁵Rb₂ molecules from pairs of colliding ultracold ⁸⁵Rb atoms. The single-event transfer yield is shown to have a near-unity value for wide resonances, while the ensemble-averaged transfer yield is shown to be higher for narrow resonances. The ARPA yields are compared with that of (the experimentally measured) ‘Feshbach molecule’ magneto-association. Our findings suggest that an experimental investigation of ARPA at sub-μK temperatures is warranted.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Adiabatic Raman photoassociation (ARPA) of ultracold atoms was introduced [1–3] as a practical way of producing ultracold diatomic molecules in their ground electronic and vibrational states. As illustrated in figure 1, the method consists of photoassociating two colliding atoms by two (‘dump’ and ‘pump’) laser pulses that are mutually coherent and partially overlapping in space and time. As in three-level ‘stimulated Raman adiabatic passage’ (STIRAP) [4–8], one uses the ‘counter-intuitive’ pulse ordering [4] in which the ‘dump’ pulse, connecting the final bound state to an intermediate excited bound state, precedes the ‘pump’ pulse, connecting the continuum to the latter state. In this way, one executes a smooth ‘adiabatic passage’ from an (ultracold atom-scattering) continuum to deeply bound molecular states [1–3].

The main problem with the above approach is the small ‘Franck–Condon’ (FC) overlap factors between the intermediate bound state and the continuum. The introduction of a (‘Feshbach’) resonance which is expected to better overlap with the intermediate bound state can alleviate this problem [9, 10]. As we show below, a Feshbach resonance also induces an important dynamic effect of prolonging the lifetime of the spatial region (the ‘FC window’) in which photoassociation occurs. In this way, a larger fraction of the atom pairs becomes available for photoassociation. This aspect has not been considered in previous works on photoassociation via Feshbach resonances [10], where it was concluded that wide resonances are more effective in promoting photoassociation than narrow ones. While we agree with [10] concerning the outcome of a single pair collision, we differ in our conclusions regarding the ensemble averaged yields. Based on our calculation of the number of recombining atoms per laser pulse pair, we find that narrow resonances are in fact more effective than wide ones, because by prolonging the lifetime of the FC window, narrow resonances allow for more recombination events to occur. This mechanism more than compensates for the smaller energetic widths of the narrow resonances.

The structure of this paper is as follows: in section 2, we develop the working equations for the ARPA process, based on representing the continuum as a discrete set of ‘effective modes’ [11]. In section 3, we present calculations of the ARPA population dynamics for a single pair of ultracold ⁸⁸Rb atoms, and demonstrate how the FC window lifetime and spatial extent are being extended by the resonance. In
section 4, we compare the yield of ARPA with that of magnetoassociation [12–16] in which a pair of atoms in a Feshbach resonance are transformed into a stable molecule by sweeping over an external magnetic field, thereby pushing the resonance energy to lie below the molecular dissociation limit. We show that the two schemes lead to similar scaling of molecular production yield, but that ARPA is expected to be more efficient. Finally, in the appendix we show that the action of the pulses is tantamount to quantum projective measurements on the initial continuum wave packet [2, 3]. Concluding remarks are provided in section 5.

2. Theory

2.1. The basic formulation

As illustrated in figure 1, ARPA involves a Λ-type level structure, similar to 3-state STIRAP, in which two, mutually coherent, temporally and spatially overlapping, laser pulses induce adiabatic passage from a molecular continuum (representing two colliding atoms) to the target bound level |1⟩, using an excited bound state |2⟩ as an intermediate. The Hamiltonian of the system is written as (in atomic units)

\[ \hat{H} = \hat{H}_0 - 2\hat{\mu} \sum_{n=1,2} \epsilon_n(t) \cos \omega_n t, \]

where \( \hat{H}_0 = E_1 |1⟩⟨1| + E_2 |2⟩⟨2| + \int_{E_{th}}^{\infty} E |E⟩⟨E| \, dE \)

(2)

is the 'material' Hamiltonian. The bandwidth of the pulses ranges from being of order of 100 \( \mu K \), down to tens of nK, which, when compared to the vibrational energy separation, makes it valid to include no other bound states than \(|1⟩\) and \(|2⟩\). The second term in equation (1) describes the interaction of \( \hat{\mu} \), the transition dipole moment, with the 'dump' (n = 1) and 'pump' (n = 2) laser pulses, whose respective amplitudes and central frequencies are \( \epsilon_n(t) \) and \( \omega_n \). We tune \( \omega_2 \), the pump centre frequency, to be in near resonance with \( \omega_{2,E} \), the transition frequency between the intermediate state \(|2⟩\) and the continuum states \(|E⟩\), and \( \omega_1 \), the dump centre frequency, to be in resonance with \( \omega_{2,1} \), the intermediate-to-final-state transition frequency. We assume that the laser fields do not vary significantly over the range of atom–atom distances in which photoassociation occurs, thereby justifying the elimination of the spatial variation of the fields.

As state |1⟩, we choose a deeply bound rovibrational level belonging to the ground electronic potential. Given this choice, the intermediate state |2⟩, taken to belong to an excited electronic potential, is chosen to be a vibrational state that overlaps well with the |1⟩ state. The main feature of the continuum we explore here is the embedding of a (Feshbach-type) resonance, leading to a sharp energy dependence of continuum–bound transition-dipole matrix elements \( \mu_{2,E} = ⟨2 | \hat{\mu} | E⟩ \) [9, 10, 17].

