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Rotational wavepacket revivals for phase modulation of ultrafast pulses

M. Comstock *, V.V. Lozovoy, M. Dantus

Department of Chemistry and Physics, Michigan State University, 50 Chemistry Building, East Lansing, MI 48824, USA

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Abstract

Phase modulation of ultrafast laser pulses has been demonstrated recently by taking advantage of the time-dependent refractive index that takes place during rotational wave packet revivals in a gaseous sample [Phys. Rev. Lett. 88 (2002) 013903]. Here we explore the effect of laser intensity, physical properties of molecules, and temperature on rotational wavepacket revivals by femtosecond transient grating spectroscopy. Theoretical analysis of experimental data is used to predict the optimum conditions for the phase modulation and compression of ultrafast laser pulses.

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1. Introduction

Rotational wavepacket revivals have been studied for many years. Techniques used to observe rotational revivals range from Optical Kerr Effect Spectroscopy [1] to laser-induced fluorescence [2], to six-wave mixing [3]. Spectroscopic techniques based on rotational wavepacket revivals can determine rotational constants with high precision and can yield important structural information about large molecules [4–11]. Concentration measurements and couplings between rotational and vibrational degrees of freedom have been investigated through similar techniques [8,12–15]. The initial rotational dephasing has been used to probe the vector dynamics of chemical reactions [16]. In addition, interest has developed in the use of rotational revivals as a means of enhancing laser-induced alignment [17–20]. Recently, several techniques have been introduced to use Raman scattering of gas phase molecules for pulse shaping and pulse compression [21–23]. Optimization of these methods requires an understanding of the molecular dynamics and the time dependence of the nonlinear susceptibility of the sample. In this Letter, we address the physics of rotational revivals and their application to pulse shaping of UV pulses as proposed by Kalosha and Ivanov [22] and demonstrated by Bartels et al. [23].

When a pump laser is introduced in a gaseous medium a rotational wavepacket is induced impulsively through off-resonance Raman interactions of the field and the molecular anisotropic polarizability. The aligned rotational wavepacket evolves in time, dephasing and reviving at regular

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[*] Corresponding author. Fax: 1-517-353-1793.
E-mail address: comstock@cem.msu.edu (M. Comstock).

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intervals [1,24]. The probe pulse to be compressed is then introduced at a time delay that matches the rotational revival in the medium. The transient changes in the refractive index induce pulse broadening and imprint a time-dependent phase modulation that can be exploited for pulse compression [25]. Rotational revival pulse compression has great potential for compressing ultrashort pulses over a broad spectral region. Especially for wavelengths in the ultraviolet where the optics used in conventional pulse shapers may not be readily available. Here we focus on the essential physics of rotational revivals for the purpose of identifying some of the key parameters that optimize the generation of negative dispersion required to compress ultrashort pulses. We illustrate these effects with experimental results and simulations.

2. Theory

After a strong nonresonant femtosecond excitation pulse, a rotational wavepacket forms in the medium. The anisotropic transient polarizability of the medium $P(t)$ depends on the beat frequencies that arise from Stokes ($\Delta J = +2$) and anti-Stokes ($\Delta J = -2$) rotational Raman transitions [15]. A quantum mechanical expression for the time-dependent polarization [26] can be obtained based on the rotational beat frequencies [8]

$$P(t) \propto N\beta \sum_J \rho_J \{ \cos[2\pi c(F_{J+2} - F_J)t] + \cos[2\pi c(F_J - F_{J-2})t]\} \exp(-t/T_2), \qquad (1)$$

where $F_J = BJ(J+1) - DJ^2(J+1)^2$ [27] [1], B and D are the rotational and centrifugal distortion constants of the molecule, T is the temperature, β is the anisotropic polarizability ($\alpha_\parallel - \alpha_\perp$), N is the number density, T_2 is the coherence dephasing time, and ρ_J is the normalized rotational distribution including spin statistics (g_J) for all natural isotopes [28] [2]

$$\rho_J = g_J(2J+1)\exp(-2\pi chF_J/kT). \qquad (2)$$

Transient grating spectroscopy is a way to directly examine changes in the polarization of the medium [23,29,30]. Heterodyne, phase sensitive, transient grating spectroscopy uses two pulses overlapped in time to form a polarization grating with dynamics described by Eq. (1). The changes in the intensity of a third beam passing through this grating are given by [26]

$$S_{\text{hetero}}(t) \propto -(1/kT)\,\mathrm{d}P(t)/\mathrm{d}t, \qquad (3)$$

where the ($1/kT$) dependence arises from off resonance excitation [26]. Homodyne transient grating spectroscopy is even more sensitive, because it measures the intensity of a fourth beam diffracted from the transient grating formed in the sample [8]. The intensity of this fourth beam is given by [26]

$$S_{\text{homo}}(t) \propto (1/kT)^2|\mathrm{d}P(t)/\mathrm{d}t|^2. \qquad (4)$$

