Molecular State Reconstruction by Nonlinear Wave Packet Interferometry

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Abstract. We investigate the reconstruction of optically prepared vibrational wave packets using nonlinear wave packet interferometry. Simulated results for a model photo-dissociative diatomic demonstrate the technique's effectiveness in identifying dynamics induced by shaped laser pulses.

1. Introduction

Recent achievements in the control of chemical reactions using adaptive laser-pulse shaping strategies [1] pose the challenge of how to identify the ultrafast photoinduced molecular dynamics [2]. Optimization of an incident waveform neither directly elucidates the light-induced reaction mechanism nor identifies the optically prepared initiating state, especially when the state propagates under a poorly characterized Hamiltonian. One means for characterizing an optically prepared target state in the absence of Hamiltonian information is reconstruction of the time-dependent probability amplitude (as opposed to probability density), which provides a complete picture of the molecule's photoinduced dynamics [3-5].

Nonlinear wave packet interferometry (WPI) [4,5] uses a pair of phase-locked pulse-pairs to create a linear superposition of nuclear wave packets in an excited electronic state (*f*). In a two-color experiment the first pulse-pair accesses transitions between the ground state (*g*) and an intermediate electronic state (*e*), while the second pulse-pair drives $f \leftarrow g$ transitions. The overlap $\langle \mathrm{ref}_{421} | \mathrm{tar}_3 \rangle$ between a target state shaped by the third pulse,

$$|\mathrm{tar}_3\rangle = e^{i(\phi_3(\omega_L')+\omega_L' t_L)} e^{-iH_f t_{43}/\hbar} P_3^{fg} |\psi_g\rangle, \tag{1}$$

and a reference state created by the first, second, and fourth pulses,

$$|\mathrm{ref}_{421}\rangle = -e^{i(\phi_4(\omega_L')-\phi_{21})} P_4^{fg} e^{-iH_g t_{42}/\hbar} P_2^{eg\dagger} e^{-iH_e t_{21}/\hbar} P_1^{eg} e^{iH_g t_{31}/\hbar} |\psi_g\rangle, \tag{2}$$

is isolated by combining measurements of the total *f*-state population taken at different values of the phase-locking angles ϕ_{21} and ϕ_{43} [5,6]. The transfer of nuclear amplitude between electronic states *a* and *b* via the j^{th} pulse in the rotating wave approximation is denoted by the pulse propagator P_j^{ab} [7], $\phi_j(\omega) - \omega t_j$ is the spectral phase of the j^{th} pulse, and $t_{jk} = t_j - t_k$.

Measurements of $\langle \mathrm{ref}_{421} | \mathrm{tar}_3 \rangle$ made with fixed t_{43} and varied t_{21}, t_{32} yield a set of simultaneous equations **z=Rt**. The vector **z** stores the overlaps, and the reference matrix **R**, whose rows comprise the conjugate wave functions of (2) at different delays, is calculated from prior knowledge of the *g* and *e* electronic states. The unknown target wave function **t**, which propagates solely on the *f* state, is determined using singular value decomposition of **R** and construction of its pseudo-inverse. The fidelity of the reconstructed vector **r**, which minimizes the norm and residual of all possible solutions [5], is quantified as $f = |\mathbf{t}^\dagger \cdot \mathbf{r}| / (\|\mathbf{t}\| \cdot \|\mathbf{r}\|)$, and lies between 1 (good) and 0 (bad). For a thermally populated mixture, a weighted sum of overlaps arising from different initial states is measured. Reconstruction proceeds as before but with the reconstructed vector partitioned to characterize the different target states, and the cumulative fidelity given as a weighted sum of the individual fidelities.

2. Simulations

To demonstrate reconstruction we simulated the nonlinear WPI signal for a model nonrotating photodissociative diatomic, using equal-frequency displaced harmonic oscillators for the ground and intermediate states (frequency $2\pi c(250\ \mathrm{cm}^{-1})$, mass 63.5 amu, and displacement 0.0614 Å) and an exponentially decaying final state with Franck-Condon energy $hc(1000\ \mathrm{cm}^{-1})$ and length scale 0.1096 Å. The first, second, and fourth pulses are transform-limited Gaussians (5 fs FWHM intensity), vertically resonant with their respective electronic transitions. The third pulse is a vertically resonant Gaussian (20 fs FWHM) with a linear frequency chirp of –144 fs^2. The delays t_{21} and t_{32} are scanned through a ground-state vibrational period (τ_g = 133.4 fs) while t_{43} = 25.4 fs. At 270 K, the first five vibrational levels account for over 99% of the total population and the resulting interferogram, calculated using grid-based propagation techniques, is shown in Fig. 1.

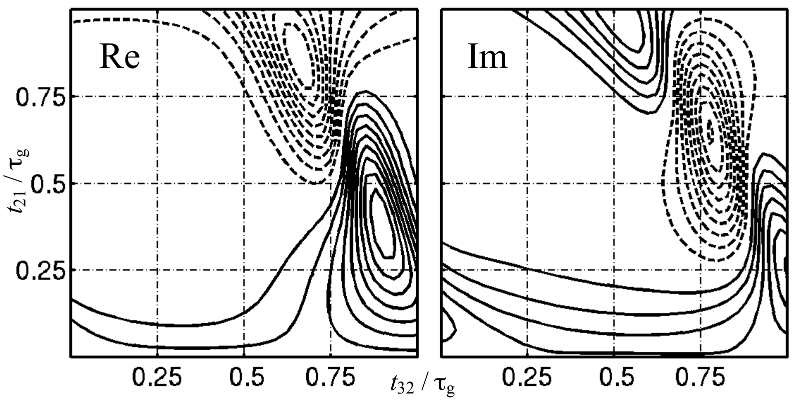

Fig. 1. Calculated interferogram for the model dissociative system. Solid (dashed) contours are separated by positive (negative) increments of 1/10 the interferogram maximum.

We apply our reconstruction procedure using the calculated interferogram with 5% uncorrelated Gaussian noise added. The first three reconstructed states and their associated target states are shown in Fig. 3. The total fidelity is 0.922. Note that individual-state reconstruction fidelity decreases with initial population;

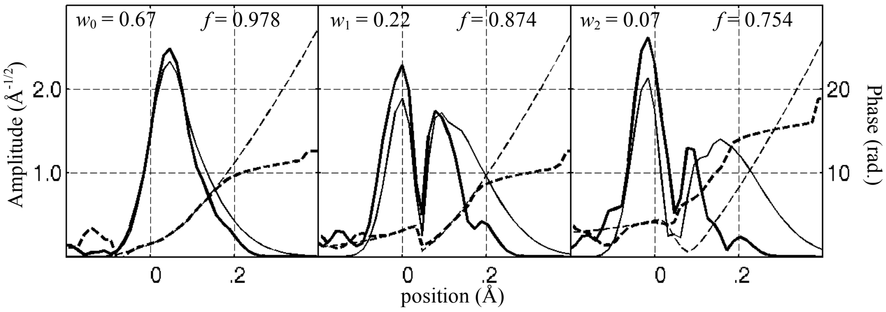

Fig. 2. Target and reconstructed states obtained with the noisy signal. Solid (dashed) lines are amplitude (phase). The target (reconstructed) state is represented by light (heavy) lines. The initial populations and individual fidelities are stated for the (left to right) ground, first, and second excited initial states.

accurate reconstruction becomes impossible for states with populations much less than the noise level. Reconstruction is also limited by the finite bandwidth of the first, second and fourth pulses, which confines the spatial range over which reference states can be effectively prepared. State reconstruction for systems with multiple degrees of freedom, including rotations, is currently being studied [8].

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