

# Two-pulse atomic coherent control

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## Abstract

Two-pulse atomic coherent control (2PACC) spectroscopy is presented. The idea is demonstrated by simulating a source consisting of a two-pulse atom laser impinging on a surface covered with a co-adsorbed atom. The controlled outcome is an Eley–Rideal chemical reaction where the controls are the time delay and relative phase between the two-pulses. The two atom laser pulses interfere with each other as well as interact with the surface leading to a reaction with a co-adsorbed atom on the surface. The new-formed molecule desorbs and the flux of the desorption has been computed showing the predicted 2PACC signal.

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## 1. Introduction

The quantum nature of matter makes it possible to exploit interference effects to reach a desired chemical goal. The realization of this approach requires a scheme to impose specific coherent properties on the wave functions of the chemical substituents. This prospect has been carried out by using coherent sources of light to imprint the coherent properties on the matter-waves and is known as coherent control [1]. The experimental demonstration of Bose–Einstein condensation of atoms opens a new source of coherent matter-waves. An output coupler termed *atom laser* [2–6] transforms the condensate into a source of either continuous or pulsed coherent matter. In this paper we want

to suggest that these sources can be employed for a coherent control of a surface mediated chemical reaction.

The current suggestion is based on a close analogy with the two-photon emission (2PPE) spectroscopy. In 2PPE spectroscopy the first photon excites the target to an intermediate level. The second photon exploits this excitation to create a measurable outcome. The method has been used to characterize both energetics and dynamics of both electrons, atoms and molecules on metal surfaces [7–13]. The application of two laser pulses gives access to probe the energetics and dynamics of the electronic states which would not be accessible if only one pulse was applied.

The source of matter-waves can be chosen from the growing list of atoms {<sup>87</sup>Rb [14], <sup>85</sup>Rb [15], <sup>23</sup>Na [16], <sup>7</sup>Li [17–19], <sup>6</sup>Li [19], K [20], H [21] and meta-stable He [22,23]}, which have been shown to go through a Bose–Einstein condensation. The existing atom lasers consist of alkali metals such as

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$^{23}\text{Na}$  [2,3],  $^{87}\text{Rb}$  [4–6]. The coherent atomic pulse is accomplished by using an external electromagnetic field to transfer the atom from a trapped to an untrapped state. The atom laser can be either continuous or pulsed.

We propose a two-pulse atomic coherent control (2PACC) spectroscopy where the optical laser pulse in the 2PPE spectroscopy is replaced by a coherent pulsed atom laser. To demonstrate this idea we simulate a process where the pulsed coherent source of atoms induces an Eley–Rideal (ER) chemical reaction. The model consists of a coherent atomic source of either hydrogen or alkali metal atoms colliding with a hydrogen atom chemisorbed on a Cu(111)-surface. The outcome is an ejected molecule in the gas phase of either  $\text{H}_2$  or an alkalihydride.

Theoretical studies of ER reactions have been performed by Jackson et al. [24–26] for an incident hydrogen atom interacting with various coated surfaces. We will show in a similar system that the application of a coherent source consisting of two atomic pulses controls molecular encounters in comparison to a single pulsed atomic beam. The control consists of the time delay as well as the relative phase between the two atomic pulses.

The dynamics of the 2PACC spectroscopy model is explored by solving the two-dimensional and two-channel time-dependent Schrödinger equation by a Newtonian propagation method [27].

## 2. The model

In 2PACC spectroscopy a sequence of two atomic pulses is applied to a surface with an adsorbed atom. An atom laser,  $Y$ , which consists of either hydrogen or alkali atoms, is applied to a Cu(111)-surface with low coverage chemisorbed hydrogen atoms. The incident atom can recombine with the target atom and a molecule is formed. The molecule may desorb from the surface and can be detected in the gas phase. The surface immobilizes the target atom and thereby the location of the atom is controlled. Here, we would demonstrate that the application of the second pulse enables us to achieve the coherent control of the reaction through the quantum interferences between the

two atom laser pulses. These interferences can either be constructive or destructive and thereby, increase or decrease the flux of the desorbing molecule in the product channel of the reaction depending on the time delay and phase between the two atomic pulses.