Expanding the time-dependent system wavefunction in the material basis set,

\[ |Ψ(t)⟩ = \sum_{i=1,2} b_i(t) e^{-i\epsilon_i t} |i⟩ + \int_{E_{th}}^{\infty} dB_E(t) b_{E}(t) e^{-iD_E t} |E⟩, \]

(3)

we obtain, using the time-dependent Schrödinger’s equation \( i\frac{d}{dt} |Ψ(t)⟩ = \hat{H} |Ψ(t)⟩ \), the orthonormality of the material states and the rotating wave approximation (RWA), that,

\[ b_1(t) = iΩ_1(t) b_2(t) \]

(4)

\[ b_2(t) = iΩ_1(t) b_1(t) - \Gamma_2 b_2(t) + i \int_{E_{th}}^{\infty} Ω_E(t) b_E(t) e^{i\Delta_E t} dE \]

(5)

\[ b_{E}(t) = iΩ_2(t) b_2(t) e^{-i\Delta_E t}, \]

(6)

where \( E_{th} \) is the continuum threshold energy, \( \Delta_E = E_2 - E - \omega_2 \) and \( \Delta_1 = E_2 - E_1 - \omega_1 \) are the detunings of the pulses and \( \Gamma_2 \) is the spontaneous decay rate of the state |2⟩. There are two Rabi frequencies in the problem, \( Ω_1(t) = \epsilon_1(t) \mu_{2,1} e^{i\Delta t} \) and \( Ω_2(t) = \epsilon_2(t) \mu_{2,E} \).

Equation (6) for \( b_E(t) \), representing a continuous set of equations for the continuously varying \( E \), is numerically difficult to solve. We therefore eliminate equation (6) by integrating \( b_E(t) \) in time,

\[ b_E(t) = b_E(0) + \int_0^t d\tau Ω_E^*(\tau) b_2(\tau) e^{-i\Delta t}, \]

(7)

and substitute this formal solution into equation (5) to obtain that

\[ b_2(t) = iΩ_1(t) b_1(t) - \Gamma_2 b_2(t) + i \int_{E_{th}}^{\infty} Ω_E(t) b_E(0) e^{i\Delta_E t} dE \]

\[ - \epsilon_2(t) \int_{-\infty}^{\infty} d\tau \int_{0}^{\infty} e^{i\epsilon_2(t) b_2(\tau) e^{-i\Delta_E t} d\tau} e^{i\Delta_E t} dE, \]

(8)
By defining $f_{\text{source}}(t)$, the source function, and $F(t - t')$, the spectral auto-correlation function, as

$$f_{\text{source}}(t) = \int_{E_0}^{\infty} \Omega_E E b_E(0) e^{i\Delta E t} dE,$$  
(9)

$$F(t - t') = \int_{E_0}^{\infty} |\mu_{2,E}|^2 e^{i\Delta E (t - t')} dE,$$  
(10)

we can transform the above (continuous) set of differential equations to a set of two integro-differential equations:

$$\dot{b}_1(t) = i\Omega_1(t) b_2(t),$$
$$\dot{b}_2(t) = i\Omega_2(t) b_1(t) - \Gamma_f b_2(t) + if_{\text{source}}(t) - \epsilon_2(t) \int_0^t \epsilon_2(t') b_2(t') F(t - t') dt'.$$  
(11)

The threshold energy $E_0$ in the source function will later in our analysis be taken as $-\infty$, since the function $b_E(0)$ is zero near the collisional threshold of the ground electronic potential, reflecting the density of states at zero kinetic energy.

### 2.2. The effective mode expansion

The simplest solution of equations (11) is obtained by the 'flat continuum' or 'slowly varying continuum approximation' (SVCA), according to which, whenever $\mu_{2,E}$ varies sufficiently slowly with energy $E$, we replace it by its value at some average energy $\bar{E}$. In this way, the spectral auto-correlation function of equation (10) is reduced to $F(t - t') = 2\pi |\mu_{2,\bar{E}}|^2 \delta(t' - t)$, and the integration in equation (11) is eliminated. Given this approximation, the dynamical equations assume, in matrix notation, the form

$$\frac{d}{dt} b = iH \cdot b + if_{\text{source}},$$  
(12)

where $b(t) \equiv (b_1(t), b_2(t))^T$, $f_{\text{source}}(t) \equiv (0, f_{\text{source}}(t))^T$, with $^T$ designating the transpose operation. The Hamiltonian matrix is defined as

$$H = \begin{pmatrix} 0 & \Omega_1^T \\ \Omega_1 & i\Gamma_{\text{eff}}(t) \end{pmatrix}$$

with $\Gamma_{\text{eff}}(t) = \pi |\mu_{2,\bar{E}}|^2 \epsilon_2(t)$.

(13)

A detailed discussion of the solutions under SVCA was made in [1–3].

The SVCA is however invalid when collisional resonances are embedded in the continuum, because in that case $\mu_{2,E}$ changes rapidly near the resonance energy [9, 17]. In order to treat this case we parametrize $\mu_{2,E}$ as [11]

$$\mu_{2,E} = \sum_{s=1}^{M} \frac{i\mu_s \Gamma_s / 2}{E - E_s + i\Gamma_s / 2},$$  
(14)

where $\mu_s$ represents the electronic transition dipole moment, $\Gamma_s$ the full-width-at-half-maximum (FWHM) and $E_s$ the centre position of each $s$ resonance. This form is capable of approximating well both wide and narrow resonances [10, 17, 18]. As will be seen below, the above parametrization allows us to greatly simplify both the analytical theory as well as the numerical propagation of the dynamical equations.

With expansion (14), the auto-correlation function $F(t - t')$ in equation (10) can be evaluated analytically as

$$F(t - t') = \sum_{s=1}^{M} \alpha_s f_s^+(t)f_s^-(t'),$$  
(15)

with

$$\alpha_s = \sum_{s} \frac{-i\mu_s \mu_s / 4}{E_t - E_s - i(\Gamma_s + \Gamma_s') / 2},$$

(16)

Using equation (15) we now define [11] the 'effective mode' variables as

$$B_s^-(t) = i\int_0^t \epsilon_2(t') b_2(t') F_s^-(t') dt',$$  
(17)

using which we transform equations (9) and (10) into

$$\dot{b}_1(t) = i\Omega_1^s(t) b_2(t),$$
$$\dot{b}_2(t) = i\Omega_2(t) b_1(t) - \Gamma_f b_2(t) + i f_{\text{source}}(t) + i\epsilon_2(t) \sum_{s=1}^{M} \alpha_s f_s^+(t) B_s^-(t).$$  
(18)