The phase modulation induced on a pulse traveling through the illuminated region can then be calculated by taking the second derivative of the changes in the index of refraction [23], which can be obtained from Eq. (1) giving

$$c(t) \propto -(1/kT)\,\mathrm{d}^2P(t)/\mathrm{d}t^2. \qquad (5)$$

This transient change in the polarization of the medium (a time-dependent refractive index) is the basis for the pulse compression method proposed by Kalosha and Ivanov [22] and carried out by Bartels et al. [23] using carbon dioxide molecules.

The magnitude of the maximum chirp that can be obtained from a sample during a revival can be estimated using the following set of expressions. First, the rotational distribution is characterized by the temperature of the sample through the

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[1] Eq. (1) also holds true for the $\Delta K = 0$ Raman transition of a symmetric top molecule, and can be applied to nearly symmetric top molecules provided the effective B constant $B_{\text{eff}} = (B+C)/2$ is used.

[2] For electronic states of gerade symmetry, Bosonic nuclei have $g_J = (2I+1)(I+1)$ if J is even, and $g_J = (2I+1)I$ if J is odd. Fermionic nuclei in gerade electronic states have $g_J = (2I+1)I$ if J is even, and $g_J = (2I+1)(I+1)$ if J is odd. For ungerade electronic states, the ratio of odd to even states is reversed. Here I is the nuclear spin of indistinguishable particles exchanged during rotation.

Boltzmann distribution. The maximum in the distribution is $J_{\max} = (kT/2\ Bch)^{0.5}$. The nth revival time is given by $\tau_R = (n/4Bc)$, and can be used to determine the rotational wave packet ‘dephasing’ rate when $n = 1$, $\gamma_R \sim J_{\max}/(\sqrt{2}\tau_R)$. With these expressions we can approximate the maximum polarization $P(\tau_R) \propto \exp(-\gamma_R^2 t^2)$. Using Eq. (5), we can obtain the magnitude of the chirp for the nth revival

$$c(\tau_R) \propto (-1)^n \beta N B \exp(-\tau_R/T_2), \tag{6}$$

where the temperature dependence expected from the $(1/kT)$ term in Eq. (5) is lost by the (kT) dependence of $(\gamma_R)^2$. This result is confirmed by calculations without approximations and experimentally. From Eq. (6) we learn that at time zero and all even revivals, the chirp is positive; the odd revivals lead to negative chirp, and because of the collisional dephasing T_2, the first revival will have the maximum amplitude. The width of the revivals can be obtained from $1/\gamma_R$ and is proportional to $(BT)^{-0.5}$, a result independently derived by Felker and Zewail [31]. For small molecules at room temperature and 1 atm pressure, the collisional dephasing time is about two orders of magnitude greater than the revival time, therefore the loss in magnitude due to collisions is small. The analysis presented here does not explicitly take into account the gain in UV pulse bandwidth resulting from self-phase and cross-phase modulation [25] in a capillary as used by Bartels et al. [23].

3. Experimental and results

Heterodyne detected transient grating measurements were recorded using a 50 fs, 1 kHz, and 800 nm regeneratively amplified titanium sapphire laser. A 60 ps transient obtained from 400 Torr of CO_2 gas at 293 K is shown in Fig. 1. The rotational revivals are observed every 21.33 ps, with half revivals in-between. The simulation of the data (using Eq. (3)) shows excellent agreement with the experiment. In order to match the heights of the full (Fig. 1b) and half revivals (Fig. 1c), we included the natural isotopes of oxygen.

