Enhancement of phase-conjugate reflectivity using Zeeman coherence in highly degenerate molecular systems

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A comprehensive theoretical analysis is developed for the vectorial phase conjugation using resonant four-wave mixing (FWM) in a highly degenerate rotational vibrational molecular system. The dynamic Stark shifts, saturation, and Doppler broadening are included for a realistic analysis. It is shown that the electromagnetically induced multilevel coherence controls the nonlinear wave mixing yielding interesting results for the phase conjugate (PC) reflectivity. It turns out that the efficiency of the PC reflectivity is decided by the relative phase of the Zeeman coherence and the population grating. When these two contributions are aligned in phase by a small detuning of the pump frequency, a large PC reflectivity (∼20%) is obtained with moderate pump intensity (∼500 mW/cm²).

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I. INTRODUCTION

For remote sensing and other imaging applications using mid-infrared (MIR) wavelengths optical phase conjugation (OPC) is required to correct phase aberration and improve the image quality in a turbulent atmosphere. However, the ideal OPC material with fast response time is rare for the middle infrared part of the spectrum. To obtain a phase conjugate reflectivity (few percent) using degenerate four wave mixing (DFWM) in transparent solid materials requires very high intensity. An intensity of ∼ a few MW/cm² was used to obtain 2% reflectivity in germanium [1]. On the other hand, resonantly enhanced four-wave mixing in highly absorbing molecular systems has shown great promises. Significant reflectivity was found using DFWM with 10.6 µm CW and pulsed CO₂ laser in absorbing SF₆ molecules [2–4]. The recent development of tunable middle infrared quantum cascade lasers (QCLs), revives the interest for efficient phase conjugation using resonant nonlinearity of rotational vibrational (RV) transitions. In this paper we explore the possibility of enhancing the phase conjugate (PC) reflectivity using the Zeeman coherence of a two-level highly degenerate Doppler broadened RV system.

Vectorial phase conjugation using Zeeman coherence in degenerate two-level and multilevel atomic systems has been highly successful [4–9]. Under steady state excitation, the PC reflectivity $R$ is proportional to $|\kappa/\text{Im}\chi|^2$, where, $\kappa$ is the FWM gain coefficient and $\text{Im}\chi$ is the absorption coefficient for the generated (signal) wave [7,9,10]. Very high reflectivity is obtained for the visible and near infrared diode lasers by reducing $\text{Im}\chi$ and enhancing $\kappa$ using electromagnetically induced transparency (EIT) or dark resonance of atomic transitions [11–16]. There has been extensive experimental and theoretical research on the significance of Zeeman coherence in vectorial phase conjugation. Lam and Abrams [17] presented a detailed theory of phase conjugation describing the role of Zeeman coherence and population grating contributions for a two-level degenerate Doppler broadened atomic system in absence of saturation and dynamic level shifts. Using four-level and three-level (A-type) Doppler broadened atomic systems Ducloy [4,5] has demonstrated the role of two photon induced Raman coherence in vectorial phase conjugation with arbitrary pump and probe intensities. Agrawal [9] has developed a nonperturbative treatment to study the Zeeman coherence effect in phase conjugation using a A-type three-level degenerate system in absence of Doppler broadening. In spite of the extensive research, a comprehensive theory of vectorial phase conjugation taking into account the effect of saturation and the dynamic level shifts in a Doppler broadened degenerate rotational vibrational molecular system with arbitrary angular momentum is still missing. The purpose of the present work is to develop such a comprehensive theory for the phase conjugation of middle infrared wavelengths.

In the absence of a strong electric or magnetic field, the molecular eigenstates are degenerate in the projection of their rotational angular momentum. Using two photon (Raman-type) interaction with right and left circularly polarized waves the Zeeman coherence can be established within the manifold of degenerate sublevels belonging to a rotational vibrational eigenstate. Therefore, for the phase conjugation in RV molecular systems we may expect to reproduce the results of the degenerate atomic systems. However, compared to an atomic system, the very different decay dynamics of the induced coherence in a pure rotational vibrational infrared transition calls for a separate treatment for the following reasons:

1. Contrary to the electronic excitations, the infrared spontaneous emission rates (∼100 Hz) are significantly weaker than the decay rates of population (∼350 kHz at ∼100 mTorr pressure) due to state changing collisions. In such cases, the decay of the sublevel coherence is dominated by the collision induced thermalization of rotational vibrational levels [18,19].

2. Pure phase changing collisions, common in electronic excitations, are rare in infrared rotational vibrational transitions.

3. In many situations, the state changing collisional rates in the ground and excited vibrational manifold are comparable.

