P H Y S I C A L   R E V I E W   L E T T E R S

Amplification of Impulsively Excited Molecular Rotational Coherence

Philip J. Bustard,[1] Benjamin J. Sussman,[1,2,*] and Ian A. Walmsley[1,†]

[1]*Clarendon Laboratory, University of Oxford, Parks Road, Oxford, OX1 3PU, United Kingdom*
[2]*Steacie Institute for Molecular Sciences, National Research Council of Canada,*
100 Sussex Drive, Ottawa, Ontario, K1A 0R6, Canada

We propose a scheme for preparation of high-coherence molecular dynamics which are phase stable with respect to ultrashort pulses. We experimentally demonstrate an example of this scheme using a phase-independent, nanosecond-duration, pump pulse to prepare a rotational coherence in molecular hydrogen. This rotational coherence is made phase stable with respect to a separate source of ultrashort pulses by seeding. The coherence is used to generate spectral broadening of femtosecond probe radiation by molecular phase modulation.

A key challenge in coherent preparation of matter is to generate particular quantum electronic and vibrational excitations with a well defined phase with respect to ultrashort probe radiation. Typically, in time-resolved spectroscopic experiments, for example, this problem is solved by using a pump-probe geometry with both pulses derived from the same source [1]. Material coherence is generated by nonlinear action of the pump, with parameters selected to maximize desired nonlinear effects. Improved excitation by increasing the pump energy may be unattainable due to deleterious competing nonlinear effects such as field ionization, for example.

The purpose of this Letter is to introduce an alternative mechanism of phase-controlled coherence generation. This scheme involves ''coherence amplification'' of an impulsively excited molecular excitation by means of an independent laser with no optical phase relationship to the ultrafast probe radiation. This technique has potential application as a route to nonperturbative control of molecular dynamics. The approach adds to the existing toolbox of coherent control processes [1] including, for example, molecular alignment [2], two-photon absorption [3], and multiphoton ionization [4]. Here we introduce the principles of the technique, present a successful demonstration of phase-stable rotational coherence preparation in hydrogen gas where we use the coherence to generate sidebands on ultrashort probe radiation by molecular phase modulation (MPM), and give a theoretical interpretation. We first give an introduction to previous MPM research, and its relevance to the problem of phase-controlled coherence preparation.

MPM uses the rapid dynamical variation of electric susceptibility in an ensemble of coherently rotating or vibrating molecules to spectrally modify radiation. In MPM, coherent superpositions of molecular eigenstates are generated by means of a rapidly changing optical pump field; various approaches have been used to generate appropriate pump fields. Impulsive techniques use the rapid rise and fall of the ultrashort pump field to drive

molecular motion and then scatter probe radiation from the decaying excitation [5–7]. This approach requires high energy pulses, of duration less than the molecular oscillation period. In contrast, adiabatic techniques drive molecular motion at the beat frequency of applied pump and Stokes fields, resulting in broadband combs of Raman sidebands produced by phase modulation [8,9]; such sidebands have been used to synthesize long trains of few-fs pulses [10]. In this technique the length of the fs pulses within the train varies from shot to shot. Full interpulse phase locking has been achieved by using a ns-duration pulse and its second harmonic as pump pulses [11]. In an alternative approach, switched wave-packet techniques have been used to drive molecular motion by adiabatic turn-on and impulsive turn-off of the pump field [2]. Similar schemes have been studied theoretically [12,13].

Shot to shot control of material dynamics with respect to ultrafast probe radiation is critical for nonperturbative quantum control experiments: in MPM, this means controlling the phase of the time-varying electric susceptibility. In this article, as an example of our technique for coherence preparation, we demonstrate phase-stable MPM of fs pulses using a phase-independent pump pulse to amplify the seeded molecular excitation.

