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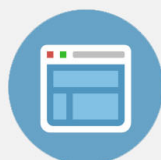
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# Time resolved dynamics of isolated molecular systems studied with phase-locked femtosecond pulse pairs

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Recent interest in developing an improved understanding of chemical reaction dynamics has led to theoretical and experimental investigations involving ultrashort laser pulses.<sup>1-4</sup> In the case of single short-pulse electronic excitation a coherent superposition of rotational and vibrational levels is prepared; such a superposition is, in general, nonstationary. Multiple-pulse excitation sequences can provide additional control of the subsequent dynamics by inducing electronic transitions from the time evolving state into portions of the molecular phase space which are otherwise difficult to access.<sup>1</sup> These sequences may require very intense pulses to induce sufficiently large population changes, and to insure that each pulse of the sequence interacts with the same molecules in the ensemble. Such sequences may also benefit from pulse shaping<sup>1(b),5</sup> to obtain the desired large population changes.

An optimization of more standard multiple-pulse excitation involves exercising control over the relative phase relationship between pulses in a sequence. The control of the phase of a series of pulses has been demonstrated and utilized by the Caltech<sup>6</sup> and Princeton<sup>7</sup> groups in studies of ensemble relaxation in "two-level" systems. Others<sup>8</sup> have used interferometric methods to generate phase coherent picosecond pulses over a few picosecond time interval.

In this Communication, we report on our recent efforts to generate and control the relative phase of pulses in a sequence. As an application, the preparation and subsequent temporal evolution of a coherent superposition of states in molecular iodine is measured. The experiment consists of recording the transient fluorescence signal as the time delay between the two pulses is incremented. The scanning is done such that the collinearly propagating pulses are always separated by an integral number ( $N$  for  $0^\circ$  and  $N + \frac{1}{2}$  for  $180^\circ$ ) of wavelengths at the locking frequency ( $\omega_{\text{lock}} = \omega_{\text{carrier}} \pm \epsilon$ ; ideally,  $\epsilon \rightarrow 0$ ). The  $250 \text{ cm}^{-1}$  FWHM bandwidth pulses prepare a rotational-vibrational coherent superposition in the  $\text{I}_2$  vapor sample and the total incoherent fluorescence is detected in a right angle geometry. The detected spectral window is limited to 570–670 nm. The relative pump-probe polarizations for the data of Fig. 1 are parallel, although measurements at the magic angle have also been performed. The phase evolution of this "wave packet" is clearly demonstrated by comparing pump-probe fluorescence signals<sup>9</sup> for pulses which are phase locked to a relative phase difference of  $\Delta\phi = 0$  or  $\pi$ . These results are shown in Fig. 1 (a) and (b). The transient in Fig. 1 (c) is for equal intensity pulses which are not phase locked.

The short (near) transform-limited pulses are created in an antiresonant ring dye laser of a new design.<sup>10</sup> The pulse

pair is generated via a phase-locked scanning Michelson or Mach-Zender interferometer. One arm of the interferometer serves as a course scanning stepper motor delay line with approximately 200 nm (double pass) resolution and  $> 100$  ps scan range. The other arm contains a position regulated