We can define a relative phase between the two atom laser pulses since the atom laser is an output coupler of a coherent source—the Bose–Einstein condensate (BEC). In a BEC all the atoms are confined in the same quantum state and thereby they can be represented by a single many-body matter-wave field wave function. This is an analog to the optical lasers where the photons in the optical cavity are represented by a single wave function. The coherent atomic pulse is accomplished by using an optical laser source to transfer the atom from a trapped (BEC) to an untrapped state (the atom laser). The relative phase between the two atom laser pulses can be utilized by phase-locking the second optical pulse relative to the first one. A time delay between the two optical lasers determine also the time delay between the two atomic laser pulses.

We chose to use a diabatic frame consisting of two potential energy surfaces (PES) to describe the process. In the reactant channel an atom approaches a chemisorbed atom residing on the surface. The PES of the reactant channel consists of a Morse potential describing the chemical bond between the hydrogen atom and the surface, and an interaction potential between the co-adsorbed atom and impinging atom. This interaction potential becomes asymptotically the triplet excited state of the molecule,  $\text{YH}$ , when both atoms are far from the metal surface.

The product channel potential asymptotically approaches a bound molecule ( $\text{YH}$ ) in the gas phase represented by a Morse potential. Upon the molecule approaches the surface a physisorption attractive potential is added representing a weak interaction between the molecule and the surface. At short range repulsive forces between the surface and the molecule dominate. The detailed parameterizations of the PES of the reactant and product channels are given in Ref. [28].

The calculation is restricted to a collinear configuration. The distance between the metal surface and the hydrogen atom (the alkali atom) is denoted

$z_h(z_y)$ . The coordinate set  $(z_h, z_y)$  is transformed to new set of coordinates  $(r, Z)$  where  $r = z_y - z_h$  is the intramolecular distance and  $Z = (m_h z_h + m_y z_y) / M$  is the center of mass coordinate. The mass of atoms, H and Y, are  $m_h$  and  $m_y$ , respectively. The total and reduced mass of the system are denoted  $M$  and  $\mu$ .

The initial state of the calculation describes an approaching wave of coherent matter, Y and an adsorbed hydrogen atom. This wave function evolves and splits to a back scattered atomic beam and a wave function representing the molecular outcome in the gas phase. The reaction yield as a function of initial conditions is calculated by integrating the flux of the wave function evolving into the asymptotic channels [29].

### 2.1. The atom laser

Initially, when the impinging atom is far away from the surface as well as the adsorbed atom, the wave function of the atom laser can be written as a product of a wave function on each atom. The wave function of the adsorbed atom,  $\psi_h$ , was chosen as the lowest energy eigenstate of the PES of the reactant channel with a fixed distance,  $z_s$ , between the approaching atom and the surface. The wave function of the approaching atom,  $\psi_y$ , is represented by a Gaussian wave function centered at  $z_y = z_s$  and with a variance,  $\sigma_y$ . The initial wave packet is given by

$$\Psi_{\text{atom}}(r, Z) = N \psi_H(z_h, z_y = z_s) \psi_y(z_y) e^{ik_y z_y};$$

$$\psi_y(z_y) = e^{-(z_y - z_s)^2 / \sigma_y} \quad (1)$$

where  $N$  is a normalization factor. The momentum of the approaching atom,  $k_y$ , is related to the energy,  $E$ , of the propagating atom laser. The variance is related to the dispersion of the atom laser.

### 2.2. The dynamics of 2PACC

In 2PACC spectroscopy the first atom laser pulse represented by the wave packet (1) is initialized at the reactant PES at a time  $t = 0$ . After a time delay,  $\Delta t$ , the second atom pulse is introduced given by

$$\Psi_{\text{atom},2}(r, Z) = \Psi_{\text{atom}}(r, Z) \exp(-i\theta) \quad (2)$$

where  $\theta \in [0; 2\pi]$  is the relative phase between the two atomic pulses.