Figure 1 illustrates our scheme. A fs pulse is divided into two parts, a weak seed pulse and a delayed probe pulse. The seed pulse propagates through the gas, generating a small rotational coherence with a well defined phase, interacting with the molecules by impulsive stimulated Raman scattering (ISRS). For ISRS to occur, this pulse must have a duration τ_{se} less than the molecular oscillation period $\tau_{se} < T_{osc} = 2\pi/\Omega$ where Ω is the Raman frequency shift associated with the oscillations [5]. In the frequency domain this means that the pulse has a bandwidth spanning both rotational levels, with frequency pairs satisfying the two-photon Raman resonance condition, and will generate optical phonons (delocalized rotational quanta) in the interaction region. In the next step a longer, phase-independent pump pulse generated using a second
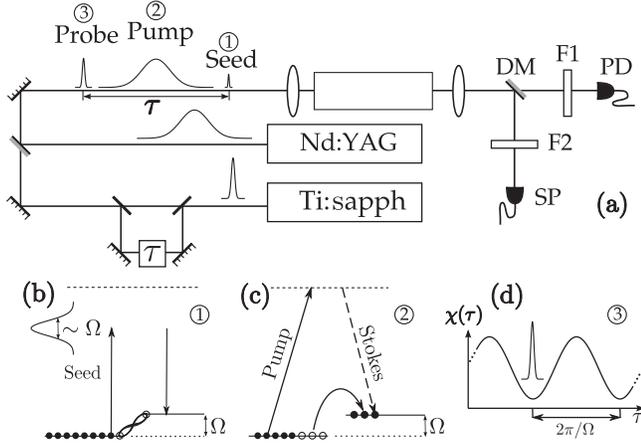
FIG. 1.   Diagram showing the experimental setup (a) and field-matter interactions (b,c,d) for phase-stable MPM. A Ti:sapphire chirped pulse amplifier laser produces a weak seed pulse and a delayed probe pulse; a Nd:YAG laser generates the pump pulse. (b) The seed excites a rotational coherence by ISRS. (c) The coherence is enhanced using a phase-independent pump pulse. (d) The probe pulse is spectrally broadened by MPM.

laser enhances the coherence by transient stimulated Raman scattering (SRS). To satisfy the condition for transient SRS, the pump pulse must have duration τ_{pu} satisfying $\tau_{pu} < \sqrt{gL}/\Gamma$ where Γ is the collisional dephasing rate, g is the Raman gain coefficient, and L is the length of the excited medium [14]. In an unseeded gas, such a pump pulse will generate a Stokes field and rotational coherence with a random phase due to initiation by spontaneous Raman scattering [14]. However, when the medium is initially seeded by ISRS, the resulting material excitation is driven parametrically by the pump, transferring energy to the medium, and to the Stokes field with frequency $\omega_{St} = \omega_{pu} - \Omega$. The resulting excitation is phase coherent with respect to the fs pulse source and may be used as an efficient phase modulator of the final fs pulse (the probe). In the final step, the probe propagates through the coherently rotating molecules and is spectrally broadened or shifted due to the rapid variation of the electric susceptibility $\chi(\tau)$ caused by the molecular motion. The MPM process may be used to imprint sidebands on, or to continuously spectrally broaden, the probe spectrum depending on its initial temporal form and arrival time with respect to the molecular motion.

We experimentally demonstrated seeding of rotational motion by ISRS, followed by coherence enhancement using a phase-independent pump pulse, and subsequent phase modulation of probe pulses. We used a home-built 1 W, 2 kHz chirped pulse amplifier Ti:sapphire laser system generating $\tau_{seed} \sim 55$ fs pulses centered at 795 nm as a source of seed and probe pulses. Pump pulses of up to 70 mJ at 532 nm were generated by a 50 Hz Quanta-Ray LAB-130-50 frequency-doubled Q-switched Nd:YAG laser system with pulse duration $\tau_L \sim 10$ ns, running in an unseeded configuration. The lasers were synchronized

electronically. The seed and probe beams were linearly polarized in orthogonal directions. The pump beam was circularly polarized to give maximum gain for the rotational Raman transition [15]. All beams were collimated to a $1/e^2$ intensity beam waist $w_0 \sim 3$ mm and focused collinearly into the 90 cm gas cell using a 50 cm singlet lens. The cell was tilted at an angle to avoid optical feedback from the cell windows. After the cell, the seed and probe beams were spectrally separated from the pump beam and its Raman sidebands using a dichroic mirror (DM) and Schott glass filter (F2). The probe beam was spatially diffused before detection using a spectrometer (SP). The Stokes sideband of the pump laser was spectrally separated from the pump pulse and any higher order Raman sidebands using interference filters (F1), before detection using a fast response photodiode (PD).

Hydrogen (H_2) gas was selected because of its rapid rotational period ($T_{osc} = 57$ fs) on the $S_{00}(1)$ transition, comparable to the pulse duration of our Ti:sapphire laser system. This is the dominant Raman transition at room temperature because $\simeq 66\%$ of population is in the ($v = 0$, $J = 1$) level. Hydrogen has low dispersion in the visible and near-IR, making it ideal for use with fs pulses.