In this way, the original set of continuous equations for $b_E(t)$ is replaced by a discrete set of equations for $B_s^-(t)$. We can further simplify the structure of the equations by defining $B_s^+(t) = \sqrt{\pi\alpha_s} f_s^+(t) B_s^-(t)$, and mode-dependent Rabi frequencies, $\Omega_2^s(t) \equiv \epsilon_2(t) \sqrt{\pi\alpha_s}$. With these definitions equations (18)–(20) assume the form

$$\dot{b}_1(t) = i\Omega_1^s(t) b_2(t),$$
$$\dot{b}_2(t) = i\Omega_2(t) b_1(t) - \Gamma_f b_2(t) + i f_{\text{source}}(t)\sum_{s=1}^{M} \alpha_s f_s^{(+)}(t) B_s^-(t),$$

(19)

$$B_s^-(t) = i\int_0^t \epsilon_2(t') b_2(t') F_s^-(t') dt',$$  
(20)

Writing these equations in matrix notation, we have that

$$\frac{d}{dt} b = iH \cdot b + if_{\text{source}},$$  
(21)

$$\begin{bmatrix} \dot{b}_1(t) \\ \dot{b}_2(t) \end{bmatrix} = \begin{bmatrix} B_1(t) \\ B_2(t) \end{bmatrix},$$
$$\begin{bmatrix} f_{\text{source}}(t) \\ f_{\text{source}}(t) \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} - \begin{bmatrix} \Omega_1^T \\ \Omega_1 \end{bmatrix}$$

where

$$H = \begin{pmatrix} \Omega_1^T & 0 & 0 & \cdots \\ 0 & \Omega_1 & 0 & \cdots \\ \Omega_2^{(1)} & \Omega_2^{(1)} & \Omega_2^{(2)} & \cdots \\ 0 & \Omega_2^{(2)} & -\chi_1 & 0 & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{pmatrix},$$  
(25)
The 'effective mode' amplitudes $B_i(t)$ thus appear equivalent to some extra bound states of energies $E_i$ that are coupled by the Rabi frequencies $\Omega_2^{(i)}(t)$ to the state $|2\rangle$, with detuning $E_i - E_2 + \delta_0$ and decay rates $\Gamma_i/2$ as contained in $\chi_i$. The non-Hermiticity of the Hamiltonian is due not just to the decay of the effective modes, appearing as the imaginary part of $\chi_i$, but also to the Rabi frequencies $\Omega_2^{(i)}$, which are in general complex numbers, since the definition of $\alpha_i$ involves a summation over $s'$, namely the effective interaction between overlapping resonances.

Equation (24) resembles (multi-state) STIRAP [19] with $\Omega_1(t)$ and $\Omega_2^{(s)}(t)$ coupling respectively $|1\rangle$ with $|2\rangle$ and $|2\rangle$ with each of the $s$ effective modes (figure 2). We note however that the transfer dynamics differs in a significant way from ordinary STIRAP in that here the initial population does not reside in the effective modes, which get gradually populated. We can see this most explicitly for a single resonance, for which the dynamical equations assume the form

$$\dot{b}_1(t) = i\Omega_1^2(t)b_2(t)$$

$$\dot{b}_2(t) = i\Omega_1(t)b_1(t) - \Gamma_2b_2(t) + i\Omega_2^{(1)}(t)f_{\text{source}}(t)/\Omega_2^{(1)}(t) + B_1(t)$$

$$\dot{B}_1(t) = -i\chi_1B_1(t) + i\Omega_2^{(1)}(t)b_2(t).$$

By re-defining $B(t) = f_{\text{source}}(t)/\Omega_2^{(1)}(t) + B_1(t)$ we obtain

$$\dot{b}_1(t) = i\Omega_1^2(t)b_2(t)$$

$$\dot{b}_2(t) = i\Omega_1(t)b_1(t) - \Gamma_2b_2(t) + i\Omega_2^{(1)}(t)B(t)(30)$$

$$\dot{B}_1(t) = -i\chi_1B_1(t) + i\Omega_2^{(1)}(t)b_2(t) + [i\chi_1f_{\text{source}}(t)/\Omega_2^{(1)}(t) + f'_\text{source}(t)].$$

where $f'_\text{source}(t) = \frac{2}{\sqrt{2\pi\delta_0}}\int_{-\infty}^{\infty} \Delta E\mu_2,Eb_E(0)e^{i\Delta E^2/2\delta_0}dE$. We see that here it is the terms in the square bracket that populate the effective mode (see figure 2).

Another contrast with three-state STIRAP is the possibility of leakage of population from the 'dark' state. In three-state counter-intuitive pulse ordering adiabatic passage [4], the population resides initially in the adiabatic 'dark' state, which is a superposition of the initial and target states only. In that case, the adiabaticity of the pulses guarantees the completeness of the transfer from the initial to the target state, leaving the intermediate state unpopulated at all times. Because in our case the effective mode gets populated in a gradual fashion, the system wavefunction may contain non-negligible contributions from other ('bright') adiabatic states. These 'bright' states have a small overlap with the intermediate state $|2\rangle$, causing population to be lost via spontaneous emission.

3. Computations of resonant photoassociation

We view the entire ARPA process as a statistical average over collisions between individual pairs of colliding atoms. As explained above, we represent such pairs by a set of (spatially extended) coherent wave packets arriving at the FC region at different times. The choice of coherent wave packets (rather than plane waves) as the basis of our computations is merely a result of our wish to work with $L^2$ normalizeable states.

In this section, we examine the above formulation by performing a set of computations on the resonantly enhanced photoassociation of ultracold $^{85}$Rb atoms to form $^{85}$Rb$_2$ in its ground vibrational state. In keeping with our view of the process we divide the computations into two parts: (A) population transfer for each colliding pair, and (B) population transfer of the thermal ensemble of pairs of colliding atoms.

