Time-Shifting the Dynamics of Li$_2$ Multistate Rovibrational Wave Packets by State Selective Coherent Phase Control

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State-selective coherent phase control using single shaped femtosecond laser pulses is implemented to achieve forward and backward shifts in time (up to a global arbitrary phase) of the rovibrational Li$_2$(E$^1\Sigma_u^+$) wave packet evolution $\Psi(t) \rightarrow \Psi(t - t_{\text{shift}})$. Experimentally, the result is reflected as a time translation of the whole measured pump-probe transient. The wave packet is composed of eight rovibrational quantum states excited from a single selected rovibrational level (using a cw laser) of the A$^1\Sigma_u^+$ electronic state. The high degree of control over the exact coherent superposition of the wave packet states is accomplished using a pulse shaping setup incorporating a liquid crystal spatial light modulator to encode the desired phases in the pump pulse. Beyond the direct implications of this work involving the experimental implementation of coherent control, it is also relevant to the separation of linear effects from non-linear effects when the pump and probe beams overlap in time and to the possibility of probing molecular dynamics and coherent configurations that, without phase control, would occur only at long times after the wave packet excitation. This is relevant, for example, to highly dissipative environments where the wave packet dephases on short time scales.

I. INTRODUCTION

The large number of possible applications, as well as scientific insights, that are opened up by using the coherent nature of laser radiation to control the dynamics of molecular systems have driven considerable theoretical and experimental efforts in the field of co-
herent control [1–15]. Many of these studies have dealt with “coherent phase control”, where the altered and optimized parameter is the phase of the optical field [1, 4–8, 12–15]. For coherent phase control using single broadband femtosecond laser pulses, in the weak field limit, varying the relative phase between various frequency components of the driving light results in changing, and therefore controlling, the quantum interference between the states that compose the excited nonstationary wave packets and their resulting dynamics. On the experimental side, recent developments in pulse shaping techniques [16, 17] have allowed the tailoring of pulses with relatively complicated phase functions, and various coherent control experiments have implemented these features [9–13, 15].

Being one of the simplest molecular systems, Li₂ serves as a benchmark and convenient basis for coherent control studies of molecules, both experimentally [14, 15, 18] and theoretically [19, 20]. Its spectroscopy is well known, yet its electronic structure is sufficiently complicated to be interesting, as is the case for the highly anharmonic E¹Σ⁺₉ state. This state is formed with an avoided curve crossing, and thus it switches from a covalent nature on the inner turning point to an ionic one on the outer turning point. Moreover, lithium dimer is a molecular system where the rotational and vibrational dynamics occur on comparable time scales, which thus allows coherent control studies of simultaneous radial and angular (three-dimensional) molecular dynamics.

In the following, we present experimental results of state-selective phase control using single femtosecond laser pulses implemented to time-shift forward and backward (up to a global arbitrary phase) the evolution of a well defined (eight state) rovibrational Li₂(E¹Σ⁺₉) wave packet, i.e. \( \Psi(t) \rightarrow \Psi(t - t_{\text{shift}}) \), where \( t_{\text{shift}} \) is either positive or negative. The required phase functions are encoded into the exciting laser pulse using a pulse shaping setup incorporating a liquid crystal spatial light modulator. As will be discussed below, such time-shifting has implications in the context of both coherent control experimental implementation, as well as in using the control ability to study dynamics of the optically driven molecular system, which otherwise is difficult to access experimentally, for example, due to strong non-linear effects or high rates of dephasing (T₁ and/or T₂ processes).

II. EXPERIMENT

The experimental setup has been described previously [14, 15] and will be presented here only briefly. A sample of lithium metal is heated in a stainless-steel cell to 1023°K in an Ar buffer at \( \sim 2.7 \) Torr. A single mode cw dye laser (200 mW) is tuned to select a specific transition of the thermally populated Li₂ molecule from an individual X¹Σ⁺₉(\( v_X, J_X \)) state to a single rovibrational state (\( v_A, J_A \)) of the A¹Σ⁺₉ electronic state. From this state, using fs laser pulses, a wave packet is launched on the E¹Σ⁺₉ state (pump step), followed by a time-delayed ionization of the Li₂ molecule (probe step). The pump and probe pulses are
obtained from a Ti:sapphire laser system (200 kHz repetition rate), and they are of \(\sim 160\) fs duration, parallel polarizations, and \(\sim 0.5\) and \(\sim 1.5\) \(\mu\)J, respectively, implicating that, except for the period when the two fs pulses are overlapped in time, the whole experiment is conducted in the weak field regime.