We investigated the effect of seeding on generation of the pump rotational-Stokes 1 sideband (RS1). The measured RS1 signal at 549 nm is plotted as a function of pump energy in hydrogen at 760 torr for two cases (Fig. 2). In the first case, only the 532 nm pump pulse propagated through the hydrogen sample (unseeded, red crosses). In the second case, a seed pulse of energy 12 μJ propagated through the cell 1 ns before the rise time of the pump pulse (seeded, blue circles). The SRS is initiated by spontaneous Raman scattering in the unseeded experiment. A fully quantum treatment shows that the spontaneous quantum noise which initiates unseeded SRS is equivalent to one optical phonon per mode [16]. For seeded SRS the impulsively generated coherence must exceed this limit. The requisite seed energy depends on the molecular polarizability, the interac-
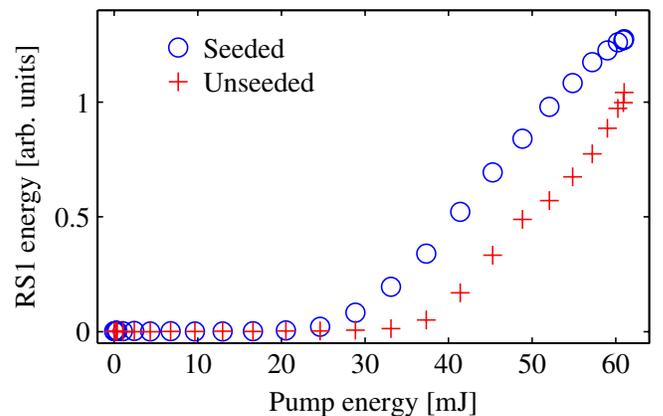

FIG. 2 (color online).   Rotational-Stokes 1 growth at 549 nm in hydrogen at 760 torr as a function of pump pulse energy for seeded (blue circles) and unseeded (red crosses) cases. Stokes growth is more efficient when a 12 μJ seed is used.

tion region geometry, and the seed pulse profile. Seeding was observed to increase the efficiency of RS1 generation for energies of a few μJ; this effect began to saturate for energies above 12 μJ. All subsequent experiments were carried out with this seed energy to minimize shot to shot fluctuations.

The properties of the material excitation, after enhancement by SRS using the pump pulse, were investigated using fundamental or frequency-doubled probe pulses from the Ti:sapphire laser. The seed pulse propagated through the hydrogen sample, followed by the temporally overlapped pump and probe pulses. Figure 3 shows the spectrum of the 24 μJ, 800 nm probe pulse after propagation through the cell. Rotational-Stokes 1 (prRS1) and anti-Stokes 1 (prRAS1) sidebands were generated on the probe pulse when the pump pulse was on; if the pump pulse was blocked, the probe spectrum was unchanged. When a narrow band 398 nm probe pulse was used, sidebands from prRAS2 to prRS2 were generated (Fig. 3, inset). These results demonstrate that the pump pulse creates a rotational coherence capable of generating significant phase modulation on probe radiation. The phase modulation of the 400 nm probe pulse is more efficient because it is closer to single-photon resonance with the hydrogen molecules and so the field-matter interaction is stronger. The probe modulation efficiency was measured to be independent of the probe energy, confirming that the probe propagates in the linear regime.

With the pump and seed pulses on, the 800 nm probe pulse spectrum was measured as a function of delay, in 8 fs steps, relative to the seed pulse from an initial delay of 3.9 ns. Delay-dependent oscillations are apparent in the probe spectrum [Figs. 4(a)–4(c)]. A spectral peak at $\Omega = 587$ cm^{-1}, corresponding to the $S_{00}(1)$ transition, is appar-

ent in the Fourier spectra of the probe spectrum line outs [Figs. 4(d) and 4(e)]. The delay-dependent oscillations in the probe spectrum demonstrate that the rotational excitation is phase coherent with the probe pulse. When the seed pulse is not present, the SRS is initiated by spontaneous Raman scattering. As a result, the phase of the rotational excitation varies randomly from shot to shot and no delay-dependent oscillations are seen: the excitation is not phase correlated with the probe pulse. However, in the seeded case shown here (Fig. 4), the SRS is parametrically initiated by the impulsively seeded coherence and so the rotational excitation is phase correlated with the probe pulse. The phase coherence with respect to the fs laser is maintained throughout the coherence enhancement despite the use of a phase-independent pump laser.