3.1. The single collision transfer yields

Following the model of [2, 3], we consider a pair of $^{85}$Rb atoms colliding on the ground electronic potential. We assume that at $t = 0$, chosen to occur before the onset of the pulses, all the population resides in the continuum wave packet and none in state $|1\rangle$ or $|2\rangle$. The shape of $|\Psi(0)\rangle = \int_{-\infty}^{\infty} dEb_E(0)e^{-iE^2/2E}\{E\}$, the initial continuum wave packet of equation (3), with $E_{th}$ being the lower energetic limit (which is extended to $-\infty$), is determined by the $b_E(0)$ function, chosen here to be an energetically-narrow Gaussian [1–3]:

$$b_E(0) = \frac{1}{(2\pi \delta_0^2)^{1/4}}\exp\left[-\frac{(E - E_0)^2}{2\delta_0^2}\right] + i(E - E_0)\alpha_0.$$
The peaking shape of the resonance represents the enhancement of the FC factor. Centre of the resonance is (depending on the actual physical system, an even larger height value can be used, which favours a lower cost of laser amplitude required). The peaking shape of the resonance represents the enhancement of the FC factor. Centre of the resonance is $E_{\text{res}} = 100 \mu K$.

$t_0 = 1.2 \, \mu s$ [1, 2]. The pair of pulse spectral widths are then chosen to have a good overlap with the energetic spread of the atomic wave packet. This requirement translates in the time domain to $\mu$s pulse durations.

The scattering continuum is assumed to contain a narrow resonance, whose shape is given by equation (14). Figure 3 shows the shape of a resonance centred at $E_{\text{res}} = E_0 = 100 \mu K$ for three different widths. Since the (Feshbach) resonance position can be tuned (magnetically), we can optimize the transfer by tuning $E_{\text{res}}$ to be always equal to $E_0$. In this way, one achieves the maximal FC enhancement (as confirmed by the numerical calculation presented in figure 5, bottom panel).

The bound-to-bound matrix element is chosen to have a numeric value $\mu_{21} = 0.0051$ au. This numeric value can be different depending on the actual experimental setup, but our results only depend on the Rabi frequency $\Omega_1(t)$, which is proportional to the product of this bound-to-bound matrix element with the laser amplitude. An increase (decrease) of the matrix element translates into a proportional decrease (increase) in the laser amplitude required. The spontaneous decay rate from level [2] is $\Gamma_2 = (30 \, \text{ns})^{-1}$ [1–3]. The central frequency of the dump pulse is chosen to coincide with $E_2 - E_1$, and the central frequency of the pump pulse to coincide with $E_2 - E_0$. The field amplitudes $\epsilon_1(t)$ and $\epsilon_2(t)$ are taken as Gaussian functions, peaking, respectively, at 1.05 and 1.55 $\mu$s, respectively. The duration of both fields is 0.22 $\mu$s, and their peak intensity is $3 \times 10^5$ W cm$^{-2}$ [2].

With these specifications, equations (21)–(23) simplify to yield

$$\dot{b}_1(t) = i\Omega_1^*(t)b_2(t)$$

(33)

$$\dot{b}_2(t) = i\Omega_1(t)b_1(t) - \Gamma_f b_2(t) + i f_{\text{source}}(t) + i\Omega_2^{(1)}(t)B_1(t)$$

(34)

$$B_1(t) = -\frac{(\Gamma_{\text{res}})}{2} B_1(t) + i\Omega_2^{(1)}(t)b_2(t),$$

(35)

where the Rabi frequencies are $\Omega_1(t) = \epsilon_1(t)\mu_{21}$ and $\Omega_2^{(1)} = \epsilon_2(t)\mu_{\text{res}}\sqrt{2\pi\Gamma_{\text{res}}}/2$. Note here that the FC factors contained in $\mu_{21}$ and $\mu_{\text{res}}$ always appear as a product with the field amplitudes $\epsilon_{1,2}(t)$. So the intensities of the dump and pump fields really are determined by the respective FC factors between the intermediate and target states, and between the continuum and the intermediate states. An enhancement on either of the the FC factors will result in the same order decrease in the laser amplitude (square-root of the intensity) needed.

In figure 4, we display the results of numerically integrating the equations for $b_1(t)$, $b_2(t)$ and $B_1(t)$, given that $b_1(0) = b_2(0) = B_1(0) = 0$. We plot the populations of the states [1] and [2] for a wide ($100 \mu K$) resonance and a narrow ($6 \mu K$) resonance. The most striking feature of this plot is that the wide resonance gives rise to an essentially complete population transfer (>90%), while the transfer probability via the narrow resonance is only $\sim 23\%$. Since the target state is the ground state, no loss of population can occur after a single photoassociation event. Loss of population is however possible when subsequent collisions with the gas of atoms and/or the action of subsequent pulses are considered. As shown in the lower panel, due to the adiabatic nature of the process and the ‘counter-intuitive’ pulse ordering, the population of the intermediate level [2] remains very low, even while the pulses are on.

3.2. Ensemble transfer yield

In agreement with [10], we have shown in sub-section 3.1 that for each event the transfer yield via a wide resonance is greater than that of a narrow resonance (figure 5, top panel). The situation is however different for an ensemble of colliding atoms, where, as we show below, the transfer yield of the narrow resonances is greater. The reason is that for narrow resonances the number of colliding pairs which can react to the light is greater, essentially because for narrower resonances one can work with narrower pulse bandwidths, hence longer pulses. The increase in the number of effective collisions occurring during the increased pulse durations more than compensates for the reduction in the individual event transfer yield.

An alternative way of viewing this effect is to examine the role of the discrete effective modes which replace the continuum in our theory. These modes are to all intents and purposes resonances [20]. The only difference between the
Figure 4. The target state and intermediate state populations as a function of time for two resonance widths. Top panel: the pump and dump field amplitudes. Middle panel: the target state probability $|b_1(t)|^2$. The transfer yield is 90% for the wide (100 μK) resonance, but only 23% for the narrow (6 μK) resonance. Bottom panel: the intermediate state population $|b_2(t)|^2$. (Notice the large difference in the vertical scale relative to the middle panel.)