It is easy to see that the above decay characteristics of RV transitions will not permit an ideal dark resonance as in atoms. However, our recent study has shown that in $Q$-type ($J \rightarrow J$) RV transition, the electromagnetically...
induced transparency arises due to an interference of the strongly coupled \( \Lambda \)- and \( V \)-type excitation channels in an ‘\( N \)'-type configuration [20]. In this paper we like to investigate how the multilevel coherence in an ‘\( N \)'-type configuration shapes the PC reflectivity in presence of saturation and dynamic level shifts.

For the vectorial phase conjugation we consider orthogonal circular polarizations for the forward and backward pump beams. The spatial hole burning, which severely degrades the PC reflectivity, is avoided with the orthogonal pump waves. To minimize the angle (maximize the overlap) between the pump and probe beams, we choose the polarizations of the forward pump and probe to be orthogonal. The pump and probe waves are assumed to be nearly resonant with the molecular transition, i.e., their detunings are much smaller than the Doppler width. With the choice of orthogonally polarized copropagating pump and probe waves, Zeeman coherence is established within the manifold of degenerate sublevels of the rotational states for the entire Doppler velocity group. In the following, we derive an analytic expression for the third-order polarization responsible for the four-wave mixing in a RV molecular transition. There are two main contributions to the FWM polarization, the Zeeman coherence and the cross population. Our numerical analysis, which takes into account the FWM polarization, the Zeeman coherence and the cross polarization, reveals that these two contributions add in opposite phases severely degrading the PC reflectivity. We show here, how the population and the Zeeman coherence contributions can be aligned in phase by a small detuning of the pump within the Doppler profile to significantly improve the PC reflectivity.

II. GENERATION OF PHASE CONJUGATE WAVE IN A DEGENERATE RV SYSTEM

Figure 1(a) shows how the Zeeman sublevels of overlapping ‘\( N \)'-type configuration can be coupled using nearly resonant right and left circularly polarized waves in a two-level RV system with the rotational angular momentum \( J \). Figure 1(b) shows the arrangement for generating phase conjugate reflection using FWM with the circularly polarized pump and probe waves. With a left circular probe wave, the conservation of angular momentum requires the signal or the PC wave to be right circularly polarized.

The nonlinear polarization at frequency \( \omega_S = \omega_P - \omega_P + \omega_B \) responsible for the generation of a right circularly \( (\sigma^+) \) polarized phase conjugate signal wave is given by

\[
P(\omega_S) = \sum_M \sigma_{[gM]}(\omega_S)|\mu_{gM}^+|g_M\rangle. \tag{1}
\]

Here, \( M \) is the quantum number for the projection of the rotational angular momentum \( J \) and \( |g_M\rangle \) represents the \( M \)th Zeeman sublevel of the ground state. Similarly \( |e_{M+1}\rangle \) represents the \( M + 1 \)-th Zeeman sublevel of the excited state. \( \sigma_{[gM]}(\omega_S)|\mu_{gM}^+|g_M\rangle \) is the off-diagonal density matrix representing the coherent superposition of the ground \( |g_M\rangle \) and the excited \( |e_{M+1}\rangle \) Zeeman sublevels. \( \mu_{[gM]}(\omega_S) \) is the corresponding transition dipole matrix element. \( \sigma_{[gM]}(\omega_S)|\mu_{gM}^+|g_M\rangle \) is generated by the scattering of the pump beams from the modulation of either the Zeeman coherence or population. The density matrix elements representing the molecular coherence under the action of various optical fields can be described by the coupled density matrix equation of the form [21]

\[
\frac{d\sigma_{nm}(\omega)}{dt} + i \Delta_{nm}(\omega)\sigma_{nm}(\omega)
= i \sum_{\nu,v} E^{+}_{\nu} \left[ \mu_{\nu,v}^+\sigma_{nm}(\omega - \omega_\nu) - \sigma_{nm}(\omega - \omega_\nu)\mu_{\nu,v} \right] \\
+ i \sum_{\nu,v} E^{-}_{\nu} \left[ \mu_{\nu,v}\sigma_{nm}(\omega + \omega_\nu) - \sigma_{nm}(\omega + \omega_\nu)\mu_{\nu,v} \right], \tag{2}
\]

where \( \sigma_{nm}(\omega) \) is the density matrix elements between states \( |n\rangle \) and \( |m\rangle \), \( E_i \) are the optical fields at frequency \( \omega_i \) and \( \mu_{\nu,v} \), etc., are the transition dipole moments. The detuning \( \Delta_{nm}(\omega) = \omega - \omega_{mn} - i\gamma_{nm} \) is the relaxation rate for the coherence described by \( \sigma_{nm} \). Under steady state optical excitation the solutions of Eq. (2) can be found using a diagrammatic technique developed in Ref. [21]. Consistent with the phase matching condition, using this diagrammatic method in the following sections we derive the expression for \( \sigma_{[gM]}|\mu_{gM}^+|g_M\rangle \) generated by various possible scattering processes. An example of our graphical derivation is worked out in the Appendix for the scattering of backward pump \( E_B \) from the multilevel Zeeman coherence induced by the Raman coupling of the forward pump with the probe wave.