We describe the system using a semiclassical model for the molecular ensemble of number density N, with two rotational levels, separated by $\hbar\Omega$ in energy, and coupled by the molecular polarizability interaction Hamiltonian, $H_{int} = -\frac{1}{2}\hat{\alpha}E^2$ where E is the full electric field and $\hat{\alpha}$ is the polarizability operator. We define analytic fields $A_{se}(z,\tau)$, $A_{pu}(z,\tau)$, $A_{St}(z,\tau)$, and $A_{pr}(z,\tau)$ for the seed, pump, Stokes, and probe, respectively, where z is the propagation coordinate and τ is the comoving time coordinate. Using the Liouville equation for the density matrix evolution, and the slowly varying envelope wave equation, we obtain coupled equations for the field and excitation $Q(z,\tau) = \rho_{12}(z,\tau)e^{i\Omega\tau}$ where ρ_{12} is the off-diagonal density matrix element [13,14]. For fs pulses,

$$\partial_\tau\rho_{12}(z,\tau) = i(\Omega + i\Gamma)\rho_{12} - i\kappa_{se,pr}|A_{se,pr}(z,\tau)|^2,$$
$$\partial_z A_{se,pr}(z,\tau) = -i\beta_{se,pr}(\rho_{12} + \rho_{12}^*)A_{se,pr}(z,\tau), \tag{1}$$

where Γ is a phenomenological damping constant, $\kappa = \frac{\alpha_{12}(\omega)}{4\hbar}$ and $\beta = \frac{\omega N\alpha_{12}(\omega)}{2\epsilon_0 c}$. For the Stokes field,
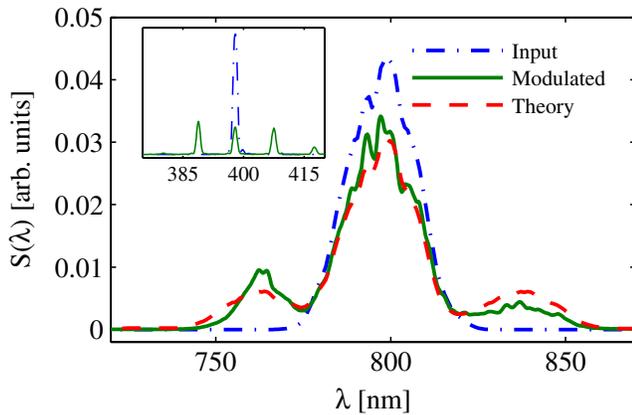

FIG. 3 (color online).   The 800 nm probe spectrum after propagation through the seeded hydrogen gas at 1500 torr with (solid green line) and without (dash-dotted blue line) the pump. MPM broadens the probe spectrum when the pump is on. The theory plot (dashed red line) is generated by numerical solution of the equations describing the one-dimensional Raman field-matter interaction. Inset: 400 nm probe spectrum with (solid green line) and without (dash-dotted blue line) the pump.
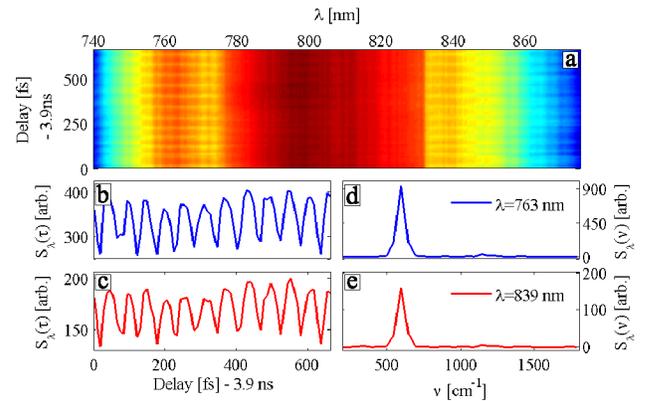

FIG. 4 (color online).   (a) Probe spectrum as a function of delay relative to the seed pulse from an initial delay of 3.9 ns. Line outs from the probe spectrum at $\lambda = 763$ nm (b) and $\lambda = 839$ nm (c). Peaks at Ω in the Fourier spectrum of the line outs (d), (e). The delay-dependent oscillations at Ω demonstrate phase coherence of the excitation with respect to the probe pulse.

$$\partial_\tau Q(z, \tau) = -\Gamma Q - i\kappa_{St}A_{pu}(\tau)A_{St}^*(z, \tau),$$
$$\partial_z A_{St}(z, \tau) = -i\beta_{St}A_{pu}(\tau)Q^*(z, \tau). \quad (2)$$

We assume no depletion of the lower rotational level, and no depletion of the seed or pump pulses [14].