Figure 5. Top panel: the target population, $|b_1(t \to \infty)|^2$, for different resonance widths. Bottom panel: $|b_1(t \to \infty)|^2$ as a function of the centre of the resonance $E_{\text{res}}$, for $E_0 = 100 \, \mu K$; this shows that transfer is optimal when the centre of the resonance coincides with the central energy of $b_E(0)$.

 modes and scattering resonances is that the effective modes do not originate from a *real* bound state embedded in a continuum. Thus, as clearly seen in equation (35), the rate of de-populating an effective mode is proportional to $\Gamma_{\text{res}}$—the resonance-width of that mode. Hence, narrower resonances, corresponding to smaller rates of depopulation, increase the interaction times of the effective modes with the intermediate level $|2\rangle$, thereby prolonging the duration of the FC window.
Figure 6. The magnitude of the window functions $f_W(t)$ for different (single) resonance widths $\Gamma_{\text{res}}$ and fixed height $\mu_{\text{res}}$. Longer tails of $|f_W(t)|$ are observed for narrower resonances.

In figure 6, we examine these trends in a quantitative way by displaying $f_W(t)$, the field normalized source term, given as

$$f_W(t) = \frac{f_{\text{source}}(t)}{\epsilon_2(t)} = \int_{-\infty}^{\infty} \mu_2(E) b_E(0) e^{i\Delta E t} dE,$$  \hspace{1cm} (36)

for resonances of changing widths. Clearly in evidence is the prolonged duration of $f_W(t)$ when switching to narrower resonances.

The temporally stretched population source is also beneficial when we consider the action of a pulse pair that is delayed relative to $t_0$, the arrival time of the incoming wave packet. Figure 7 shows the transfer efficiency as a function of such delay times for three different resonance widths. For a narrow resonance, despite the drop in the peak value, the single collision transfer efficiency remains large for longer times. This means that atom pairs which started their collision at an earlier time can still be transformed into bound molecules with non-negligible probability.

In order to obtain the delay time averaged molecular production yield for an atomic ensemble we need to calculate the area under the transfer-yield curves of figure 7. Figure 8 displays the dependence of the delay time averaged yield for various resonance widths. We first note that the yield changes relatively slowly for resonance width larger than 1000 $\mu$K. This is because in this case the resonance width by far exceeds $\delta_0$, the energetic spread of the initial atomic ensemble, and we approach the flat-continuum limit. As the width of the resonance drops to a few $\mu$K, the molecular production yield rises to a maximum value, but drops significantly due to spontaneous emission for yet narrower resonances. Thus, there exists an optimal resonance width for which the molecular production yield is maximal. Comparing the optimal molecular production yield, obtained for a (narrow) resonance value of $\sim 8$ $\mu$K, with the yield in the flat-continuum limit, we see an improvement factor of 1.56.

3.3. Scaling behaviour with ensemble temperature

We now explore, as was done in [1], how the process varies as the average ensemble energy, $E_0$, and energy spread, $\delta_0$, are scaled down by a factor of $s > 1$, i.e. $E_0 \rightarrow E_0/s$, and $\delta_0 \rightarrow \frac{\delta_0}{s^2}$. In [1], we showed that the equations are invariant to this scaling provided the peak time was scaled up by the same factor $t_0 \rightarrow st_0$, and the initial wave packet amplitude is scaled as $b_E(0; E, t_0) \rightarrow \sqrt{s}b_E(0; \frac{E}{s}, st_0)$. We now consider the effect, in addition to the above, of scaling the resonance shape as $\mu_2(E, \Gamma_{\text{res}}) \rightarrow \mu_2(E, \frac{\Gamma_{\text{res}}}{s^2})$. In order to match the spectral profile to the scaled $b_E(0)$, we need to scale up the centre frequencies and durations of the two pulses by the same $s$ factor. Since we can choose the intensity (amplitude) of the fields, we scale $\epsilon_1(t) \rightarrow \frac{\epsilon_1(t)}{s}$ and $\epsilon_2(t) \rightarrow \frac{\epsilon_2(t)}{s}$. As a result, the source function scales like $f_{\text{source}}(t, t_0, \Gamma_{\text{res}}) \rightarrow s^{-1} \cdot f_{\text{source}}(st, st_0, \frac{\Gamma_{\text{res}}}{s^2})$. The above scaling leaves the dynamical equations (equations (33)–(35)) essentially unchanged, except for the spontaneous decay rate which cannot be scaled. As we scale the relevant times by a
factor of $s$, the deleterious effect of the spontaneous emission becomes more and more pronounced.

In figure 9, top panel, we display the dependence of the single collision photoassociation yield on the spontaneous decay rate. Note that a change of one order of magnitude for the spontaneous decay rate only affects our results negligibly. When we compare the results to those displayed in figure 5, top panel, where the transfer yield is plotted as a function of the resonance width, we see that the transfer yield is not greatly affected at ensemble temperatures of a few $\mu$K to a few $10^2 \mu$K. As the ensemble temperature goes down by three orders of magnitude, the single collision transfer efficiency goes down too, by $\sim 67\%$ of its original value. The effect is more pronounced for narrower resonances, because the longer interaction times enhance the effect of the spontaneous decay. However, as shown in the lower panel of figure 9, it is possible to combat the effect of spontaneous decay at very low temperatures, e.g. in nK range, by increasing the amplitude (intensity) of both laser fields.

One can summarize these results by saying that the optimal resonance width is always $\sim 8\%$ of the ensemble temperature, and that the optimal molecular production efficiency by ARPA is $\sim 56\%$ higher than that of the wide resonance (flat continuum) case.

3.4. Thermalization

At long times, the cumulative action of many pulses can change a region (or regions) in phase space corresponding to the recombining atoms, thereby affecting the initial wave packet amplitude $b_E(0)$. However, an atomic ensemble can thermalize sufficiently fast, on the order of milliseconds, to yield the typical atomic trap setting of $100 \mu$K temperature and $10^{11} \text{ cm}^{-3}$ density [24]. This means (depending on the...
repetition rate of the pulses) that after a few thousand $\mu s$ pulse pairs, the atomic ensemble can thermalize back to its original phase-space distribution, re-validating the ensemble-averaged form we used for $b_p (0)$.