(a) Scattering of the forward pump \( E_F \) from the modulation of population is shown schematically in Fig. 2(a). The scattering process generates a phase matchable contribution to the FWM polarization \( \sigma_{[gM]}|\mu_{gM}^+|g_M\rangle \) given by

\[
D_\Sigma^+|gM\rangle|\mu_{gM}^+\rangle E_F N^e_{M+1}(\omega_B - \omega_P) - D_\Sigma^-|gM\rangle|\mu_{gM}^-\rangle E_F N^e_{M}(\omega_B - \omega_P). \tag{3}
\]

\( N^e \) refers to the Fourier component of the population at frequency \( \omega_B - \omega_P \) in the ground
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\[
D_1 = (\omega_B - \omega_P - i\gamma_c)^{-1}
\]

\[
D_2 = (\omega_B - \omega_P - i\gamma_c)^{-1}
\]

\(\gamma_c\) and \(\gamma_c\) are the decay rates for the populations in the excited and ground rotational vibrational states, respectively. \(D_1\), \(D_2\), and \(D_B\) are the single photon resonant denominators associated with the signal wave, the probe wave, and the backward pump wave, respectively. The single photon resonant denominators are given by \(D_j(\omega_j) = (\omega_j - \omega_0 - i\gamma_j)^{-1}\), where \(\omega_j\) refers to \(\omega_S\), \(\omega_P\), \(\omega_B\), or \(\omega_F\). \(\omega_0\) is the resonant frequency for the rotational vibrational transition, \(\gamma_j\) is the relaxation rate for the coherence described by the density matrix \(\sigma_{e(\omega_j)}^{\epsilon(\omega_j)}\) between the ground and excited \(\text{Zeeman sublevels} \{g_M\}\) and \(\{e_M\}\). In many situations of infrared rotational vibrational transitions in the absence of pure phase changing collisions, the decay rate \(\gamma_j\) is given by \(\approx \frac{1}{2}(\gamma_c + \gamma_c)\). Since the product of the resonant denominators in Eq. (4) is a sensitive function of Doppler detunings, the Doppler averaging over all possible velocity groups will generate significant contribution only at the line center.

(b) Scattering of the backward pump \(E_B\) from the ground and excited \(\text{Zeeman coherence is described schematically in Fig. 2(b). The phase-matching contribution to the FWM polarization generated by this scattering process is given by}

\[
D_3 D_3 D_3 B(\omega_B - \omega_P)\mu^{\epsilon(\omega_B)}_{\epsilon(\omega_B)} \mu^{\epsilon(\omega_B)}_{\epsilon(\omega_B)} \mu^{\epsilon(\omega_B)}_{\epsilon(\omega_B)} \\
\times (N_{M-1}^R - N_{M-1}^S) E_F E_B E_P.
\]

The Fourier component of the ground and excited \(\text{Zeeman coherence is described in the Appendix). Substituting these solutions in Eq. (5) leads to the following expression for the FWM polarization:

\[
D_3 D_3 D_3 B(\omega_B - \omega_P)\mu^{\epsilon(\omega_B)}_{\epsilon(\omega_B)} \mu^{\epsilon(\omega_B)}_{\epsilon(\omega_B)} \mu^{\epsilon(\omega_B)}_{\epsilon(\omega_B)} \\
\times (N_{M-1}^R - N_{M-1}^S) E_F E_B E_P.
\]

or excited state \(\text{Zeeman sublevel} M\). The populations of population \(N_{M-1}^R(\omega_B - \omega_P)\) and \(N_{M-1}^S(\omega_B - \omega_P)\) in the ground and excited states are generated by the interference of the forward propagating probe wave \(E_P\) with the counter propagating pump wave \(E_B\). This contribution has been described as cross population by Lam and Abrams [17]. Graphical solutions (see example in the Appendix) of the relevant density matrix elements under steady state excitation lead to the following expression for the contribution given in Eq. (3):

\[
D_3 D_3 D_3 B(\omega_B - \omega_P)\mu^{\epsilon(\omega_B)}_{\epsilon(\omega_B)} \mu^{\epsilon(\omega_B)}_{\epsilon(\omega_B)} \mu^{\epsilon(\omega_B)}_{\epsilon(\omega_B)} \\
\times (N_{M-1}^R - N_{M-1}^S) E_F E_B E_P.
\]
\[ + D_SD_D_F \mu^+_{\langle |e_{M\perp}|, |e_{M\perp}| \rangle \mu^-_{\langle |e_{M\perp}|, |e_{M\perp}| \rangle} \times (N_{M+1} - N_{M}^F) E_F E_B E_P^* \]  