Under strong-field conditions, there is a ‘kick towards alignment’ during the initial pulse [17]. While this ‘kick’ is not explicitly accounted for in our simulations, greater alignment leads to greater phase modulation, as more molecules are involved in the initial rotational ensemble. This results in an increase in the overall transient grating signal. Strong fields, however, can also induce a bending deformation [32], and hence a change in the observed revival and phase profile [15,33]. Fig. 2a

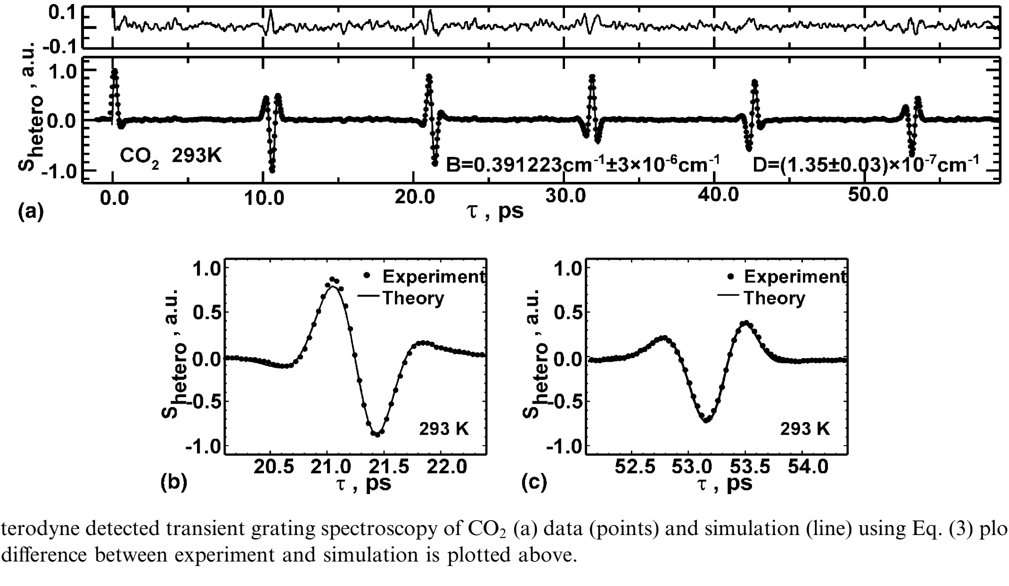

Fig. 1. Heterodyne detected transient grating spectroscopy of CO_2 (a) data (points) and simulation (line) using Eq. (3) plotted for first 60 ps; the difference between experiment and simulation is plotted above.

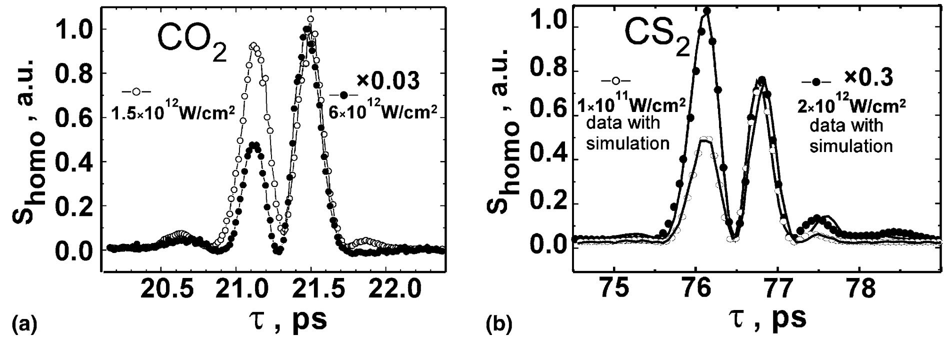

Fig. 2. Homodyne detected transient grating spectroscopy of molecules after strong-field excitation, (a) CO_2 at 1.5×10^{12} and 6×10^{12} W/cm^2 and (b) data and simulation (Eq. (4)) of CS_2 at 1×10^{12} and 2×10^{12} W/cm^2 showing evidence of bond deformation.

shows strong-field effects on the homodyne detected rotational revivals of CO_2 using the same laser system and the forward box geometry. A 3× increase in the pump laser intensity results in a 30× increase in signal. The shape of the revival is also distorted, because the CO_2 molecules are deformed in the presence of the strong field, this deformation can be beneficial for pulse compression. Fig. 2b shows similar effects in the first full recurrence of CS_2. The CS_2 Homodyne data were obtained with a 55 fs, 30 Hz, and 620 nm amplified CPM laser source in the forward box geometry, the setup has been described previously [8]. The structure of the recurrence was successfully simulated (using Eq. (4)) by assuming that 30% of the population experienced a bending deformation to 160° S–C–S bond angle ($B_{\text{eff}} = 0.11025$ cm^{-1}) [32]. The Gaussian transverse mode profile of the laser, upon focusing, delivers 70% of the intensity within the central 30%. The surrounding 70% of the molecules experience a lower intensity. The structural deformation experienced by the molecules can actually increase the magnitude of the phase modulation at the revival, however, further increases in laser power (above 10^{13} W/cm^2) can produce self-focusing and filamentation, generating fields strong enough to cause sample breakdown and plasma formation [34]. Under these conditions the rotational revivals are no longer observed.

