

Selective Excitation of Vibrational Wave Packet Motion Using Chirped Pulses

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Chirped ultrashort pulses are used to selectively excite vibrationally coherent populations in the ground and excited electronic states of a molecule in liquid solution. Negatively chirped pulses are shown to enhance the nonstationary ground state component, while positively chirped pulses discriminate against its formation. Separation of the ground and excited state contributions to the signal allows us to obtain state-specific information about the vibrational dephasing.

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Ultrashort pulse formation is determined by the ability to control the phase structure across the pulse spectrum: Intuitively, one wants all the frequency components to have zero relative phase, yielding a transform-limited (TL) pulse in which all the colors arrive simultaneously. Control of the phase structure of the laser pulse opens up possibilities beyond simply performing an experiment with the highest possible time resolution. The idea that one might time the arrival of the different frequency components of the pulse in order to coherently control the temporal evolution of the wave function has been the subject of considerable theoretical work [1–4]. Chirped pulses have been used to adiabatically transfer population in I_2 vapor [5], and quantum control of wave packet evolution has also been demonstrated in the same system [6]. Such tailored wave functions are potentially very powerful probes of molecular dynamics [7,8], and recently chirped pulses have been used to obtain information about the time scale of electronic dephasing in solution [9]. In this work we analyze the amplitude, phase, and damping of oscillations excited by chirped ultrashort pulses and demonstrate that such pulses can selectively excite coherent wave packet motion on either the electronic ground or excited state potential energy surface of a molecule. This selectivity aids in the interpretation of the observed dynamics.

The mechanism by which we achieve selectivity has been observed previously in numerical simulations of chirped pulse excitation [10] and can be thought of as a one-photon variant of the “pump-dump” process [11]. Figure 1 shows a schematic of the process that gives rise to the effects we observe. In the wave packet picture [12], the first field interaction places amplitude on the S_1 excited state where it starts to slide down the potential energy surface. A second field interaction either can bring more amplitude up, creating population in the excited state, or it can bring the amplitude from the first field interaction back down to S_0 , creating a displaced hole in the ground state [13]. In this latter case, the two sequential field interactions form an impulsive resonant Raman process that transfers momentum from the light

pulse to the S_0 wave function using the S_1 state as an intermediary. Since the wave packet on S_1 is moving from higher optical frequencies to lower, this process is enhanced when the color components of the pulse are ordered in time such that red follows blue. Thus a negatively chirped (NC) pulse favors the creation of a nonstationary ground state component while a positively chirped (PC) pulse discriminates against it. Although pump-probe experiments are often assumed to probe only dynamics on the excited state, a short pulse interacting with a molecular system can always induce motion in the ground state through this mechanism, introducing ambiguity into the interpretation of the observed dynamics [14–16]. Chirping the pump pulse provides a way to experimentally enhance wave packet motion on either the ground or excited state and allows one to selectively probe dynamics on those states.

The molecule studied in these experiments is the laser dye LD690 (LD) whose optical response is dominated by a 586 cm^{-1} ring-breathing vibrational mode [17]. The laser system used to produce the ultrashort pulses in this experiment has been described before [14,18], and for these experiments produces an amplified pump pulse of

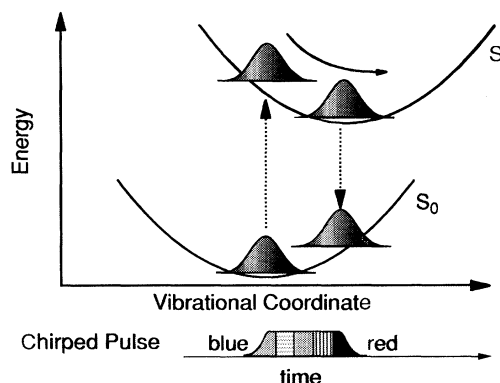


FIG. 1. Diagram of the time-dependent resonant Raman process leading to ground state wave packet oscillations, along with the frequency components as a function of time for a negatively chirped (NC) pulse which enhances this process.

12 fs duration and a slightly shorter 10 fs probe pulse, both centered at 620 nm with approximately 70 nm of bandwidth. This bandwidth is enough to coherently excite up to four vibrational states of the 586 cm^{-1} mode. The chirp of the pump pulse is modified by changing the separation of the pulse compression gratings. The actual chirp of the pulse is measured by cross correlating a 60 fs narrow band pulse with the 12 fs pulse in a $100\text{ }\mu\text{m}$ KDP crystal and analyzing the spectrum of the upconverted signal [18,19]. A polynomial fit to the plot of group velocity delay versus frequency shows that the chirp varies linearly with grating separation, as predicted [20], but with residual higher order chirp terms due to the limitations of the grating-prism pulse compression. We refer to the shortest duration pulse as transform limited (TL) for the sake of convenience.