(6)

The resonant denominators are given by

\[ D_3 = (\omega_F - \omega_P - i\gamma_e)^{-1} \]  
\[ D_4 = (\omega_F - \omega_P - i\gamma_e)^{-1}. \]

Note that here we have used \( \gamma_e \) and \( \gamma_e \) for the relaxation of excited and ground state Zeeman coherence \( \sigma_{\langle |e_{M\perp}|, |e_{M\perp}| \rangle} \) and \( \sigma_{\langle |g_{M\perp}|, |g_{M\perp}| \rangle} \). As pointed out in the Introduction, this is consistent with the dominant decay mechanism of the sublevel coherence due to collision induced thermalization of population. It should be noted that pure orientational relaxations are less common for a reasonable pressure of a few hundred mTorr at room temperature. Moreover, for sufficiently large rotational angular momentum \( J \) compared to the nuclear spin, hyperfine depolarization is negligible and the decay rates are independent of the magnitude \( J \) [22]. Since the forward pump \( E_F \) and the probe wave \( E_P \) are copropagating the resonant denominators \( D_3 \) and \( D_4 \) are Doppler free. However, the products \( D_SD_F \) or \( D_SD_B \) involve counter propagating resonant fields and are subject to Doppler broadening. The result of Doppler averaging over all velocity groups yields significant contribution only at the line center. The superposition of the cross population [Eq. (4)] and the Zeeman coherence [Eq. (6)] contributions define the FWM polarization responsible for the generation of a phase conjugate wave. As we will see later in our numerical analysis, these two terms contribute with opposite phases reducing the PC reflectivity. In the following we describe two more terms in the FWM polarization \( \sigma_{\langle |g_{M\perp}|, |g_{M\perp}| \rangle}(\omega_S) \). These terms are generated by the coherent interaction of the phase conjugate (PC) signal wave with the forward and backward pumps and are responsible for the dynamic level shifts and EIT type transparency for the signal wave.

(c) Coherent interaction of the PC wave with copropagating backward pump is described schematically in Fig. 2(c). The interaction generates a contribution to PC polarization:

\[ D_SD_B \mu^+_{\langle |e_{M\perp}|, |e_{M\perp}| \rangle} \times (N_{M+1} - N_{M}^F) E_B E_P^* \]  

(7)

\[ \times (N_{M+1} - N_{M}^F) E_F E_B E_P^*. \]

The Fourier component of ground and excited state Zeeman coherence \( \sigma_{\langle |g_{M\perp}|, |g_{M\perp}| \rangle} \) and \( \sigma_{\langle |e_{M\perp}|, |e_{M\perp}| \rangle} \) at frequency \( (\omega_S - \omega_B) \) is generated by the coherent coupling of the right circularly polarized signal wave \( E_S \) with the left circularly polarized backward pump \( E_B \). Substituting the steady state solution for the density matrix \( \sigma_{\langle |g_{M\perp}|, |g_{M\perp}| \rangle}(\omega_S - \omega_B) \) and \( \sigma_{\langle |e_{M\perp}|, |e_{M\perp}| \rangle}(\omega_S - \omega_B) \) in Eq. (7) we get the following contribution to the FWM polarization at frequency \( \omega_S \):

\[ D_SD_B \mu^+_{\langle |e_{M\perp}|, |e_{M\perp}| \rangle} \times (N_{M+1} - N_{M}^F) E_F E_B \sigma_{\langle |g_{M\perp}|, |g_{M\perp}| \rangle}(\omega_S - \omega_B). \]

(9)

This term originates due to coherent scattering of the forward pump \( E_F \) from the modulation of population \( N_{M}^F(\omega_S - \omega_F) \) and \( N_{M}^F(\omega_S - \omega_F) \) in the ground and excited states due to interference of counter propagating forward pump \( E_F \) and the signal wave \( E_S \). Using the steady state solution of the density matrix we get

\[ D_SD_B \mu^+_{\langle |e_{M\perp}|, |e_{M\perp}| \rangle} \times (N_{M+1} - N_{M}^F) E_F E_B \sigma_{\langle |g_{M\perp}|, |g_{M\perp}| \rangle}(\omega_S - \omega_B). \]

(10)

\[ \times (N_{M+1} - N_{M}^F) E_F E_B E_P^*. \]

The first term in Eq. (10) contributes to the dynamic Stark shift induced by the forward pump. The second term represents the contribution due to coherent coupling of the signal wave with the counter propagating forward pump, and is therefore sensitive to Doppler detuning. Under Doppler averaging this contribution becomes significantly smaller than the Doppler free contribution described earlier in Eq. (8).