Based on the accurate description of rotational revivals under weak- and strong-fields, we consider the conditions that optimize this effect for pulse shaping. The magnitude of $c(t)$ is independent of temperature, but proportional to $NB\beta$ (see Eq. (6)). Therefore, rotational cooling, as proposed by Bartels et al., should not enhance the phase modulation. The magnitude of phase modulation depends on the number density, which should be kept as high as possible while preventing condensation. Samples should have very large anisotropic polarizability, making linear molecules ideal candidates.

Finding the best conditions for compression of a given pulse will require balancing the maximum value of negative phase modulation and the time during which the chirp is within 10% of its minimum value, the ‘compression window’. Rotational cooling of the sample can be used to broaden the compression window. However, because of the square-root dependence, significant cooling would be required to achieve a significant effect, and this could lead to condensation when using the gas-filled capillary method [23]. With supersonic beam expansion it is possible to achieve significant cooling but then the number density would be significantly smaller, therefore decreasing the overall magnitude of phase modulation that can be achieved. It will be more practical to find a molecular sample with the appropriate rotational constant to get the desired compression window. Bulk samples at room temperature are the most practical and efficient for pulse compression.

Fig. 3a shows the calculated (Eq. (5)) effect of temperature on the compression window for CO_2. Notice that, as predicted above, the magnitude of the phase modulation is not affected by temperature but the width of the phase modulation window

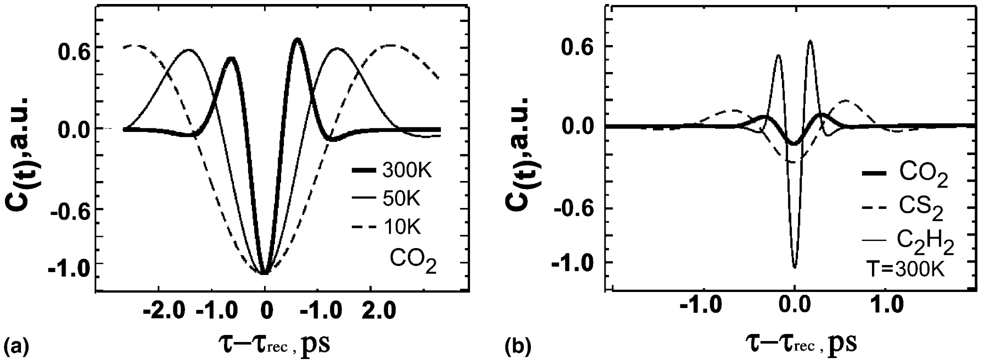

Fig. 3. Predicted phase modulation using Eq. (5) for (a) three different temperatures (constant density) and (b) for three different molecules (same density and 300 K).

is inversely proportional to temperature. Fig. 3b shows the calculated (Eq. (5)) phase modulation that can be obtained for several different molecules, C_2H_2, CO_2, and CS_2 at room temperature. This simulation takes into account the relative polarizabilities of the molecules and assumes identical numerical densities. Pulse compression, assuming positively chirped seed pulses, resulting from self phase modulation [25] in a capillary, takes place in the region where maximum negative chirp is observed. This occurs near the center of the first rotational revival.

Based on the pulse compression requirements, one must determine the temporal chirp in the medium that will produce the desired compression results. Here we assume that one can take advantage of the transient negative phase modulation within the compression window, and that a slight deviation from linear chirp is acceptable for producing pulse compression. For seed pulses longer than 40 fs, CS_2 has a first rotational revival at 76.5 ps [15], with a compression window of ~170 fs and can provide a factor of two greater phase modulations than CO_2, which has a compression window of ~90 fs. Unfortunately, CS_2 has a lower threshold for ionization than CO_2. We propose the use of acetylene molecules; the first revival is at 7.08 ps, with a compression window of ~50 fs. Another molecule to be considered for compressing short pulses is NO. It can provide 80% of the negative dispersion that acetylene can, it has a recurrence at (7.08 ps) and is less prone to fire or explosion.

4. Conclusions

In summary, rotational revival pulse compression requires molecules with high nonlinear susceptibility that can withstand strong-field excitation. The window available for phase modulation has to match the duration of the pulse being compressed. The number density should be kept as high as possible for more efficient pulse compression. The magnitude of phase modulation produced by a sample is essentially temperature independent. The laser intensity of the pump pulse must be strong enough to create a large degree of alignment while avoiding the destruction of the molecular medium.

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