The experimental setup also incorporates a pulse shaping assembly, composed of two gold-coated gratings (1200 lines/mm), two cylindrical lenses (30 cm focal length), and a liquid crystal spatial light modulator (SLM). The SLM consists of two one-dimensional liquid crystal arrays placed between two sheet polarizers. Each array is composed of 128 independent pixels whose effective refractive index is computer-controlled by an applied voltage, manipulating the spectral phase and/or amplitude of the various frequency components of the dispersed light to modify the amplitude and/or phase of each rovibrational component state of the excited wave-packet. The experimental wavelength resolution of our pulse shaping assembly is \(\sim 4.2\) cm\(^{-1}\) per pixel, and the accuracy for an applied phase (0–360°) is less than 1°, depending on the particular phase.

Figure 1 shows a schematic picture of the experiment, including the relevant Li\(_2\) potential curves and the ion electronic ground state. In the present experiment, the selected intermediate state is \(A^1\Sigma_u^+(v_A = 14, J_A = 18)\), and the wave packet components are \(E^3\Sigma_u^+(v_E = 13 - 16, J_E = 17, 19)\) (eight states). The locations of these rovibrational states within the pump pulse energy spectrum are shown in Fig. 2. The pulse is centered around 12430 cm\(^{-1}\) with a FWHM of \(\sim 150\) cm\(^{-1}\).

III. TIME-SHIFTING THE WAVE PACKET EVOLUTION BY PHASE CONTROL

In the following we present the procedure to achieve a shift in time of the wave packet evolution through the phase shaping of the pump laser pulse. Since the theory for describing our experimental scheme in the weak field limit is well established and has already been described [14, 19], we emphasize here only the details and parameters that are essential to the present work.

The superposition state \(\Psi(t)\) excited by the pump pulse (after the pulse is ended) from an initial state \(i\) is given at time \(t\) after excitation by [14]

\[
\Psi(t) \propto \sum_n c_n \epsilon_{pump,n} \vert n \rangle \exp \left[ -i \left( \frac{E_n}{\hbar} t + \Phi_{pump,n} \right) \right]
\]

where the index \(n\) stands for a state composed in the excited wave packet, \(\vert n \rangle\) is its eigenfunction, and \(E_n\) represents its energy. The coefficient \(c_n\) is the matrix element of the \(i \rightarrow n\) transition, and \(\epsilon_{pump,n}\) and \(\Phi_{pump,n}\) are the electric field amplitude and phase, respectively, of the pump pulse at the transition frequency \(w_{ni} = E_n - E_i\). The phases
\( \Phi_{\text{pump},n} \) are the physical quantities subjected to our direct experimental control through the pulse shaping setup.

In order to shift (up to a global arbitrary phase) the time evolution of the wave packet \( \Psi(t) \) corresponding to the given initial phases \( \Phi^{(0)}_{\text{pump},n} \) by a constant time offset \( t_{\text{shift}} \) which is either positive or negative, i.e. \( \Psi(t; \Phi^{(0)}_{\text{pump},n}) \rightarrow \Psi(t - t_{\text{shift}}; \Phi_{\text{pump},n}) \), the applied phases \( \Phi_{\text{pump},n} \) should depend linearly on the state energy with a slope proportional to \( t_{\text{shift}} \) (linear phase sweep):

\[
\Phi_{\text{pump},n} = \Phi^{(0)}_{\text{pump},n} - \frac{t_{\text{shift}}}{\hbar} E_n ;
\]  

(2)

In other words, up to a global arbitrary phase, all the superposition states of the wave packet that for \( \Phi^{(0)}_{\text{pump},n} \) would exist at time \( t \), following the application of this linear phase sweep would occur at time \( t + t_{\text{shift}} \); A negative slope of the linear phase sweep corresponds to a shift forward (\( t_{\text{shift}} > 0 \)), while a positive slope corresponds to a shift backward (\( t_{\text{shift}} < 0 \)).