As the wave packet propagates population is transferred from the reactant to the product PES through the non-adiabatic coupling. The dynamics of the 2PACC is visualized by solving the time-dependent two-channel Schrödinger equation which is given by

$$\begin{bmatrix} H_{11}(r, Z) & H_{12}(r, Z) \\ H_{21}(r, Z) & H_{22}(r, Z) \end{bmatrix} \begin{pmatrix} \phi_1(r, Z) \\ \phi_2(r, Z) \end{pmatrix} = i \frac{\partial}{\partial t} \begin{pmatrix} \phi_1(r, Z) \\ \phi_2(r, Z) \end{pmatrix} \quad (3)$$

The wave functions in the reactant and product channels are denoted  $\phi_1$  and  $\phi_2$ , respectively. The diagonal elements in the Hamiltonian operator have the following form

$$H_{ii}(r, Z) = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial Z^2} - \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} + V_i(r, Z) \quad (4)$$

where the first two terms are the kinetic energy operator for the two degrees of freedoms and the last term is the potential energy operator. The off-diagonal elements of the Hamiltonian operator are the non-adiabatic coupling between the two-channels and they are represented by:

$$H_{12}(r, Z) = H_{21}(r, Z) = h_{12} e^{-(r-r_{yh}^e)^2} e^{-\beta Z} \quad (5)$$

where  $\beta$  and  $h_{12}$  are the non-adiabatic coupling strength and element. The intramolecular equilibrium distance is denoted  $r_{yh}^e$ .

Using the Newtonian method [30] a grid based wave function has been propagated. The scattered wave function is removed at large values of  $r$  and  $Z$  by absorbing complex potentials [31]. The 2PACC signal has been evaluated by integrating the flux passing through a dividing line at the product channel. The integrated flux has been determined as a function of the time delay and the phase-relation between the two atom laser pulses.

## 3. Result and discussion

The dynamics of the 2PACC spectroscopy are demonstrated for a hydrogen atom laser source