According to previous estimates [1, 2], the total number of pulse pairs needed to transfer an entire atomic ensemble of density $10^{11}$ cm$^{-3}$ (at a temperature of 100 $\mu$K) is around $10^7$. Therefore, a few thousand pulses is indeed a very small fraction of the total number of pulses needed, and the thermalization is fast compared to the ensemble size molecular conversion time.

One is also inclined to pose the practical question of how to hide the newly formed molecule in the state $|1\rangle$ from subsequent pulse pairs. In accordance with more detailed discussions in [1, 2], this can be done, for example, by allowing the newly formed molecules in the state $|1\rangle$ to ‘leak’ away from the laser focus, which is possible because they react differently from the atoms to the confining laser frequency. A molecular trap can then be placed just below the atomic trap.

4. The ARPA yield dependence on the phase-space density and comparison to magneto-association

Following [1, 3], we now present a detailed calculation of ARPA efficiency in a thermal ensemble. In order to estimate the fraction of atoms photoassociated per pulse pair, we multiply $P(E)$, the single collision photoassociation probability at the energy $E$, by the number of collisions experienced by a given atom while the pulses are on. This is equivalent to averaging over all possible values of $t_0$ as performed above.

The number of collisions during the pulses is calculated as follows: at a given energy $E$, the velocity of a given atom is $v = (2E/m)^{1/2}$ and the distance traversed by it during a pulse of $\tau_{\text{user}}$ duration is $v\tau_{\text{user}}$. The cross-section for collision is $\pi b^2$ where $b$ is the impact parameter. For $s$-wave collisions, the semiclassical estimate is $b = h/2p = h/(2\sqrt{2mE})$. Hence, the number of collisions experienced by the atom during the two pulses is $n = N\pi b^2 v\tau_{\text{user}}/V$, where $N$ is the number of atoms in the trap, and $V$ is its volume. Putting all this together, we obtain that the fraction of atoms photoassociated per pulse pair is

$$f(E) = \frac{P(E)\pi N\tau_{\text{user}}}{4Vm^{3/2}(2E)^{3/2}}. \quad (37)$$

Estimating the photoassociation yield for the case of flat continuum, we can set $P(E) \simeq 1$ [3], and assume that all collisions occur at the temperature of the relative motion $T_{\text{rel}} = 2T$. Further, when optimizing the yield for an atomic ensemble, we must choose $\tau_{\text{user}} \simeq 2\pi h/kT_{\text{rel}}$ because the bandwidths of the pump and dump pulses should match the energy spread in the ensemble. Thus, we obtain

$$f(T) \simeq \frac{\pi^2 N\hbar^3}{V(2mkT_{\text{rel}})^{3/2}}. \quad (38)$$

As pointed out above, a narrow resonance can enhance this fraction by a factor of 0.56, i.e. for a narrow resonance $f_{\text{narrow}}(T) = 1.56 f(T)$, with $f(T)$ given by equation (38).

We now consider the yield of magneto-association. In this process, a time-varying external magnetic field is ‘swep’ in magnitude, thereby moving $E_{\text{sa}}$, the position of the Feshbach resonance of interest, to lie below $E_{\text{sa}}$, the onset of the continuum. In this way, the Feshbach resonance is stabilized to become a ‘Feshbach molecule’ [12–16]. The magneto-association is then followed by a traditional three-bound state STIRAP [15, 16].

The efficiency of this scheme is limited by the yield of the first step. In this step, two atoms may form a molecule if prior to sweeping the magnetic field they are within, approximately, $\Theta_1$ volume of phase space from each other [22]. Therefore, at low to moderate phase space densities, the probability for a given atom to participate in a magneto-association process is

$$f(T) \simeq N \Theta_{\text{association}}/\Theta_{\text{whole}} = \frac{N h^3}{8V(2mkT_{\text{rel}})^{3/2}}. \quad (39)$$

where $\Theta_{\text{whole}} = V \times (2mkT_{\text{rel}})^{3/2}$ is the single-particle phase space volume at temperature $T$ and $V$ is the trap volume.

Comparing equations (38) and (39) we see that the ARPA yield scales with temperature in exactly the same fashion as the magneto-association yield. However, in absolute numbers our estimates are such that at low to moderate phase space densities the ARPA yield is $1.56 \times 8\pi^2 \simeq 120$ times higher than the magneto-association yield. These findings strongly suggest that an experimental investigation of ARPA at sub-$\mu$K temperatures is warranted.

5. Conclusions

In this paper, we have shown that adiabatic Raman photoassociation of ultracold atoms proceeding via collisional resonances is an efficient way of producing ultracold diatomic molecules in deeply bound states. We have done that by replacing the resonance-dominated molecular continuum by a discrete set of ‘effective modes’ acting like a set of resonances. Though when the scattering resonance width is narrow it covers a smaller region in phase space (relative to the case of wide resonances), resulting in a drop of the single collision transfer efficiency, this drop is amply compensated for by the (as much as an order of magnitude) longer durations for which the photoassociating pulses can effectively act. In this way, each pair of (pump and dump) laser pulses can act on more colliding atoms. The overall effect is that the narrow-resonance molecular production yield can be as much as ~56% higher than the wide resonance yield. For atomic temperatures in the $\mu$K range, we find that the optimal conditions are attained for resonances whose widths are about 8% of the ensemble temperature. We have also shown that the efficiency of the ARPA scheme compares favourably with the efficiency of magneto-association, with the yields of both schemes scaling with temperature in exactly the same manner. We have demonstrated that the ARPA process is a projective quantum measurement by the pulses of the initial continuum...
wave packet. This feature is a result of the single collision transfer efficiency being proportional to the degree of overlap between a function set by the pulses and the initial wave packet.

