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VOLUME 141

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INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more and be broadly educated with respect to a large domain of science has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, and the desire to remain educated persists in all scientists. This series, *Advances in Chemical Physics*, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, a field that we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

STUART A. RICE

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NEW ADVANCES IN MID-IR PULSE SHAPING AND ITS APPLICATION TO 2D IR SPECTROSCOPY AND GROUND-STATE COHERENT CONTROL

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I. INTRODUCTION

Science often advances only as quickly as technology allows. This trend is especially evident in the field of molecular spectroscopy, where the science of studying molecular structures, dynamics, and chemical reactions has progressed in step with the technology of manipulating electromagnetic fields. For example, nuclear magnetic resonance (NMR) spectroscopy, which is now used to determine the structures of proteins, was made possible by radio-frequency technology developed in the 1950s. Likewise, laser-guided control of excited-state chemistry became possible in the 1990s with technology for temporally shaping visible and

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near-infrared (near-IR) femtosecond laser pulses [1–3]. In this review chapter, we highlight a new generation of shaping technology—femtosecond mid-infrared (mid-IR) pulse shaping—and review some of the novel spectroscopies and experiments that can now be implemented. With this new shaper, ground-state vibrational motions can be coherently controlled [4] and sophisticated new two-dimensional infrared (2D IR) spectroscopies implemented [5]. Experiments will be reviewed that incorporate mid-IR pulse shaping to expand our knowledge of vibrationally excited molecules in condensed phases, give us control over vibrational motions, and allow us to probe intricate molecular motions such as those that occur during protein folding.

Our desire for pulse shaping in the mid-IR stems from the impact such technology could have on multidimensional IR spectroscopies and coherent control of ground-state vibrations, among other possibilities. In the absence of a mid-IR pulse shaper, the only shaped pulses that are straightforward to generate in the mid-IR are linearly chirped with either material dispersion or pairs of gratings. In fact, the first experiments with linearly chirped pulses were performed in 1998 by Heilweil and co-workers [6]. They showed that it was possible to improve vibrational excitation and even invert vibrational populations with linearly chirped picosecond pulses in a process that has become known as ladder climbing. Ladder climbing is now possible using broad-bandwidth femtosecond pulses so that much higher vibrational states can be accessed. It is often routine to see excitations reach $\upsilon = 6$ or 7 in metal–carbonyl systems even without chirped pulses. While impulsive interactions that rely on transform limited electric fields can excite numerous vibrational quanta, achieving control of specific vibrational motions within complex potential landscapes requires equally complex laser pulses.

An interesting consequence of the slow development in mid-IR pulse-shaping technology is that the theory for manipulating molecules lies far ahead of experiments [1, 2, 7]. There are a number of theoretical research articles simulating possible experiments that might be done with shaped mid-IR light. These include articles using shaped pulses to enhance specific features in 2D IR spectra [7], controlling vibrational excitation on ground molecular states [8, 9], controlling chemical reactions like proton transfer [10], condensing Bose–Einstein condensates in gases [11], and using vibrations for quantum computing [12, 13]. Complicated pulse shapes have also been suggested for enhanced ladder climbing, such as those by Meier and Heitz, who predicted that pulses with sophisticated time and frequency profiles can improve vibrational excitation and attain at least partial quantum selectivity [8]. Many of these control experiments rely on aspects of abiabatic rapid passage and STIRAP (stimulated Raman adiabatic passage) methodologies [1, 14–16]. Theory could only be compared to experiment in the case of ladder climbing, as arbitrarily shaped mid-IR pulses have only recently become available. Thus, while a few experiments have been performed with shaped mid-IR pulses, theory suggests that the field of mid-IR-based coherent control is in its infancy.

Femtosecond pulse shaping in the visible and near-IR regions of the spectrum has been possible for more than a decade [17]. Indeed, there are numerous methods available for shaping visible pulses. The most widely adopted method (Fig. 1) disperses the femtosecond pulses using a grating so that the pulse spectrum is spread over a finite spatial distance. With the spectrum spatially resolved, the amplitudes and phases in the pulse can be manipulated in the Fourier plane using a programmable modulator and then transformed back into the time-domain using a second grating. The final pulse shape is simply the inverse Fourier transform of the mask, convoluted with the pulse spectrum. Thus, waveforms can be synthesized with a level of complexity only constrained by the bandwidth of the pulse and the specifications of the modulator, including its frequency resolution, phase resolution, and absorption profile.