(e) The saturable single photon polarization for the signal wave is

\[ D_SD_B \mu^+_{\langle |e_{M\perp}|, |e_{M\perp}| \rangle} \times (N_{M+1} - N_{M}^F) E_S. \]

(11)

Collecting all contributions from Eqs. (3)–(11), and using Eq. (1) we get the nonlinear polarization for the phase conjugate wave:

\[ P(\omega_S) = \chi(\omega_S) E_S + \kappa(\omega_S) E_P^*. \]

(12)
where

\[
\chi(\omega_S) = \frac{D_S |\mu_+^{[gS]|e_{M+1}}|^2}{Z} \times \left[ \left( N^e_{M+1} - N^g_M \right) \right.
\]
\[
- D_S D_B |\Omega^B_{[eS]|e_{M+1}}|^2 \left( N^e_{M+1} - N^g_M \right) - D_S D_B |\Omega^B_{[gS]|e_{M+1}}|^2 \left( N^e_{M+1} - N^g_M \right)
\]
\[
- \left. D_F^* (D_7 + D_8) |\Omega^F_{[eS]|e_{M+1}}|^2 \left( N^e_{M+1} - N^g_M \right) \right].
\]

(13)

The real and imaginary part of the susceptibility \(\chi(\omega_S)\) determines the dispersion and the absorption of the signal wave, respectively. The gain coefficient \(\kappa(\omega_S) = \kappa_Z(\omega_S) + \kappa_P(\omega_S)\), where the Zeeman coherence gain \(\kappa_Z\) is given by

\[
\kappa_Z(\omega_S) = \frac{D_S \mu_+^{[gS]|e_{M+1}}}{Z} \times \left[ D_S D_F |\Omega^F_{[gS]|e_{M+1}}|^2 |\Omega^B_{[eS]|e_{M+1}}|^2 \mu_+^{[gS]|e_{M+1}} \left( N^e_{M+1} - N^g_M \right)
\]
\[
- D_S D_F |\Omega^F_{[gS]|e_{M+1}}|^2 |\Omega^B_{[eS]|e_{M+1}}|^2 \mu_+^{[gS]|e_{M+1}} \left( N^e_{M+1} - N^g_M \right)
\]
\[
- D_S D_F |\Omega^F_{[gS]|e_{M+1}}|^2 |\Omega^B_{[eS]|e_{M+1}}|^2 \mu_+^{[gS]|e_{M+1}} \left( N^e_{M+1} - N^g_M \right)
\]
\[
+ D_S D_F |\Omega^F_{[gS]|e_{M+1}}|^2 |\Omega^B_{[eS]|e_{M+1}}|^2 \mu_+^{[gS]|e_{M+1}} \left( N^e_{M+1} - N^g_M \right).
\]

(15)

and the gain \(\kappa_P\) due to the modulation of population is given by

\[
\kappa_P(\omega_S) = \frac{D_S \mu_+^{[gS]|e_{M+1}}}{Z} \times \left[ D_S (D_B - D_F) |\Omega^F_{[gS]|e_{M+1}}|^2 |\Omega^B_{[eS]|e_{M+1}}|^2 \mu_+^{[gS]|e_{M+1}} \left( N^e_{M+1} - N^g_M \right)
\]
\[
+ D_S (D_B - D_F) |\Omega^F_{[gS]|e_{M+1}}|^2 |\Omega^B_{[eS]|e_{M+1}}|^2 \mu_+^{[gS]|e_{M+1}} \left( N^e_{M+1} - N^g_M \right)
\]
\[
+ D_S (D_B - D_F) |\Omega^F_{[gS]|e_{M+1}}|^2 |\Omega^B_{[eS]|e_{M+1}}|^2 \mu_+^{[gS]|e_{M+1}} \left( N^e_{M+1} - N^g_M \right).
\]

(16)

where

\[
Z = 1 - D_S D_B |\Omega^B_{[gS]|e_{M+1}}|^2 - D_S D_B |\Omega^B_{[eS]|e_{M+1}}|^2 - D_S (D_7 + D_8) |\Omega^F_{[eS]|e_{M+1}}|^2.
\]