Low pump pulse energies ensure that the signal is linear with pump intensity and the $\chi^{(3)}$ limit holds. The sample is a $70\text{ }\mu\text{m}$ thick flowing jet of LD690 dissolved in methanol with a probe transmission of at least 50%. The transient absorption of the probe is detected either by spectrally filtering the probe after the sample with a monochromator, and using differential detection in conjunction with lock-in amplification, or by detecting all probe wavelengths simultaneously in an optical multichannel analyzer [21].

Data were obtained at various probe wavelengths, with the most dramatic chirp effects seen in the red part of the transient absorption spectrum. Figure 2 shows the pump-probe signal at 640 nm along with the Fourier power spectra of the oscillatory component. For the data shown here, the pulse widths derived from the intensity autocorrelations are 33, 12, and 20 fs for the PC, TL, and NC pulses, respectively. The quadratic phase terms corresponding to these pulse widths are approximately $\Phi''(\nu) = 5200, -200,$ and -6100 fs^2 , respectively. As we put negative chirp on the pulse, the oscillations at 640 nm are first enhanced, with a maximum enhancement

occurring at a chirp corresponding to a pulse about twice as long as the TL pulse (this maximum is shown in Fig. 2), and are then slowly washed out as the pulse gets longer than the vibrational period. At the maximum the 586 cm^{-1} peak from the NC data is roughly 5 times larger than that of either the TL or PC data. By moving the grating in the opposite direction and putting a corresponding positive chirp on the pulse, we find that the amplitude of the oscillations is slightly diminished, and further chirping the pulse eventually kills the oscillations. This is most clearly seen in the early time (first 400 fs) data, since different damping times for the oscillations excited by a PC as opposed to a TL pulse (see below) can broaden and diminish the Fourier peaks of the long time traces shown in Fig. 2. The fact that, for a given pulse width, positively or negatively chirped pulses yield very different signals shows that these effects are not just due to the temporal broadening of the pulses.

If the frequency of the 586 cm^{-1} mode changed in going from S_0 to S_1 as previously claimed [22], then it would be a simple matter to determine whether the enhanced oscillations originate from S_0 or S_1 . Our resonance Raman measurements and Fourier transforms of long-time pump-probe traces show no evidence of this, however, and we use calculations and an analysis of the wavelength-dependent phase and damping times of the oscillations to determine their origin.

We calculate the differential pump-probe signals using the time-dependent perturbation formalism employed previously for the modeling of 4-wave-mixing signals [17,23]. LD is a large molecule with many vibrational degrees of freedom, and our calculation takes into account its 18 optically coupled vibrational modes and an electronic dephasing function obtained from previous resonance Raman and photon echo data [17]. In the case of LD, the 586 cm^{-1} mode dominates the multimode response, and the other modes serve mainly as an effective electronic dephasing through their destructive interference at early times [17]. The calculation does not take vibrational relaxation or the possibility of mode-mode coupling into account. The electric field of the pump pulse is derived from a Fourier transform of the magnitude of the experimentally measured pulse power spectrum multiplied by a frequency-dependent phase function obtained from the cross-correlation measurements. The shapes and temporal widths of the experimental pulse autocorrelation and cross correlation are well reproduced by the calculated pulses. Figure 3 shows the calculated signal at 640 nm along with its decomposition into ground and excited state components. As in the experiment, the largest effect is seen in this spectral region, with negative chirp greatly increasing the ground state contribution to the oscillations and positive chirp slightly decreasing it. The excited state contribution is degraded by both positive and negative chirp because the longer excitation event broadens the wave packet. It is important in these experiments

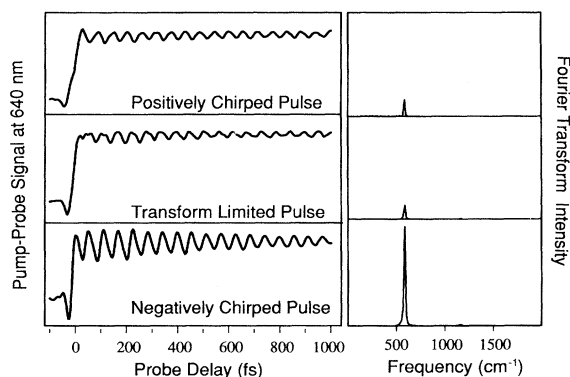


FIG. 2. Experimental pump-probe data at 640 nm using positively chirped (PC), transform-limited (TL), and negatively chirped (NC) pump pulses.

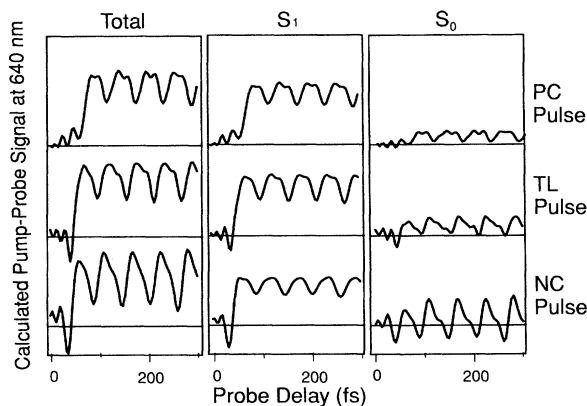


FIG. 3. Calculated pump-probe signal at 640 nm, with its decomposition into S_0 and S_1 contributions, using PC, TL, and NC pump pulses.

to take the actual phase structure of the pulse into account. Figure 3 shows that the experimental pulses do not achieve completely selective excitation, and this is due mainly to the higher order phase distortions present. Calculations using Gaussian pump pulses with a purely linear positive chirp show almost complete suppression of the ground state oscillations. A comparison of theory and experiment at the other probe wavelengths also shows qualitative agreement, except at the far red and blue edges of the spectrum. The edges of the spectrum probe the regions of the potential energy surface far from the minima, where the simple harmonic model assumed in our calculations would be expected to break down.