The major problem with extending these shaping methods into the mid-IR is the availability of a suitable modulator. There are many different types of phase and amplitude modulators that work in or near the visible, including liquid crystal modulators (LCM), TeO_2 and fused silica acoustooptic modulators

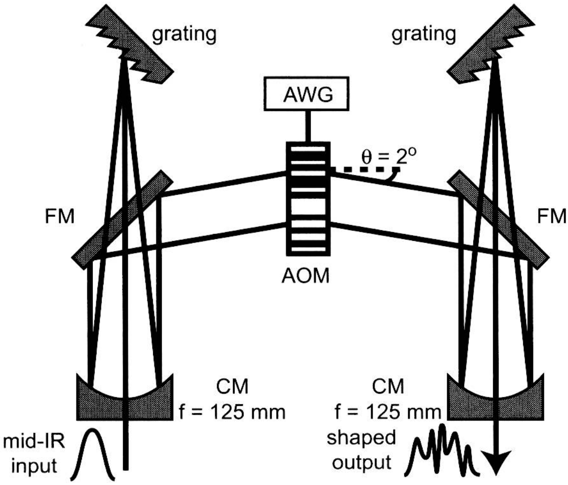

Figure 1. Experimental setup of the pulse shaper: AOM, Ge acousto-optic modulator; AWG, arbitrary waveform generator; CM, cylindrical mirror; grating, 200-g/mm ruled grating. Pulses are dispersed by the grating, focused at a CM, shaped at the AOM, collimated at a CM, and recombined at a grating.

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(AOM), and deformable mirrors, but none are suitable for the mid-IR: Liquid crystal modulators transmit in the visible and near-IR, TeO_2 and fused silica acoustooptic modulators operate in the visible and ultraviolet regions of the spectrum, respectively, and deformable mirrors only allow full-phase control for wavelengths <900 nm. Even though these modulators do not currently operate directly in the mid-IR, they can be used to indirectly create modulated mid-IR pulses by shaping in the near-IR and then transferring that shape to the mid-IR via difference frequency mixing [18–21]. Parametric transfer makes a large-wavelength regime available for phase and amplitude tailoring. However, difference frequency mixing scales nonlinearly with electric field, and thus the intensity of mid-IR light generated in this manner depends on the desired pulse shape. Furthermore, the frequency resolution is suboptimal, because the near-IR pulses are convoluted through the finite thickness of the mixing crystal. As a result, indirect shaping methods have limited utility in IR spectroscopy and coherent control. It is better to shape directly in the mid-IR so that the resolution and efficiency is dictated only by the design of the pulse shaper.

In the past two years, we have developed a pulse shaper that operates directly on mid-IR light. Our design is largely based on the work of Warren Warren [22, 23], who developed pulse shaping for visible frequencies using a TeO_2 acoustooptic modulator. Our shaper uses a germanium acoustooptic modulator that permits shaping between about 2 and 18 μm with fidelity comparable or better than most visible masks. By working directly in the mid-IR rather than by difference frequency mixing, it is possible to create intense and accurately shaped mid-IR pulses. With this shaper, many of the theoretically proposed experiments are now possible. In what follows, we first review some simple experiments demonstrating that ground-state vibrational motion can be controlled with even very simply shaped pulses. We then illustrate how our mid-IR shaper can be used to simplify and automate 2D IR data collection for improved insight into vibrational couplings and molecular structures. We think that this new technology will permit rapid advances in both controlling and understanding ground-state chemistry.

II. MID-IR PULSE-SHAPING TECHNOLOGY

The germanium pulse shaper works by modulating the intensity and phase of the frequency spectrum of each mid-IR pulse. The broader the frequency spectrum, the more intricately shaped the pulses can be. We generate mid-IR pulses with >500-nm bandwidth using a modified optical parametric amplifier (OPA) pumped by a short-pulse Ti:Sapphire regenerative amplifier (800 nm, <50 fs). The optics and nonlinear crystals in the OPA have been optimized for large bandwidth and high mid-IR intensity (typically 4.5 μJ at 6 μm when pumped with 800 μJ of 800 nm) [24]. These pulses serve as the shaper input.