Summation over the magnetic quantum number \(M\) for all possible molecular orientation (\(M_i = 0\)) is implied in Eqs. (13), (15), and (16). \(\Omega^F_{[eS]|e_{M+1}}, \Omega^B_{[gS]|e_{M+1}}\) are the Rabi frequencies associated with the forward pump field \(E_F\) or the backward pump field \(E_B\) coupling the ground \(|g_S|\) with the excited state Zeeman sublevels \(|e_{M}\). With the present choice of polarization, the forward pump will connect the ground state \(|g_S|\) with the excited state \(|e_{M+1}\) and the backward propagating field will couple \(|g_S|\) with \(|e_{M-1}\). Under steady pumping condition, the saturation of the ground and excited state Zeeman population are described by the following set of coupled equations:

\[
N^e_M = N_0 - \tau_s \beta_F |\Omega^F_{[gS]|e_{M+1}}|^2 \left( N^e_{M+1} - N^g_M \right)
\]
\[
- \tau_s \beta_B |\Omega^B_{[gS]|e_{M+1}}|^2 \left( N^e_{M+1} - N^g_M \right)
\]
\[
N^e_{M+1} = \tau_e \beta_F |\Omega^F_{[gS]|e_{M+1}}|^2 \left( N^e_{M+1} - N^g_M \right)
\]
\[
+ \tau_e \beta_B |\Omega^B_{[gS]|e_{M+1}}|^2 \left( N^e_{M+1} - N^g_M \right)
\]
\[
N^e_{M-1} = \tau_e \beta_F |\Omega^F_{[gS]|e_{M+1}}|^2 \left( N^e_{M+1} - N^g_M \right)
\]
\[
+ \tau_e \beta_B |\Omega^B_{[gS]|e_{M+1}}|^2 \left( N^e_{M+1} - N^g_M \right).
\]

(17)

where \(\tau_s\) and \(\tau_e\) are the collisional relaxation times of the ground and excited rotational levels:

\[
\beta_F = i D_F + cc \quad \text{and} \quad \beta_B = i D_B + cc
\]
The solutions of the coupled equations (17) for the Zeeman population can be used in Eqs. (12)–(16) to find the expression for the susceptibility \( \chi \) and gain \( \kappa \). The PC reflectivity \( R \) is given by [9,10]

\[
R = \frac{|\chi|^2/|\text{Im}\chi|^2}{|1 + \cot(g)| |\chi|^2/|\text{Im}\chi|^2 - 1|^2},
\]

where

\[
g = aL\sqrt{|\chi|^2/|\text{Im}\chi|^2 - 1}, \tag{19}
\]

\[
a = \frac{\omega_2 N}{2\epsilon_0} \text{Im}\chi. \tag{20}
\]

\( \alpha \) is the nonlinear absorption coefficient for the phase conjugate optical field \( E_S \), \( N \) is the number density of resonant molecules, and \( L \) is the propagation length through the molecular medium.

### III. NUMERICAL ANALYSIS

In the following numerical analysis we consider the case of a nearly degenerate FWM (NDFWM), where the pump frequency is held fixed and the probe frequency is tunable around the line center. The pump frequency may have a finite detuning much smaller than the width of the Doppler broadened molecular transition.

Under this arrangement the single photon resonant denominators are

\[
D_F = \frac{1}{f - \delta_D - i\gamma}, \quad D_B = \frac{1}{f + \delta_D - i\gamma},
\]

\[
D_P = \frac{1}{\Delta - \delta_D - i\gamma}, \quad D_S = \frac{1}{2f + \Delta + \delta_D - i\gamma}, \tag{21}
\]

where \( f \) is the fixed frequency detuning for the pump waves, \( \delta_D \) is the Doppler shift of the molecular resonance for a certain velocity group, \( \Delta \) is the variable probe detuning from the line center, \( \gamma = \gamma_e \) is the decay rate for the optically induced molecular coherence \( |\langle \mu | e \rangle| \). We have assumed \( \gamma_e \approx \gamma \approx \gamma_e \), which is generally true for pure rotational vibrational transitions as discussed earlier in this paper and in Ref. [18].

The PC reflectivity is calculated as a function of probe detuning for a \( Q(10) \) Doppler broadened transition in the \( \nu_3 \) vibrational band of NO\(_2\) molecule (6 \( \mu \)m mid-infrared wave). We have recently shown that for a \( Q \)-type \( RV \) transition, the transparency of a weak beam is enhanced in presence of Zeeman coherence induced by Raman coupling of the weak beam with a cross polarized strong pump [20]. The electromagnetically induced transparency for the signal wave enhances the effective gain factor \( |\chi_{\text{Im}}| \) significantly improving the PC reflectivity.

After substituting the numerical solutions for the population described by the set of Eqs. (17), we evaluate the nonlinear susceptibility using Eqs. (12)–(16) for a given pump intensity and detuning.