Experimentally, the wave packet time evolution is reflected in the pump-probe ionization signal \( S_{\text{pump-probe}}(\tau) \) measured as a function of the pump-probe delay time \( \tau \) [14]:

\[
S_{\text{pump-probe}}(\tau) = S_{\text{const}} + \sum_{m,n;m \neq n} |A_{mn}| \cos \left( \frac{E_m - E_n}{\hbar} \tau + \Phi_{mn}^\text{pump} + \Phi_{mn}^* \right)
\]  

(3)

with

\[
\Phi_{mn}^\text{pump} = \Phi_{\text{pump},m} - \Phi_{\text{pump},n}
\]  

(4)

where \( S_{\text{const}} \) is a constant signal level, and the time-dependent part of the signal is composed of cosine terms corresponding to the various \((m,n)\) quantum beats with amplitudes \(|A_{mn}|\). The phase of each beat has been separated into \( \Phi_{mn}^\text{pump} \), which is being controlled here, and \( \Phi_{mn}^* \), which contains all the other contributions to the phase not under control in the current experiment. This includes the molecular phases corresponding to both the pump (bound-bound excitation) and probe (ionization) steps, as well as possible phases introduced externally by the probe laser pulse. In general, all these various phases have direct implications in the context of coherent control, and they can serve as a tool to gain insight into the structure of the ionization continuum [8], however here they are regarded as given non-controllable parameters. Other experiments, which have been conducted in our lab, have dealt with these aspects [21].

For \( \Phi_{\text{pump},n} \) given by Eq. (2), the phase difference \( \Phi_{mn}^\text{pump} \) has the form

\[
\Phi_{mn}^\text{pump} = -\frac{t_{\text{shift}}}{\hbar} (E_m - E_n) ;
\]  

(5)

This implies that a time-shift of the wave packet evolution \( \Psi(t) \rightarrow \Psi(t - t_{\text{shift}}) \) is directly reflected as a time-shift of the whole measured pump-probe transient \( S_{\text{pump-probe}}(\tau) \rightarrow S_{\text{pump-probe}}(\tau - t_{\text{shift}}) \).
IV. RESULTS AND DISCUSSION

Figure 3 shows an experimental pump-probe transient (only the time-dependent part) taken without any phase manipulation up to pump-probe delay times of 80 ps, together with its corresponding FFT spectrum up to 120 cm\(^{-1}\). The contribution from higher frequency components (120 to 256 cm\(^{-1}\)) is less than 3%. All the prominent Fourier components in the spectrum (marked with "*") are identified and correlated with specific pairs of states out of the wave packet states \(E^1\Sigma_g^+ (v_E = 13 - 16, J_E = 17, 19)\). This experimental identification of the energy differences between the various wave packet components is a crucial component of the present experiment, since in order to achieve the time-shifting the applied phases should follow the specific linear phase sweep of Eq. (2). The precise locations of the various rovibrational states within the pump pulse energy (see Fig. 2) were found experimentally by monitoring the amplitude of the Fourier components involving specific rovibrational states while blocking various frequencies in the shaped pump pulse.

Following the control scheme described in Sec. III, we have demonstrated translation in time of the wave packet originally excited with the non-shaped pulse ("unshaped wave packet") by 5, 7 and 9 ps, applying linear phase sweeps over the various rovibrational states (see Eq. (2)) with a slope of -54.0, -75.6 and -97.1 °/cm\(^{-1}\), respectively. The corresponding pump-probe transients are shown in Fig. 4(b,c,d), together with the transient corresponding to the unshaped wave packet (Fig. 4(a)). Here, \(\Phi_{\text{pump},n}^{(0)}\) stands for any chirp that exists in the unshaped pulse upon arrival in the interaction region of the heat pipe.

In order to illustrate the achieved translation in time, Fig. 5 presents all four experimental pump-probe transients one on top of the other; each one is shifted back numerically by its corresponding time shift relative to the transient of the unshaped wave packet. As can be seen, all the transients agree with each other within the experimental error bars, demonstrating both forward and backward time-shifting of the wave packet evolution from any configuration to any other one out of the four configurations. Thus, as a whole, the time-shift has been shown here for \(t_{\text{shift}} = \pm 2, \pm 4, \pm 5, \pm 7, \text{ and } \pm 9 \text{ ps}\). The only exception in the agreement between the various experimental transients is the additional signal around \(\tau = 0\) appears in the unshaped wave packet transient, which originates from the non-linear processes occurring when the pump and probe pulses are overlapped in time. These non-linear processes are very sensitive to the power, alignment, focusing conditions and temporal shape of the pulses and thus are less desirable for precise phase control, although such highly non-linear effects are the subject of recent investigations [12]. Here, the time shift introduced by the phase control permits the clear separation in time of the signal (and the corresponding wave packet dynamics) that originate from the linear behavior from the ones that originate from the non-linear effects around zero delay time.