A schematic of the pulse shaper is shown in Fig. 1. The pulse shaper functions through the use of a pair of diffraction gratings (200 grooves/mm) and a pair of cylindrical mirrors ($f = 125\,\mathrm{mm}$). In this geometry the gratings, cylindrical mirrors and AOM are all separated by the mirror focal length with the Ge AOM placed in the center of the Fourier plane, as is typical of the 4-f geometry. The shaper design incorporates gratings placed in quasi-Littrow configuration and tilted vertically, allowing for easy adjustment to multiple light sources, such as HeNe or mid-IR. Before inserting the Ge AOM, the 4-f geometry of the cylindrical mirrors and gratings was initially set using three parallel propagating HeNe beams diffracted from the first grating in 7th, 8th, and 9th order. The Ge AOM, when placed in the Fourier plane, deflects the mid-IR at a Bragg angle of $\sim 2^\circ$ with amplitude and phase according to the acoustic wave passing through the crystal. Since the HeNe beam does not transmit through Ge, we compensate for the 2° angular deviation using the folding mirrors (FM, Fig. 1) immediately before and after the Ge AOM. To create a desired mid-IR pulse, the properly shaped acoustic wave is coupled into an RF amplifier using a 300-Msample/s arbitrary waveform generator. The amplified waveform drives a piezoelectric bonded to the Ge crystal, creating an acoustic wave across the crystal aperture. Since the acoustic wave velocity is negligible relative to the mid-IR pulses traversing through the Ge AOM, this wave acts like a static modulated grating. Thus, by shaping the acoustic wave, the desired mid-IR frequencies are deflected with amplitude and phase specified by that acoustic wave. As a result, the phase and intensity of the shaped mid-IR pulses are set by the phase and intensity of the acoustic wave.

The frequency resolution of the shaper is dictated by the product of the time aperture Δt and the usable RF bandwidth, Δf. The acoustic wave propagates along the length of the AOM at 5.5 mm/μs, the speed of sound in Ge. Given a crystal aperture of 5.5 cm × 1 cm, the time aperture of the AOM is $\Delta t = 10\,\mu\mathrm{s}$. The AOM was designed to operate at a 75-MHz center frequency and has a bandwidth of $\Delta f = 50\,\mathrm{MHz}$. Thus, for our design, $\Delta t \cdot \Delta f = 500$, which indicates a maximum of 500 equivalent resolvable elements across the crystal aperture.

III. PERFORMANCE OF Ge AOM SHAPER

Figure 2 illustrates the phase and amplitude resolution of our device. Shown in this figure is a spectrum collected for a shaped pulse generated by a series of 3-ns acoustic waves separated by 665 ns, shown in Fig. 2b. Each wave deflects a particular frequency in the mid-IR pulse spectrum to create a comb of frequencies. The resulting peaks each have an fwhm of 5 nm and are separated by 63 nm, demonstrating the high resolution and contrast ratio of the pulse shaper. Considering that the 3-ns duration of each acoustic pulse is smaller than

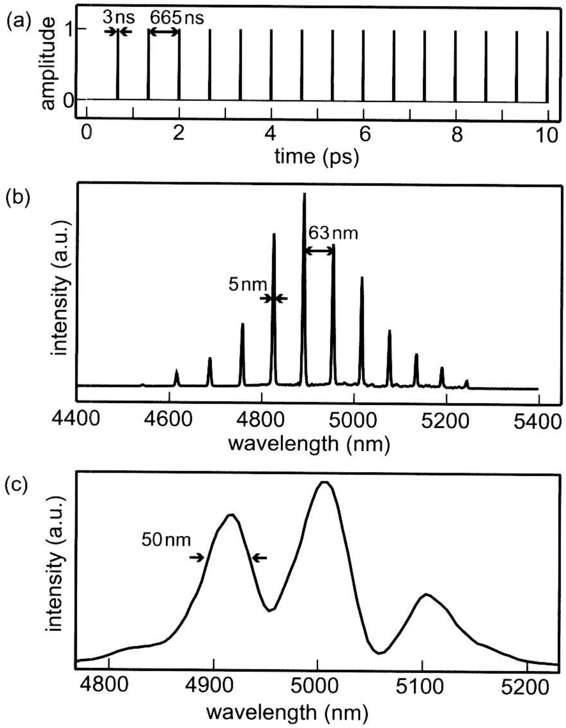

Figure 2. (a) Periodic RF signal used to modulate the frequency spectrum. (b) Spectrum resulting from the modulated RF signal in (a). (c) Pulse shaped by two π-jumps in an effort to create a comb spectrum using parametric transfer.