The PC reflectivity is then calculated using the Doppler averaged susceptibility:

\[
\langle \chi \rangle_D = \frac{1}{\Delta_D \sqrt{\pi}} \int_{-\infty}^{\infty} \chi(\delta_D) e^{-\frac{\delta_D^2}{\Delta_D^2}} d\delta_D,
\]

where \( \Delta_D \) is the \( \frac{1}{2} \) width of the Doppler velocity distribution.

The molecular parameters (the decay rates, transition dipole moments, absorption coefficients, etc.) used in the numerical simulation are derived from Refs. [19,23,24]. Figure 3 shows the PC reflectivity for a \( Q(10) \) transition (in the \( \nu_3 \) vibrational band of NO\(_2\)) as a function of the probe detuning while the pump frequency is held fixed at the line center. 5% reflectivity is obtained with a small normalized pump intensity \( f = 0.5 \) and an unsaturated field optical density \( \alpha L = 1 \) for a low gas pressure of \( \sim 100 \) mTorr. At this gas pressure the collisional relaxation rate \( \gamma \approx 350 \) kHz. \( I_S \) is the saturation intensity for the rotational vibrational transition given by \( I_S = \frac{\omega_2^2}{2\epsilon_0} \) and corresponds to the pump field Rabi frequency \( \frac{\omega_2}{\gamma} = \gamma \), where \( \mu \) is the transition dipole moment for the vibrational excitation. Using a recently measured transition dipole moment of \( \mu = 0.3 \) Debye for the \( \nu_3 \) vibrational band of NO\(_2\), at a pressure of

![FIG. 3. (Color online) Doppler free PC reflectivity as a function of the probe detuning \( \Delta \) at a normalized pump intensity \( f = 0.5 \). The pump frequency is held fixed at the line center. The unsaturated field optical density \( \alpha L = 1 \).](image)

![FIG. 4. (Color online) Signal absorption \( -\text{Im}\chi \) (dashed line) and the amplitude of the FWM Gain |\chi| (solid line) as a function of the probe detuning \( \Delta \). The pump frequency is fixed at the line center; the pump power and the optical density correspond to Fig. 3.](image)

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FIG. 5. (Color online) (a) Dispersion of the imaginary part of the FWM gain due to Zeeman coherence ($\kappa_Z$, solid line) and due to modulated population ($\kappa_P$, dashed line). Pump intensity and optical density correspond to Fig. 3. FWM net gain $\kappa = \kappa_Z + \kappa_P$. (b) The dispersion of the real part of the FWM gain due to Zeeman coherence (Real $\kappa_Z$, solid line) and modulation of population (Real $\kappa_P$, dashed line). The pump power and the optical density correspond to Fig. 3.

$\sim 100$ mTorr, $I_S$ is estimated to be $\approx 7$ mW/cm$^2$. A typical room temperature Doppler full width of 90 MHz ($\sim 260\gamma$) for NO$_2$ is used in the numerical simulation [24]. Figure 4 shows the optical susceptibility $\text{Im} \chi$ describing the nonlinear absorption of the signal wave and the four wave mixing gain coefficient $|\kappa|$ as a function of the probe detuning $\Delta$. The signal absorption is reduced at the line center due to the combined effect of pump induced saturation of absorption and the EIT type transparency due to the coherent interaction of the signal wave with the pump wave. Figure 5(a) compares the imaginary part of the FWM gain coefficient $\kappa_Z$ due to Zeeman coherence with the contribution $\kappa_P$ due to the modulation of population. Likewise, Fig. 5(b) compares the dispersion of the real parts of the two gain contributions. Figures 5(a) and 5(b) show that although the Zeeman coherence ($\kappa_Z$) and the population ($\kappa_P$) terms have the same structure, they contribute to the net FWM gain with opposite phases, thus, reducing the achievable PC reflectivity. However, in this case the Zeeman term dominates as it originates from the coherent interaction of the copropagating forward pump with the probe wave and

FIG. 6. (Color online) (a) The PC reflectivity at higher pump intensity $I_S = 100$ as a function of probe detuning $\Delta$. The pump frequency is held fixed at the line center and the field optical density $\alpha L = 1$. (b) The imaginary part of the gain due to Zeeman coherence ($\kappa_Z$, solid line) and population modulation ($\kappa_P$, dashed line) as a function of probe detuning with pump frequency fixed at the line center. The opposite phase and comparable magnitudes of these two contributions reduces the PC reflectivity. The pump intensity and optical density correspond to Fig. 6(a).
FIG. 7. (a) Imaginary part of the gain $\kappa_Z$ (Zeeman coherence, solid line) and $\kappa_P$ (population term, dashed line) as a function of Doppler shift $\delta_D$ for the pump intensity $I/I_s = 0.5$. The pump and probe frequencies are held fixed at the line center. The contributions from the various Doppler groups cancel to produce a small $\kappa_P$. (b) Imaginary part of the gain $\kappa_Z$ (Zeeman coherence, solid line) and $\kappa_P$ (population term, dashed line) as a function of Doppler shift $\delta_D$ for the pump intensity $I/I_s = 100$. Pump and probe detunings are zero. The Doppler averaged amplitude of the population term $\kappa_P$ is comparable to the Zeeman term.

is relatively Doppler free. The population term, on the other hand, is generated from the interference of counter propagating backward pump and the probe wave and is sensitive to the Doppler detuning.