Future applications will deal with time-dependent resonances. We envision combining ARPA with a dynamical sweep of the Feshbach resonance across the threshold energy range. As the sweep will render the resonances narrower, the laser pulses will be made narrower so as to transfer the atomic gas into molecules in an optimal piecewise manner.

Acknowledgments

Support by NSERC Discovery Grant, by a Major Thematic Grant from UBC’s Peter Wall Institute for Advanced Studies, and by the US DoD DTRA program are gratefully acknowledged. ES acknowledges the Institute of Theoretical Atomic, Molecular, and Optical Physics (ITAMP) for support during a visit to ITAMP facilities.

Appendix A. ARPA as a projective measurement of the initial continuum wavefunction

We showed in [2] that if the continuum is flat, then ARPA implements a projective measurement of the initial wavefunction of two colliding atoms. Basically, the profiles of the laser pulses \( \epsilon_j(t) \) define a wave form \( f^{(\text{ARPA})} \) that is adiabatically coupled to the target state [1]. An initial scattering state which overlaps \( f^{(\text{ARPA})}(t) \) well will undergo population transfer to [1], while a state orthogonal to \( f^{(\text{ARPA})} \) will not. By controlling the laser pulse profiles and implementing ARPA, one is essentially measuring the wavefunction of the colliding atoms.

In this appendix we extend the treatment to a resonance-dominated continuum, and relate the effect of collision resonances to our ability to control \( f^{(\text{ARPA})}(t) \). We start by noting that in the adiabatic limit the solution of the equations of motion ((12) and (13)) is of the form [1, 2]

\[
\begin{align*}
\text{(A.1)} \quad b_1(t) &= i \cos \theta(t) \int_0^t \mathrm{d}t' \exp \left[ i \int_0^{t'} \mathcal{E}_+(t'') \mathrm{d}t'' \right] \\
&\quad \times \sin \theta(t) f_{\text{source}}(t') - i \sin \theta(t) \\
&\quad \times \int_0^t \mathrm{d}t' \exp \left[ i \int_0^{t'} \mathcal{E}_-(t'') \mathrm{d}t'' \right] \cos \theta(t'') f_{\text{source}}(t'), \\
\text{(A.2)} \quad b_2(t) &= i \sin \theta(t) \int_0^t \mathrm{d}t' \exp \left[ i \int_0^{t'} \mathcal{E}_+(t'') \mathrm{d}t'' \right] \\
&\quad \times \sin \theta(t') f_{\text{source}}(t') + i \cos \theta(t') \\
&\quad \times \int_0^t \mathrm{d}t' \exp \left[ i \int_0^{t'} \mathcal{E}_-(t'') \mathrm{d}t'' \right] \\
&\quad \times \cos \theta(t') f_{\text{source}}(t'),
\end{align*}
\]

where

\[
\mathcal{E}_\pm(t) = \frac{1}{2} [i \Gamma_{\text{eff}}(t) \pm \sqrt{4 |\Omega_{12}(t)|^2 - \Gamma_{\text{eff}}(t)^2}],
\]

and

\[
\tan \theta(t) = \mathcal{E}_+(t)/\Omega_{12}(t).
\]

The final yield of the ARPA process is defined as the probability \( P_l = |b_1(t \to \infty)|^2 \). Using equations (A.3) and (A.4), we see that \( \cos \theta(t \to \infty) = 0 \), and the excited bound state amplitude \( b_2(t \to \infty) \) indeed vanishes. Substituting \( \cos \theta(t \to \infty) = 0 \) and \( \sin \theta(t \to \infty) = 1 \) in equation (A.1) we obtain that

\[
b_1(t \to \infty) = \int_0^\infty f_{\text{ARPA}}^{(0)}(t) f_{\text{source}}(t) \mathrm{d}t \equiv \left[ f_{\text{ARPA}}^{(0)} \right] f_{\text{source}},
\]

where

\[
f_{\text{ARPA}}^{(0)}(t) = -i \exp \left[ i \int_0^t \mathcal{E}_-(t') \mathrm{d}t' \right] \cos \theta(t).
\]

Thus, the photoassociation amplitude \( b_1(t \to \infty) \) is given as the projection of the source function \( f_{\text{source}} \) onto the specific wave form \( f_{\text{ARPA}}^{(0)} \) whose shape is controlled by the amplitudes and the phases of \( \Omega_2(t) \) and \( \Omega_1(t) \). Wave packets that are orthogonal to \( f_{\text{ARPA}}^{(0)} \) do not photoassociate in the ARPA process, while the ones that project well onto \( f_{\text{ARPA}}^{(0)} \) do. By tailoring the amplitudes and phases of the laser pulses, one can choose which continuum waveform is transferred into the target state [2].

In the main part of the paper we have shown that resonance-dominated ARPA is most efficient when the resonance is narrow and the pump pulse has a narrow bandwidth relative to the initial ensemble temperature. These arguments allow us to replace in (9) \( E_\text{th} \) by \( -\infty \) and obtain, via the convolution theorem,

\[
f_{\text{source}}(t) = \epsilon_1(t) f_0(t) \times W(t) \\
\equiv \epsilon_2(t) \int_{-\infty}^\infty W(\tau) f_0(t - \tau) \mathrm{d}\tau,
\]

where

\[
W(t) = \frac{1}{2\pi} \int_{-\infty}^\infty \mu_{2,E}(E) e^{i\Delta\tau E} \mathrm{d}E,
\]

and

\[
f_0(t) = \int_{-\infty}^\infty b_0(E) e^{i\Delta\tau E} \mathrm{d}E.
\]

\( f_0(t) \) is the phase-space envelope [21] of the initial wave packet of continuum states. Semiclassically, it corresponds to the incoming wavefunction as a function of time \( t \), measured at the turning point of a classical trajectory of energy \( E_0 \). The positive values of \( \tau \)—the time variable in the convolution integral of equation (A.7)—correspond to an outgoing motion, and negative values to an incoming motion [21].