the design resolution, we determine an actual resolution of 190 equivalent pixels across the entire aperture, after adjustment for monochromator resolution. The ideal resolution is not reached because under the focusing conditions of our 4-f geometry, we have a spot size of 250 μm at the Ge crystal, which is roughly twice the size of a resolvable frequency element. Tighter focusing at the crystal by either expanding the mid-IR beam or using shorter-focal-length cylindrical mirrors will improve the resolution. Nonetheless, the intensity and phase of each of these resolvable elements can be adjusted to create sophisticated shaped pulses. For example, the resolution dictates the maximum time delay, τ, by which two pulses in a pulse pair can be separated, where $\tau = 2\pi/\omega$. Thus, with 190 resolvable elements, we can generate a pair of pulses separated by a time delay as large as 13 ps. With 500-pixel resolution, a delay of 35 ps can be achieved. Given that most condensed-phase vibrational lifetimes are < 10 ps, our configuration is adequate for properly resolving spectral features without obfuscation from the ringing that arises with temporal truncation.

The frequency comb spectrum also serves to calibrate the position of the Ge AOM aperture to the wavelength. To accurately shape in the time domain, a second calibration is also necessary to compensate for the chirp in the input mid-IR pulses emanating from the OPA (which are not usually compressed) as well as a linear chirp created by the Bragg deflection angle of the AOM. To account for these chirps, we use an autocorrelator with a 0.5-mm-thick type I $AgGaS_2$ ($\theta = 33^\circ$) doubling crystal and vary the second- and third-order dispersion coefficients (ϕ_2 and ϕ_3) to maximize the second harmonic signal. Neglecting acoustic nonlinearities, the desired temporal shape is simply a Fourier transform of the product of the acoustic profile and frequency spectrum, adjusted by the two calibrations.

IV. COMPARISON TO PARAMETRIC TRANSFER

For comparison, we also show in Fig. 2c the comb spectrum generated not with our Ge AOM shaper, but by parametric transfer from the near-IR. Before developing our Ge AOM shaper, we first began creating shaped mid-IR pulses following the methods developed by other groups using difference frequency mixing to shift a shaped near-IR pulse into the mid-IR [18–21]. Following their methods, we used a 4-f geometry and a phase controllable liquid crystal modulator to shape the signal beam in an optical parametric amplifier, which was then difference frequency mixed with the idler beam stretched to 1 ps. The spectrum in Fig. 2c was created by phase modulating the signal beam in an effort to place a series of evenly spaced dips in the mid-IR spectrum. At best, we were able to create a frequency profile consisting of three distinct peaks, each approximately 50 nm in width. Clearly, the frequency resolution attainable from parametric transfer is much poorer than by shaping directly in the mid-IR, although we do note that other groups have reported better resolution using indirect transfer [18, 20]. Another drawback of parametric transfer is that the intensity of the tailored mid-IR depends strongly on its pulse shape, because the transfer is a nonlinear optical process. As a result, much more intense pulses can be made when shaping directly in the mid-IR.

V. COHERENT CONTROL OF GROUND-STATE VIBRATIONAL DYNAMICS

Advances in the theory and implementation of femtosecond pulse shaping have spurred a revolution in the coherent control of atomic and molecular processes. By creating complex vibrational and/or electronic wavefunctions with tailored pulses, it is now possible to guide many chemical and physical processes such as photodissociation, ionization, electron transfer, fluorescence and vibrational excitation [1, 3]. Most studies so far have focused on the excited electronic states of systems because the wavelength ranges accessible to existing pulse shapers only span the visible and near-IR spectral regions. This limited wavelength range is unfortunate, because simulations suggest that it should be possible to control chemical reactions using ground-state vibrations [10]. Among these simulations are studies concluding that tailored pulse shapes can control intra- and intermolecular proton transfer [10, 25–28], that electron transfer can be controlled using vibrational excitation [29], and that mid-IR excitation can direct isomerization [30, 31]. Thus, extending the techniques developed for visible pulse shaping into the mid-IR promises to open a new class of experiments geared toward understanding and optimizing ground state control.