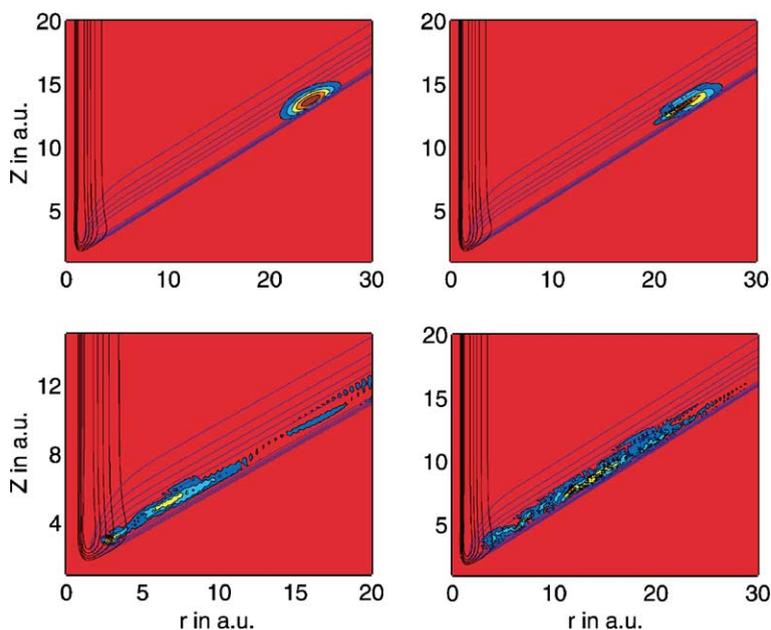


Fig. 1. The evolution of the wave packet of the atom lasers applied to a Cu(111)-surface coated with hydrogen atoms on the reactant PES is shown for a time delay,  $\Delta t = 2.42$  fs and the phase,  $\theta = 1.5\pi$ . The contours of the PES of the reactant and the product channel for are shown with blue and black lines, respectively. The wave packet at the reactant channel is given for  $t = 0$  fs (upper left),  $t = 2.42$  fs (upper right),  $t = 111$  fs (lower left) and  $t = 198$  fs (lower right), respectively (1 a.u. is  $0.529 \text{ \AA}$ ). The initial wave packet is a product of the a wave function of each atom. The wave function of the adsorbed atom is the lowest eigenstate along the line;  $z_y = 13.6 \text{ \AA}$ . For the impinging atom the following parameters are used  $\sigma_y = 1.26 \text{ \AA}^2$  and  $k_y = -18.9 \text{ \AA}^{-1}$ . The non-adiabatic coupling and element are  $1.89 \text{ \AA}^{-1}$  and  $0.027 \text{ eV}$ , respectively.

impinging on to a Cu(111)-surface coated with hydrogen atoms. The parameters for the wave packet of the atom laser are specified in Fig. 1. The binding energy of the lowest eigenstate of the adsorbed hydrogen atom is  $-2.3 \text{ eV}$ . The wave function of the approaching atom is represented by a one-dimensional Gaussian wave packet. The total energy of the initial 2D-wave packet. The PES of the reactant and product channel as well as the initial one pulse wave packet ( $t = 0$ ) of the atom laser are displayed in Fig. 1 (upper left).

The initial wave function for the two-pulse calculation is generated by first using the signal pulse wave function, letting it propagate for the prespecified time delay and then placing the second wave function in the original position of the first wave packet. The relative phase between the two wave packet at the initial position may be different e.g.  $\theta \neq 0$ . Snapshots of the evolution of the wave packet on the reactant and the product

channel are shown in Figs. 1 and 2, respectively, for  $\theta = 1.5\pi$  and  $\Delta t = 2.24$  fs.

Fig. 1 shows the progress of the wave function toward the non-adiabatic crossing seam where part of the wave function is transferred to the molecular state where it can exit. This means that the approaching hydrogen atom has reacted with the co-adsorbed hydrogen and created an  $\text{H}_2$  molecule. The wave function of product channel shows that the newly formed hydrogen molecule either is adsorbed on the surface e.g. is trapped in potential well or it desorbs and leaves the surface highly vibrationally excited.

The predicted 2PACC signal, which is the difference between a one pulse and two-pulse desorbed molecular outcome is calculated from the total integrated flux at  $t = 339$  fs. Fig. 3 shows the 2PACC signal as a function of the time delay and relative phase between the two-pulses. The 2PACC signal shows a variation with respect to both

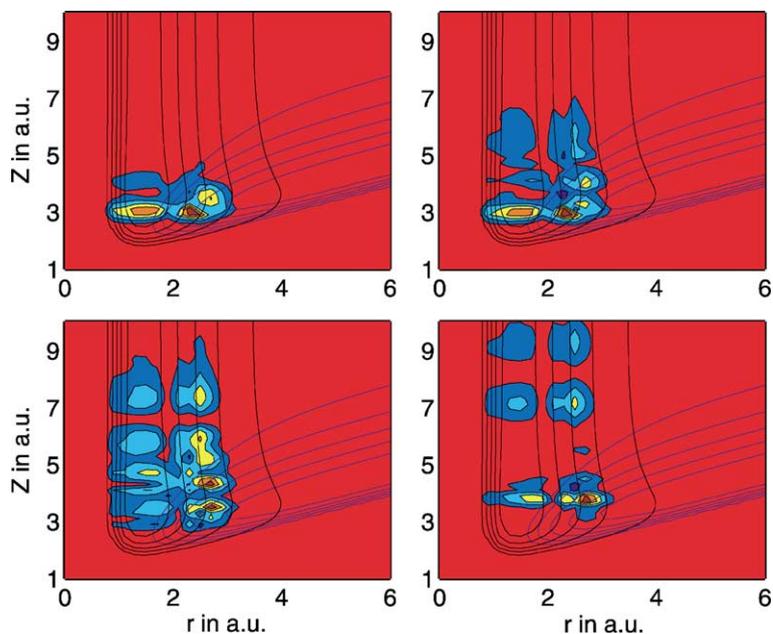


Fig. 2. The evolution of the wave packet on the product channel for  $t = 111$  fs (upper left),  $t = 140$  fs (upper right),  $t = 169$  fs (lower left) and  $t = 198$  fs (lower right), respectively, are shown for time delay of  $\Delta t = 2.42$  fs and phase,  $\theta = 1.5\pi$ . Notice the exciting wave packet on the reactive channel at  $t = 198$  fs.

