

Phase Modulation of Ultrashort Light Pulses using Molecular Rotational Wave Packets

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We demonstrate experimentally how the time-dependent phase modulation induced by molecular rotational wave packets can manipulate the phase and spectral content of ultrashort light pulses. Using impulsively excited rotational wave packets in CO₂, we increase the bandwidth of a probe pulse by a factor of 9, while inducing a negative chirp. This chirp is removed by propagation through a fused silica window, without the use of a pulse compressor. This is a very general technique for optical phase modulation that can be applied over a broad spectral region from the IR to the UV.

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Ultrashort pulses have a wide variety of applications in science and technology. For some applications such as high-harmonic generation, THz measurements, surface SHG generation, or time-resolved chemical reaction dynamics, very short optical pulses are desirable [1–3]. However, the bandwidth available directly from laser systems is limited. Several techniques exist for broadening the spectrum of a light pulse, followed by compression to a shorter pulse. Recent advances in the field of coherent control of matter [4–9] enable new techniques for manipulating light pulses. In this Letter, we describe the use of a rotational wave packet created by an ultrashort light pulse to induce a rapid phase modulation on a time-delayed probe pulse.

A common pulse compression scheme is to use the electronic Kerr nonlinearity to produce a temporal self-phase modulation (SPM) that is proportional to the pulse intensity [10–13]. The SPM process imparts a positive chirp on the pulse that must then be compensated for by a diffraction grating or prism pulse compressor [14,15]. Moreover, because SPM is a third-order nonlinear process, it is very sensitive to variations in the input pulse shape and energy and amplifies any instabilities in the input pulse. In recent years, several exciting alternative approaches for the modulation of light based on molecular motion have been demonstrated. One method uses intense quasi-cw lasers to excite a series of high-order vibrational Raman lines, producing a broad frequency-comb spectrum [16]. In another technique, an ultrafast laser pulse excites a strong vibrational coherence in SF₆, also creating many high-order Raman sidebands [17]. Compressing the spectra from either technique produces a pulse train with narrow temporal structure (predicted to be sub-fs) given by the separation of the highest-order Stokes and anti-Stokes sidebands. Compression schemes based on rotational modulation of the index of refraction of a molecular gas have recently been proposed, predicting compression to 3 fs duration using rotationally excited H₂ [18] and to ~1 fs using N₂ [19].

In this work, we demonstrate experimentally that rotational wave packet revivals [20] in a molecule (CO₂) can be used to phase modulate and self-compress single, ultra-

short, light pulses. A short pump pulse excites a rotational wave packet in the gas that undergoes periodic full revivals at time delays of $T_r = h/2B$, where h is Planck's constant and B is the rotational constant of the molecule. In the case of CO₂, full revivals occur at $T_r = 42.8$ ps. Because these revivals are separated by many ps (even though they contain rapid structure during each revival), the probe pulse experiences a nonperiodic phase modulation allowing for single pulses to be generated which are phase modulated in a simple, controlled way. We also measured the phase induced by the time-dependent index of refraction during the rotational revival of a wave packet. Finally, we show that soliton-like pulses can be generated at arbitrary intensities using this scheme.

Provided electronic excitations and rovibronic couplings are negligible, the rotational motion of the molecules can be described by a simple rigid rotor model [21,22]. The total wave function Ψ will be expanded in terms of rotational eigenstates $|JM\rangle$ of the field-free Hamiltonian H_0 , whose corresponding energy eigenvalues are $BJ(J+1)$, where J is the angular momentum quantum number and M is its laboratory frame z -axis projection. The interaction between the linearly polarized pump pulse and a linear molecule is through an induced electric dipole moment, describable in terms of the effective angular potential energy $V = -[\varepsilon(t)^2/2](\alpha_{\parallel} \cos^2\theta + \alpha_{\perp} \sin^2\theta)$. Here $\varepsilon(t)$ is the electric field of the laser pump pulse, θ is the angle between the electric field and the internuclear axis, and $\alpha_{\parallel}, \alpha_{\perp}$ are the components of the anisotropic polarizability for fields respectively parallel and perpendicular to the axis. The full Hamiltonian for a rotating molecule interacting with the pump pulse is

$$H(t) = H_0 - \frac{1}{2}\varepsilon(t)^2(\Delta\alpha \cos^2\theta + \alpha_{\perp}), \quad (1)$$

where $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$.