The actual phases applied experimentally across the pump pulse spectrum to achieve the various time shifts of the unshaped wave packet are shown in Fig. 6. The phase value at
each rovibrational state is the residual from the division of the required total phase by 360°. Figure 7 displays the corresponding intensity cross-correlation profiles taken between the phase-shaped pump pulses and the original unshaped Gaussian pulse using the second-order response of a GaAsP photodiode. The cross correlation width of the unmodified pump pulse is 227 fs (FWHM) and it increases to more than 1 ps after introducing the phases depicted in the Fig. 6. The cross-correlation profiles are also reflected in the pump-probe transients around zero delay time, when the shaped and unshaped beams are overlapped in time. However, for the phase-shaped pulses the transients and the profiles are not identical, since following the increase in the pulse duration the instantaneous field strength has decreased, and the linear and non-linear effects around zero have become of very close magnitudes.

One should note that applying the above time-shifting phases to the discrete set of rovibrational levels indeed shifts the wave-packet dynamics, however it does not time-shift the pulse itself by $t_{\text{shift}}$. For a detailed discussion of such experimental time-shifting of the pulse itself, including the limitations arising from the pixellated nature of the SLM, the reader is referred to Refs. [16, 17]. In the context of the present experiment, the pixellation of the SLM is not a limiting factor since each of the discrete rovibrational states composing the wave packet lies within a separate pixel, thus experimentally the applied phases can follow the needed form of Eq. (2).

V. CONCLUSIONS

Following from the experimental demonstration of this work, based on the description given in Sec. III, one direct conclusion is that an experimental time-shifting can be applied to any given wave packet state composed of a well defined discrete set of levels, well separated in the energy domain. For example, once the phases of the wave packet components are optimized to produce partial localization of the wave packet at a given time, and as a result to maximize or minimize the ionization yield [15], the achieved minimum or maximum can be shifted in time.

Extending the time translation to a much longer time-shift will allow the probing of molecular dynamics and coherent configurations that, without phase control, would occur only at long times after the wave packet excitation. This might be significant, for example, in highly dissipative environments where the wave packet dephases on relatively short time scales.

Future experiments will be conducted to investigate in further detail the experimental limitations, as well as the possible applications, of such time-shifting of the wave packet dynamics.
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REFERENCES


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FIG. 1: Relevant potential energy curves for Li₂ and Li²⁺ [22, 23].

FIG. 2: Spectral profile of the laser pulse. The vertical lines indicate the excitation energies of the various rovibrational states of the E¹Σ⁺ₕ state composing the excited wave packet. They are labeled with the corresponding vibrational and rotational quantum numbers.

FIG. 3: (a) Experimental pump-probe transient taken with non-shaped pump pulse and (b) the corresponding FFT spectrum. The Fourier components identified to correlate with specific pairs of states out of the wave packet states E¹Σ⁺ₕ(νₑ = 13 – 16, Jₑ = 17, 19) are marked with "*" (see text).

FIG. 4: Experimental pump-probe transients obtained for (a) the unshaped wave packet, and for various time-shifts of it: (b) 5 ps, (c) 7 ps, and (d) 9 ps.

FIG. 5: The experimental transients shown in Fig. 4 one on top of the other; each one is shifted back numerically by its corresponding time shift relative to the transient of the unshaped wave packet (Fig. 4(a)).

FIG. 6: The phases applied experimentally across the pump pulse spectrum to achieve the time shifts of the unshaped wave packet by 5 ps (dotted line), 7 ps (dash-dotted line) and 9 ps (solid line).

FIG. 7: Intensity cross-correlation traces between the phase-shaped and the original unshaped Gaussian pulse, obtained with GaAsP photodiode. They correspond to the various phase configurations shown in Fig. 6.
Fig. 2
Fig. 3
Ionization Signal (arb. units)

Pump-Probe Delay (ps)

- Unshaped
- $t_{\text{shift unshaped}} = 5\;\text{ps}$
- $t_{\text{shift unshaped}} = 7\;\text{ps}$
- $t_{\text{shift unshaped}} = 9\;\text{ps}$

Fig. 5