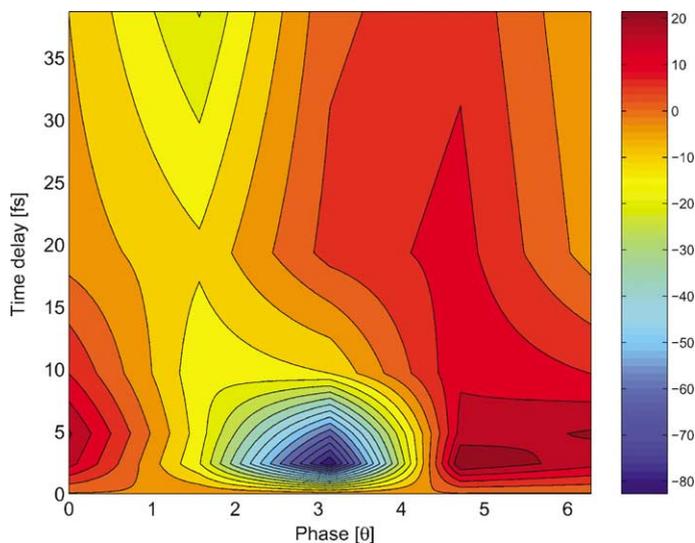


Fig. 3. The 2PACC signal relative to the output for one pulse (in %) are shown as a function of the time delay (in fs) and the relative phase ( $\theta$ ) between the two atomic pulses for an initial wave packet with energy  $-1.6$  eV and  $-2.2$  eV. The predicted 2PACC signal are calculated from the integrated flux along a divided line on the product channel at  $t = 339$  fs and  $t = 388$ . Areas of enhancement are in red and depletion are in blue.

control parameters meaning that the outcome of the ER reaction is coherent controlled by the time

delay and relative phase between the two atomic pulses. The amount of control of the 2PACC sig-

nal demonstrated in this model is an enhancement of 27% for  $\theta = 2.5\pi$  and  $\Delta t = 2.24$  fs relative to one atomic pulse compared with a suppression of 80% at  $\theta = 1.5\pi$  and  $\Delta t = 2.24$  fs.

#### 4. Conclusion and outlook

The 2PACC spectroscopy has been presented for a hydrogen atom laser impinging on a Cu(111)-surface coated with hydrogen atoms. The reaction of the atom laser with a co-adsorbed atom on the surface can lead to a desorbed molecule. Two atom laser pulses are applied and they interfere with each other. This interference is essential in the process of achieving the coherent control of the chemical reaction. Controlling the time delay and relative phase between the two atomic pulses we have observed an enhancement of the 2PACC signal relative to one atom laser pulse. Furthermore, the 2PACC spectroscopy utilizes the coherent control of the biatomic or bimolecular recombination reaction.

The methodology of the 2PACC spectroscopy can be applied for other atom laser sources as well as other coated surface. Simulations of the 2PACC spectroscopy for an atom laser consisting of a beam of Na and Rb [2–6], are in progress.

In principle the model could be extended to the full 6D with the result of a control of the internal state of the desorbing molecule. Considering other surface degrees of freedom, such as phonons and electron/hole pairs, it is known that they influence the outcome of ER reactions. But in the present 2PACC context their contribution can mostly be ignored. The surface related degrees of freedom are incoherent relative to the atom laser pulse. The signal as in 2PPE is the difference between the single and two-pulse experiment therefore it excludes incoherent processes.

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