The function \( W(t) \), the ‘FC window’, describes the residence time of the system in the ‘FC region’, the spatial region for which the FC factors are substantial. The temporal width \( \Delta \tau_W \) at which \( W(\tau) \) is substantial corresponds to \( \Delta R \),

\[4\] At ultracold temperatures the semiclassical point of view underlying the above carrier-envelope interpretation of the wavefunction is invalid for long-range van der Waals interactions, i.e. at interatomic distances from several up to hundreds of atomic units. However, our approach predicts what happens to the wavefunction after the photoassociation is complete, at large interatomic distances where the semiclassical expression for the wavefunction is correct.
the spatial extension of the FC window. In the flat continuum case, \( W(\tau) = \mu\delta(\tau) \), and the time of residence in the FC region is zero. In contrast, a narrow resonance can cause the system to be greatly delayed in the FC window. In that case, an incoming continuum wave packet does not leave the FC system to be greatly delayed in the FC window. In that case, \( W(\tau) \) is greatly defined by the laser pulses and by the continuum structure encoded in the window function \( W(\tau) \).

Thus, the shape of the wave form scooped from continuum by a laser pulse pair is equally defined by the laser pulses and by the continuum structure encoded in the window function \( W(\tau) \).

Expanding the bound–continuum transition spectrum into effective modes (equation (14)) we have
\[
W(\tau) = -\sum_s \frac{\mu_s \Gamma_s}{2} \times \exp\left[\left(i(E_s - \omega - E_\pm) - \frac{\Gamma_s}{2}\right)\tau\right] \theta(\tau),
\]
where \( \theta(\tau) \) is the Heaviside function. Therefore,
\[
f_{\text{ARPA}}^{(W)}(t) = -\varepsilon_2(t) \sum_s \frac{\mu_s \Gamma_s}{2} \int_0^\infty d\tau \times f_{\text{ARPA}}^{(0)}(t + \tau) e^{i(E_s - \omega - E_\pm) - \frac{\Gamma_s}{2}\tau}.
\]

Equations (A.5) and (A.13) present the main result of this appendix. They show that, similar to the case of a flat continuum, the profiles of the pump and dump pulses define the shape of coherent wave forms which can be transferred from the continuum into the target state. However, the dwelling of the wavefunction due to the resonances decreases the ability to control these wave forms. If due to the resonances the dwell time \( \Delta t_W \) exceeds the durations of the laser pulses, then by equation (A.11) we know that in addition to photoassociating atoms that arrive at the FC at \( t_0 \), there is a non-negligible probability of photoassociating atoms which get there before or after \( t_0 \).

References

[1] Vardi A, Abrashkevich D, Frishman E and Shapiro M 1997 *J. Chem. Phys.* **107** 6166
[2] Shapiro E A and Shapiro M 2009 Adiabatic Raman photoassociation with shaped laser pulses *Cold Molecules: Theory, Experiment, Applications* ed R Krems, W Stwalley and B Friedrich (New York: Taylor and Francis) pp 291–316
[3] Shapiro E A, Shapiro M, Pe’er A and Ye J 2007 *Phys. Rev. A* **75** 013405
[4] Vitanov N V, Fleischhauer M, Shore B W and Bergmann K 2001 Coherent manipulation of atoms and molecules by sequential laser pulses *Adv. At. Mol. Opt. Phys.* **46** 55
[5] Oreg J, Hise F T and Eberly J H 1984 *Phys. Rev. A* **29** 690–7
[6] Gaozbat U, Rudeckii P, Scinemann S and Bergmann K 1990 *J. Chem. Phys.* **92** 5363–76
[7] Coulston G W and Bergmann K 1992 *J. Chem. Phys.* **96** 3467–75
[8] Bergmann K, Theuer H and Shore B W 1998 *Rev. Mod. Phys.* **70** 1003–25
[9] Pellegrini P, Gacesa M and Cote R 2008 *Phys. Rev. Lett.* **101** 053201
[10] Kuznetsova E, Gacesa M, Pellegrini P, Yelin S F and Cote R 2009 *New J. Phys.* **11** 055028
[11] Frishman E and Shapiro M 1996 *Phys. Rev. A* **54** 3310
[12] Kohler T, Goral K and Julienne P 2006 *Rev. Mod. Phys.* **78** 1311
[13] Hodby E, Thompson S T, Regal C A, Greiner M, Wilson A C, Jin D S, Cornell E A and Wieman C E 2005 *Phys. Rev. Lett.* **94** 120402
[14] Danzl J G, Haller E, Gustavsson M, Mark M J, Hart R, Bouloufa N, Dulieu O, Ritsch H and Nagele H-C 2008 *Science* **321** 1062–6
[15] Ni K-K, Ospelkaus S, de Miranda M H G, Pe’er A, Neyenhuis B, Zirbel J J, Kotochigova S, Julienne P S, Jin D S and Ye J 2008 *Science* **322** 231–5
[16] Danzl J G, Mark M J, Haller E, Gustavsson M, Hart R, Aldegunde J, Hutson J M and Nagele H-C 2010 *Nat. Phys.* **6** 265–70
[17] Fanou U 1961 *Phys. Rev.* **124** 1866
[18] Li X, Thannopulos I and Shapiro M 2011 *Phys. Rev. A* **83** 033415
[19] Kral’ P, Thanopulos I and Shapiro M 2007 *Rev. Mod. Phys.* **79** 53
[20] Taylor J 1972 *Scattering Theory* (New York: Wiley)
[21] Shapiro E A 2000 *J. Exp. Theor. Phys.* **91** 449
[22] Shapiro E A, Spanner M and Ivanov M Yu 2005 *J. Mod. Opt.* **52** 897 and references therein
[23] Shapiro E A, Walmsley I A and Ivanov M Yu 2007 *Phys. Rev. Lett.* **98** 050501
[24] Hodby E, Thompson S T, Regal C A, Greiner M, Wilson A C, Jin D S, Cornell E A and Wieman C E 2005 *Phys. Rev. Lett.* **94** 120402
[25] Vardi A, Shapiro M and Anglin J R 2002 *Phys. Rev. A* **65** 027401
[26] Madison K W 2010 private communication