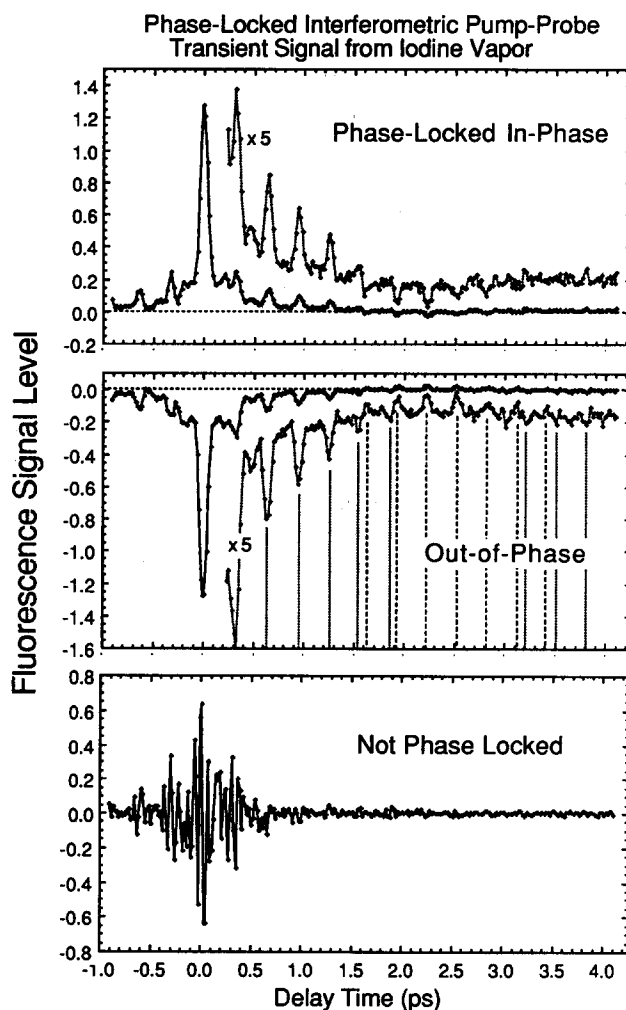


FIG. 1. Phase locked pump-probe signals detected from iodine vapor at 300 K. Both pump and probe pulses are at 611 nm and are 65–70 fs in duration. Fluorescence is detected at right angles as a function of time delay between the pulses. A double modulation scheme was used so that the fluorescence signal results only from molecules influenced by both pulses (i.e., is zero background). (a) Pump and probe pulses have the same phase; (b) pump and probe pulses are phase shifted by  $180^\circ$ ; (c) no active phase locking between pump and probe pulses is used. The dotted vertical lines in (b) indicate features with the same net phase as the probe pulse. Dashed vertical lines indicate recurrence features with the opposite net phase. All three scans are over the same time delay interval and identical  $t = 0$  positions. There are 256 pts/scan.

piezo electric transducer (PZT). The PZT undergoes sinusoidal modulation with amplitude of  $< \lambda / 10$  at  $\approx 300$  Hz. The PZT also functions to make the small ( $< \lambda / 2$ ) corrections to the relative phase of the pulses following each stepped advance of the scanning delay line, and is capable of 10 nm resolution.

The error signal for the PZT is derived from a phase-locked-loop (PLL) which consists of a monochromator and photomultiplier, a high stability lock-in amplifier and a differential amplifier to the PZT controller. The lock-in detects the change in the current from a PMT that monitors the fringe interference. The lock-in is referenced to the sinusoidal modulation of the PZT position. The monochromator also disperses the spectral components of the pulses and only a narrow-pass window ( $\approx 3 \text{ cm}^{-1}$ ) is detected. The geometrical pulse broadening in the present case is more than 50 ps.<sup>11</sup> Both pulses travel collinearly and traverse the same set of paths through the monochromator, thereby retaining the relative phase information. The maximum phase-locking time interval is dictated by the spectrally selected band-pass.<sup>12</sup>

Figures 1(a) and 1(b) shows the transient response (in fluorescence emission) which is due only to the signal from both pulses. The in-phase pump-probe case shows positive recurrences for the first 1.5 ps delay which then change to negative going spikes. Initially, as the wave packet returns to the Franck-Condon (FC) region of the coordinate, the wave packet has the same net phase factor as the second pulse. The overall phase of the wave packet, however, evolves such that the sixth through tenth recurrences occur out-of-phase with the probe pulse and lead to a decrease in the system polarization and the total fluorescence. The results for the out-of-phase locked pulse pair show the opposite behavior. Figure 1(c) shows a sharply contrasting result when the pump and probe pulses are not phase locked.

In the present case the dynamics reflect not only the FC overlap with the ground state but also the phase evolution of the excited state wave packet. The recurrence features in the fluorescence signal occur at approximately 300 fs time intervals, which corresponds to the vibrational level spacing for  $v \approx 10$ –16 in the  $B$  state of  $I_2$ . Additional lower frequencies are revealed in the change of sign and shift in the uniform time spacing between the fifth and sixth recurrence features.

The present measurements monitor both the motion and the phase evolution of the wave packet along the coordinate. Recent quantum mechanical wave-packet dynamics calculations<sup>13</sup> are in excellent agreement with our data, reproducing both the periodicity and sign reversal of the features in Fig. 1. The slower period phase modulation giving rise to the sign reversal after five recurrences results from a slowly evolving phase shift of the molecular superposition state in comparison to the phase-locked pump and probe pulses that are referenced to the phase of the carrier frequency of the laser.

Our principal result is the demonstration of the ability to monitor the evolution (both amplitude and phase) of coherent superposition states in multilevel systems. The phase control that is the central feature of these measurements also allows for the observation of an additional lower frequency

( $v \approx 2 \text{ ps}^{-1}$ ) phase modulation. In a future account we will present a complete description of the experimental apparatus and a quantitative analysis of the multilevel atomic and molecular coherent transient signals for such "two-slit"<sup>14,14</sup> measurements.

Investigators utilizing coherent pulse sequences to study solute-solvent interactions and chemical reaction dynamics in liquid media are in progress.

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