A quantum system initially in a pure $|JM\rangle$ state will be excited by the pump pulse into a coherent superposition of different $|J'M\rangle$ states. Selection rules require that the $J' = J, J \pm 2, J \pm 4, \dots$ have the same exchange symmetry as the initial J . After the pump pulse, the rotational wave

packet evolves under the field-free Hamiltonian. There are exact, periodic, full wave packet revivals at a period of $T_r = h/2B$. In addition, due to the quadratic dependence of the energy on the rotational quantum number, partial revivals occur with a period $T_{\text{partial}} = \{h/[d^2E(q)/dq^2]\}$ [23], where q is a quantum number that must increase by unity.

Our detailed model begins with a thermally averaged ensemble of different pure $|JM\rangle$ states weighted according to the Boltzmann distribution function. Next, we propagate them in time through the duration of the pump pulse, using the time-dependent Schrödinger equation, with the Hamiltonian defined in Eq. (1). In the case of a symmetric, linear molecule, e.g., CO_2 , only even J values are included in the ensemble (i.e., $J = 2q$). The dephasing and rephasing of the quantum states induce a periodic modulation of the index of refraction of the gas, which is given by

$$n^2(t) \approx 1 + \frac{N}{\epsilon_0} (\alpha_{\perp} + \Delta\alpha \langle \cos^2\theta(t) \rangle), \quad (2)$$

where N is the gas number density. The alignment cosine, $\langle \cos^2\theta(t) \rangle$, is the thermally averaged expectation value of $\cos^2\theta$. Figure 1 shows the calculated index of refraction as a function of time, for rotating CO_2 molecules at temperatures of 293 and 195 K, excited by a 20-fs, 800-nm pump pulse at intensity $3 \times 10^{13} \text{ W/cm}^2$. At $t = 0$, the pump pulse creates the coherent rotational wave packet. The peaks in $n(t)$ that occur every $T_r \sim 42.8 \text{ ps}$ are due to the rotational revivals where the wave packets rephase completely. Partial rephasings occur at intervals of $T_{\text{partial}} = T_r/4 \sim 10.7 \text{ ps}$. The partial rephasings at odd multiples of T_{partial} would not exist if both even and odd J states were allowed, e.g., for a heteronuclear molecule. Note that in Fig. 1, the molecular alignment is improved

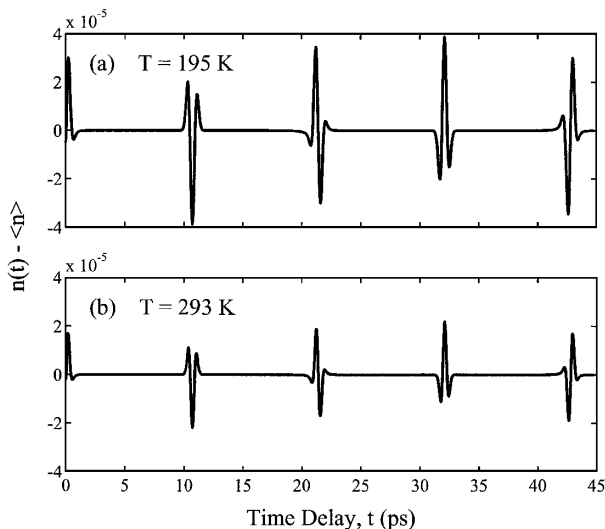


FIG. 1. Calculated index of refraction, $n(t)$, as a function of time for rotating CO_2 molecules at room temperature (a) and 195 K (b). The plots show deviations from the average value, $\langle n \rangle$, where $\langle n \rangle - 1 = 2.6 \times 10^{-4}$ for 195 K and 1.7×10^{-4} for 293 K.

by cooling the molecular gas. Cooling increases the purity of the initial state, resulting in a more coherent alignment of the ensemble of molecules and therefore a larger variation in the index of refraction.

The phase modulation imparted on the probe pulse is maximized when the delay coincides with a full or partial rotational wave packet revival. By adjusting the delay of the probe pulse to coincide with the minimum or maximum of the index of refraction, we sample a region of curvature that provides predominately either positive or negative quadratic temporal phase modulation. Furthermore, by adjusting the duration of the probe pulse to match the time separation of the inflection points of $n(t)$, we can maximize the total phase modulation. This is desirable for two reasons. First, by confining the pulse energy to that region of the phase modulation where the curvature is of the same sign (within the inflection points), we ensure that the chirp is always of the same sign. This results in a smooth spectral broadening of the pulse, ensuring a high-quality compressed pulse. In contrast, for SPM, the time-dependent refractive index $n(t)$ generated by the pulse intensity envelope has inflection points. These lead to identical frequencies being created in different temporal regions of the pulse. Interference between these frequencies leads to modulations in the spectrum of the broadened pulse, which makes temporal compression difficult.