More evidence that chirping the pulse results in selective excitation of wave packet motion is provided by an analysis of the wavelength dependent phase of the oscillations. While NC and TL pulses produce oscillatory motion on both the S_0 and S_1 surfaces, a PC pulse should result in oscillations mainly from S_1 . Examination of the data shows that the amplitude of the oscillations in the PC pulse data goes through a minimum at around 635 nm, coinciding with a 180° phase shift from the oscillations in the blue region to those in the red. The maximum of the steady-state fluorescence spectrum in methanol is close to 635 nm, which means that this wavelength corresponds to the bottom of the S_1 potential well, according to our displaced harmonic oscillator model. Since the wave packet travels through this region twice per period and also broadens at the bottom of the well [15,24], the oscillations are washed out in this spectral region and a minimum in their amplitude is observed. Neither the NC nor the TL pulse data show such a minimum because in these cases there is a significant contribution from motion on S_0 .

The last aspect of the observed oscillations we analyze are their damping times, which are directly related to the molecule's vibrational dephasing times. A single-value-decomposition analysis [25] is used to extract damping

times from the oscillatory part of the data. Figure 4 shows the long-time behavior of the oscillations at 580 nm; a NC pulse yields essentially undamped oscillations, while the TL pulse excites oscillations that decay on the order of a picosecond, and a PC pulse results in oscillations with an even faster decay time of about 0.8 ps. At 640 nm the situation is the reverse of 580 nm—a PC pulse excites oscillations with a significantly slower decay time than those excited by a NC pulse (roughly 3 ps vs 1 ps). Negative chirp yields faster decaying oscillations in the red, while positive chirp yields faster decays in the blue. A qualitative explanation of this trend makes use of the fact that higher-lying vibrational states in polyatomic molecules generally undergo faster relaxation than states close to the minimum of the potential well [26]. Thus in the NC case, where the oscillations are dominated by the ground state contribution, we see a fast damping in the red part of the spectrum (corresponding to coherences involving higher-lying states in S_0) while the oscillations in the blue region suffer much less damping, since they involve lower-lying states and motion closer to the ground state minimum. While 580 nm does not correspond exactly to the ground state minimum, it is closer than 640 nm if the well is anharmonic. The TL and especially the PC pulse data reflect mostly excited state wave packet motion. Here the fast damping at 580 nm is due to coherently excited higher-lying vibrational states in S_1 now that the S_0 motion is suppressed. The relatively slow damping at 640 nm, close to the excited state potential minimum, is again the result of wave packet motion close to the bottom of the potential well having a longer dephasing time. The fact that our pulses do not achieve exact quantitative values for the vibrational dephasing times in LD difficult, since there is probably still some mixture of S_0 and S_1 wave packet motion in the data.

The phenomenon of chirped pulses enhancing or suppressing ground state wave packet motion should be general. Optical excitation of a molecule creates a vibrational wave packet with maximum potential energy which sub-

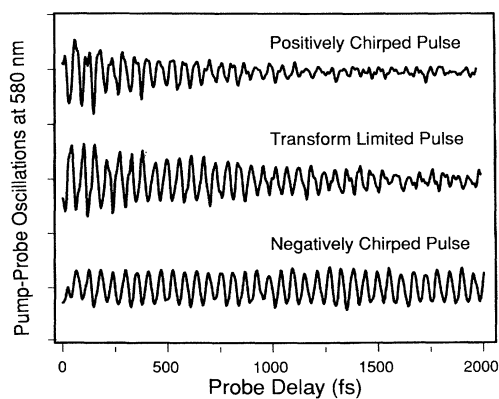


FIG. 4. Oscillatory component of the experimental pump-probe signal at 580 nm using PC, TL, and NC pump pulses.

sequently evolves to a lower point on the potential energy surface and thus to a lower optical transition frequency. In this work we have shown that ultrashort chirped pulses can substantially enhance or suppress oscillatory motion on S_0 , enabling us to experimentally distinguish between ground and excited state coherent vibrational dynamics. Using this technique, we have observed that the dephasing of a molecular vibration in liquid solution can vary by an order of magnitude, depending on the electronic surface (S_0 or S_1) and the region probed (close to or far from the minimum). Chirped pulses should also be useful in determining the origin of coherent vibrational motion observed in some photoreactive systems [16,25,27].

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