The prior lack of a suitable mid-IR pulse shaper hindered scientific progress toward ground-state control. Without a shaper that works directly in the mid-IR, experimental control of ground-state vibrational excitation is limited to using either stimulated Raman excitation with shaped Stokes and anti-Stokes pulses [32] or vibrational up-pumping with mid-IR pulses that are linearly chirped with material dispersion or a grating pair [6, 33–35]. While useful, neither of these methods provides the intensity or flexibility in pulse shape necessary for arbitrary generation of ground-state wavepackets. Taking advantage of the capabilities afforded us by a mid-IR pulse shaper, we set about optimizing vibrational ladder climbing in the ground state.

Vibrational ladder climbing is one of the most fundamental coherent control strategies. Most experimental schemes proposed for chemical control, whether it is proton transfer, electron transfer, or isomerization, require that vibrational energy be selectively deposited into one or more eigenstates with programmable phase and amplitude. Ladder climbing with linearly chirped pulses is the most intuitive way of accomplishing this task. The vibrational selection rules of harmonic potentials limit vibrational excitation to one quantum at a time. Therefore, at least near the minima of potential energy surfaces, vibrational excitation requires a driving field that is initially on resonance with the fundamental frequency and chirped to match the anharmonicity of the potential, thereby sequentially exciting the system through a series of vibratonal states analogous to climbing the rungs on a ladder. Linearly chirped mid-IR pulses can be easily generated with materials or a grating pair, and the effect of linear chirp on ladder climbing efficiency has been studied [6, 33]. Experiments on $W(CO)_6$, carbonmonoxy myoglobin (Mb-CO), and other compounds have found that a negative chirp improves vibrational excitation [6, 33–35]. If enough energy is deposited, photodissociation occurs, at least in the gas phase [34, 35].

One might expect that linearly chirped pulses are sufficient to ladder climb Morse potentials, because the slope of the chirp can be adjusted to match the anharmonic spacing of the Morse potential (the frequency difference between vibrational levels υ and υ + 1 is constant because Morse potentials only have a single anharmonic term in their expansion). Following this line of thought, a more sophisticated pulse would only be necessary for potentials with more complex curvature, such as at high excitation energies where potentials usually deviate from Morse behavior or on multidimensional surfaces where the curvature depends on couplings to other modes. However, recent simulations by Meier and Heitz show that complex pulse shapes dramatically increase ladder climbing efficiency even on Morse potentials [8]. Shown in Fig. 3a is the Wigner diagram of a shaped pulse, optimized to maximize the vibrational excitation of the carbon monoxide stretch bound to the heme of a myoglobin protein (Mb). The Wigner

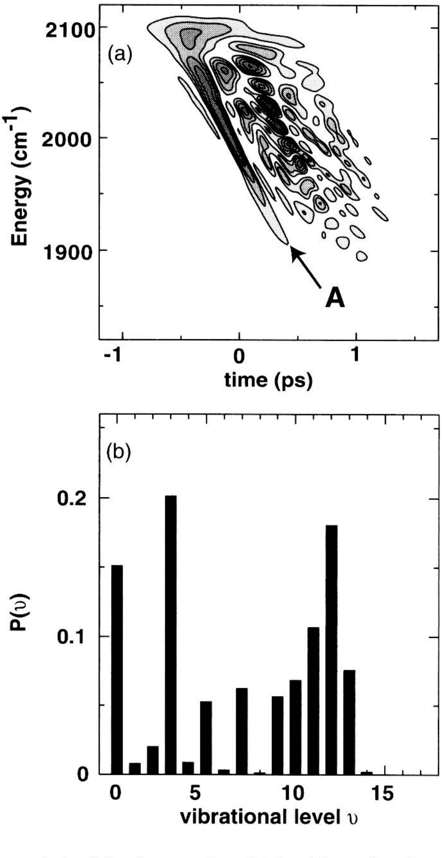

Figure 3. (a) Wigner plot of the laser pulse obtained by a local control algorithm used to optimize higher-level vibrational populations in carbon monoxyhemoglobin. (b) The vibrational distribution created by the laser pulse depicted in (a). (These figures are reproduced with permission of C. Meier and M.-C. Heitz.)

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