The second reason for matching the probe pulse length to the width of the curved portion of the induced $n(t)$ is to maximize the resultant bandwidth. Using a probe whose length is matched to the rotational revival width will result in more spectral broadening than for a shorter probe pulse. This result is seen by considering a simple expression that predicts the broadening induced on Gaussian pulses that experience a quadratic temporal phase modulation (or linear chirp) [24]

$$f = \sqrt{1 + \left(\frac{\pi c_R \tau_i^2}{2 \ln 2} \right)^2}.$$

Here τ_i is the input pulse duration and the curvature of the temporal phase, $\varphi(t) = \omega_L t + \pi c_R t^2$, defines the chirp rate c_R . The output pulse duration is $\tau_o = \tau_i/f$ and follows a $1/\tau_i$ dependence. Therefore, increasing the input probe pulse duration can yield shorter output pulses until the probe pulse length exceeds the region of curvature in $n(t)$. Group velocity walkoff between the pump and probe pulses could cause the probe to shift in time with respect to the rotational revivals into a region of opposite chirp, but it is negligible in our case ($\sim 0.56 \text{ fs/cm}$).

For our experiments, we used 15–20-fs laser pulses generated by an amplified Ti:sapphire laser system, at a 1-kHz repetition rate, a wavelength of 800 nm, and an energy of $\sim 1 \text{ mJ}$ [25,26]. A portion of the pump pulse ($\sim 30\%$) is split off for use as a probe pulse. This probe pulse is frequency doubled in either a long [25-mm KDP (KH_2PO_4)] nonlinear crystal to generate a long probe pulse ($\approx 0.6 \text{ nm}$, 270 fs, 400 nm) or in a short (2.5-mm KDP) crystal to

generate a short probe pulse (≈ 2.2 nm, 52 fs, 400 nm). The pump and probe pulses are combined with an adjustable delay and focused into a 30–60-cm long, 450- μ m diameter, hollow-core fiber filled with CO₂ gas at pressures of 100–500 torr. For our first experiment, a rotational coherence was prepared using a 0.3-mJ, 20-fs, 800-nm pump pulse propagating through 280 torr of room temperature CO₂ gas in a 30 cm, 450- μ m, hollow-core fiber. Using the short probe pulse to sample the instantaneous index variation, we measured the frequency shift (proportional to dn/dt) of the temporal phase modulation due to the first observed partial rotational revival, as shown in Fig. 2(b). These results can be integrated to obtain the phase $\varphi(t) = [n(t)\omega_0/c]L$ [Fig. 2(a)], while the chirp rate can be obtained by differentiation [Fig. 2(c)]. The probe pulse spectrum was measured as a function of delay in the vicinity of the first observed partial rotational revival. As expected, for a 52-fs probe pulse very little broadening results from the peak chirp rate of ~ 0.10 THz/fs, corresponding to $f \sim 1.17$.

We then repeated the experiment with a longer probe pulse of duration 270 fs, generated by doubling in a 25-mm thick KDP crystal. Here we used a 60-cm long fiber filled with 300 torr of CO₂ gas. The probe delay was adjusted to coincide with the first full rotational revival to give the maximum output bandwidth in a region of negative chirp. The input pulse shown in Fig. 3 (dashed line) has a minimum pulse duration of 270 fs as determined by the Fourier transform of the probe spectrum. The output probe pulse was characterized using self-diffraction, frequency-resolved optical gating (SD FROG). A 1-in. length of

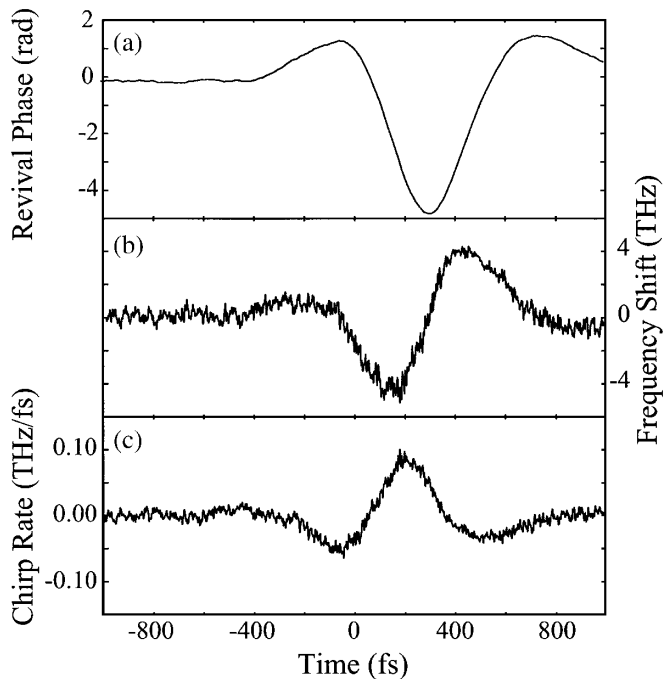


FIG. 2. Measured phase (a), frequency shift (b), and chirp rate (c) for the first observable partial rotational revival.