We consider a δ-function form for the seed pulse, $A_{se}(z, \tau) = \delta(\tau - \eta_1)$, with no initial material excitation, $\rho_{12}(z, \tau < \eta_1) = 0$, and no initial Stokes field, $A_{St}(z, \tau < \eta_1) = 0$. In the absence of a pump pulse,

$$\rho_{12}^{npu}(z, \tau) = -i\kappa_{se}e^{-\Gamma(\tau-\eta_1)}e^{i\Omega(\tau-\eta_1)} \quad (3)$$

for the excitation after the seed propagation. Assuming a pump pulse $A_{pu}(\tau)$ contained in a time window (η_1, η_2), and using $\rho_{12}^{npu}(z, \eta_1)$ as an initial condition, we continue with piecewise integration of (2) [14]. For $\tau > \eta_2$,

$$\rho_{12}^{wpu}(z, \tau) = -i\kappa_{se}e^{-\Gamma(\tau-\eta_1)}e^{i\Omega(\tau-\eta_1)}I_0(\sqrt{4pz}), \quad (4)$$

where $I_n(x)$ is the modified Bessel function of order n, $p = \int_{\eta_1}^{\eta_2} \kappa_{St}\beta_{St}|A_{pu}(\tau')|^2 d\tau'$. Using (4) we solve for the probe field propagating through the excited medium in the limit where the probe does not significantly change the excitation, $|\kappa_{pr}|A_{pr}|^2| \ll |\Omega\rho_{12}|$. In this linear limit,

$$A_{pr}(z, \tau) = A_{pr}(0, \tau)\exp[-i\delta_{mod}\sin(\Omega(\tau - \eta_1))] \quad (5)$$

for $\tau \geq \eta_2$ where

$$\delta_{mod}(z, \tau) = 2\beta_{pr}\kappa_{se}e^{-\Gamma(\tau-\eta_1)}(z/p)^{1/2}I_1(\sqrt{4pz}). \quad (6)$$

Two insights are clear from these results. First, comparison of solutions (3) and (4) shows that the pump enhances the seeded excitation by a factor $I_0(\sqrt{4pz})$ due to SRS. The excitation generated by the seed parametrically excites further Raman scattering events when the pump propagates through the seeded medium. The onset of SRS generates a Stokes field and enhances the molecular coherence (4). Second, the relative phase of the probe pulse and material excitation is independent of the pump phase, depending only on the seed-probe delay time $(\tau - \eta_1)$. Provided the ultrashort pulse satisfies the limit for ISRS, a phase-independent pump pulse can be used to enhance the coherence by transient SRS.

The analytic results given above are valid only in the limit of an undepleted pump pulse, and an undepleted molecular ground state. However, in the experimental regime discussed here, these assumptions are no longer valid. To obtain a comparison with experiment we therefore numerically solve the planar propagation problem, including the pump field and second rotational-Stokes sideband. Dispersion is neglected. In the model, the propagation distance is set to twice the confocal parameter, and all other measured experimental parameters are used. Figure 3 shows good agreement between the theoretical and experimental plots, resulting in a modulation depth of $\delta_{mod} \simeq 1$. The asymmetry in the experimental spectrum may be attributable to dispersive effects, resulting in vari-

able modulation efficiency across the probe spectrum. This effect was previously reported [17].

In conclusion, we have proposed and demonstrated a scheme for generation of a macroscopic molecular coherence which is phase stable with respect to ultrashort pulses, despite use of a phase-independent pump laser to prepare the sample. The technique has potential application as a route to generation of large molecular coherence in coherent control experiments. This scheme is an attractive candidate for spectral shifting and broadening of broadband pulses because of its relative simplicity and linearity in the probe pulse energy. Improved modulation may be possible by implementing the technique in gas-filled, hollow-core capillaries or photonic crystal fibers with higher Raman gain than free-space propagation.

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*ben.sussman@nrc.ca
†walmsley@physics.ox.ac.uk

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