fused silica glass was inserted into the beam before the SD FROG measurement apparatus to compress the pulse. The deconvolved pulse shape and phase, shown in Fig. 3 (solid and dotted lines, respectively), indicate that the pulse duration has been reduced to 30 fs, corresponding to a compression ratio of 9. This compression is achieved without the use of gratings, prisms, or chirped mirrors, so the efficiency is limited only by coupling into a hollow core fiber.

This approach to molecular modulation of light has several desirable characteristics. First, it allows for some tunability of the compressed pulses by shifting the delay of the probe pulse to a region of either positive or negative slope of the wave packet revival. Second, it can impart either a positive or negative chirp on the pulse. Third, since the phase modulation imparted by the molecular rotations is independent of the intensity of the probe pulse, spectral broadening is stable. Fourth, since a separate pulse prepares the rotational wave packet, this technique offers the potential for some control over the phase modulation [27–29]. Fifth, this process can lead to the generation of extremely short light pulses, possibly as short as 1 fs [19]. Sixth, this technique works best for *long* pulses that are relatively easy to produce, generating shorter output pulses when the duration of the probe pulses matches that of the rotational revival. Seventh, under some conditions, the time-dependent phase modulation of the rotational revival will balance the dispersion of the gas and will therefore support soliton-like propagation that is independent of pulse energy; i.e., the pulse is copropagating with an index “bubble” caused by molecular alignment. Finally, and perhaps most importantly, this technique is very general and should allow for self-compression of light over the entire transparency range of the molecular gas, spanning from the IR into the UV region of the spectrum. This is particularly important in the UV, where the higher index of refraction may make this technique more effective, and where other pulse compression techniques suffer either from high-order

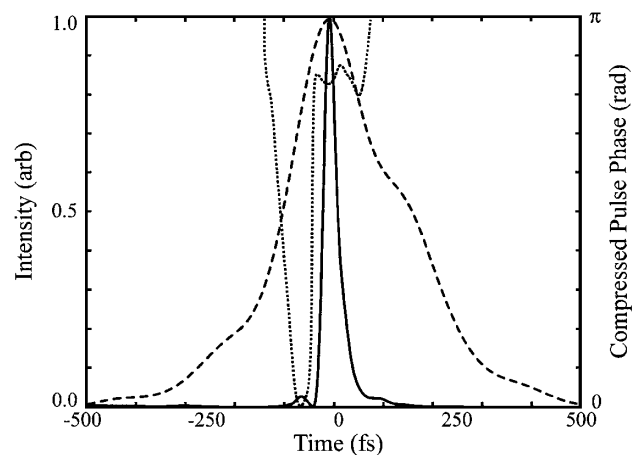


FIG. 3. Temporal profiles of the injected 270 fs pulse (dashed line) and the self-compressed 30 fs pulse (solid line) and phase (dotted line).

dispersion or high loss. For example, we expect a 100-fs pulse from a KrF laser at 248 nm, under similar conditions, to compress to a temporally smooth, sub-3-fs pulse after propagating through a 1-mm LiF window.

Further improvements such as lengthening the fiber, increasing its diameter, increasing the gas pressure, cooling the molecular gas, using a more intense pump pulse, and using a molecule with a larger difference in polarizabilities will yield even shorter, higher power, shaped pulses. By choosing a different molecule, we can adjust the time scale of the width of the rotational revivals to optimize for different input pulse durations. Last, our model predicts that shaping the spectral phase of the pump pulse can modify the structure of the revival. This presents the possibility of tailoring the wave packet to precompensate for high-order spectral phase aberrations in the compression window. Unlike techniques involving the excitation of a single vibrational or rotational level, this is possible in a wave packet because the relative phases of many rotational levels can be adjusted so that they rephase in an optimal way. If the modulation of the revival structure is strong enough, this technique could be used as a programmable molecular phase modulator operating with bandwidths exceeding 50 THz.

In summary, we present a first measurement of the phase induced by a rotational wave packet revival and demonstrate its use for phase modulation and self-compression of an ultrashort pulse. We also demonstrate the possibility of novel, energy-independent, soliton-like propagation. This scheme is relatively insensitive to the input wavelength and provides a method for self-compression in spectral regions where traditional techniques are not efficient. We expect this technique will also provide a convenient and flexible tool to manipulate and shape pulses in a wide spectral range for a wide variety of experiments.

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