Figure 6(a) shows the PC reflectivity as a function of probe detuning $\Delta$ at a higher pump intensity of $I/I_s = 100$. The pump frequency is held fixed at the line center of the Doppler broadened transition. In Fig. 6(a) the PC reflectivity is split at the line center and is reduced by more than an order of magnitude compared to its value at the low pump intensity ($I/I_s = 0.5$). Figure 6(b) explains how the PC reflectivity is reduced at higher intensity due to a destructive interference of the Zeeman contribution with an equally strong population term. Both contributions split and exhibit Rabi-like side bands due to the combined effect of dynamic Stark shift and pump induced saturation at the line center. Figures 7(a) and 7(b) compare the Doppler spectrums of the Zeeman coherence and population contributions at the two extreme pump intensities.

FIG. 8. (a) PC reflectivity versus pump intensity when the pump and probe frequencies are fixed at the line center. Field optical density $\alpha L = 1$ and the collisional damping rate 350 kHz at a gas pressure of 100 mTorr. (b) The line center net gain $\kappa$ (solid line) and the signal absorption $-\text{Im} \chi$ (dashed line) as a function of intensity. The absorption drops due to saturation and coherent interaction. The FWM gain shows a maximum as a function of intensity; at higher intensity the gain reduces due to a destructive interference of the Zeeman coherence and the population term.
The Doppler spectra are calculated using fixed pump and probe frequencies tuned to the line center of the molecular transition. At a low intensity the relatively small Doppler averaged population contribution does not affect the four-wave mixing gain. At higher intensities, however, there is a significant Doppler averaged population contribution which interferes destructively with the Zeeman term reducing the net gain. Figure 8(a) shows the line center PC reflectivity as a function of the pump intensity. The pump frequency is held fixed at the line center. The corresponding signal absorption and FWM gain at the line center are shown in Fig. 8(b). Figure 8(b) shows that the line center absorption drops with intensity due to a combined effect of the pump induced saturation and EIT. The FWM gain however shows a maximum and reduces at higher intensity due to a destructive interference of the Zeeman coherence and the population term. The PC reflectivity $R \sim |\chi_{\text{Im}}|^2$ will therefore have a maximum as a function of the pump intensity as shown in Fig. 8(a).

The above results show that in a vectorial phase conjugation the PC reflectivity degrades due to a destructive interference of the population term $\kappa_P$ with the Zeeman coherence contribution $\kappa_Z$. Aligning the phases of these two contributions might improve the PC reflectivity. The phase alignment of $\kappa_Z$ and $\kappa_P$ can be achieved by slightly detuning the pump frequency within the Doppler profile. Figure 9 shows the line center PC reflectivity (zero detuning for the probe wave) versus the pump intensity for a fixed pump detuning of 3.3 MHz $\approx 10\gamma$ from the line center. With the detuned pump, a maximum of 20% PC reflectivity is achieved for a pump intensity $I_{IS} \approx 80$. The corresponding PC reflectivity as a function of probe detuning is shown in Fig. 10(a). Figure 10(b) shows the dispersion of the FWM gain components $\kappa_Z$ (Zeeman) and $\kappa_P$ (population) for the fixed detuned pump frequency. The phase alignment of the two gain components takes place over a narrow spectral bandwidth giving rise to a sharply peaked asymmetric reflection spectrum as shown in Fig. 10(a).

The recent development [24–26] of external cavity grating tuned (ECG) mid-infrared quantum cascade lasers (QCL), producing hundreds of mW of power within a narrow spectral bandwidth ($\Delta \leq 0.0001$ cm$^{-1}$) has opened up the new possibility of phase conjugation using nonlinear optical interactions with the rotational vibrational quantum states. Using a transition dipole moment of 0.3 Debye (recently measured for the $v_3$ band of NO$_2$) [24], a quick estimate shows that the ECG QCL meets the pump intensity requirement of $\sim 560$ mW/cm$^2$ at a gas pressure of $\sim 100$ mTorr. The narrow spectral bandwidth $\sim 4$ MHz of the ECG QCL is ideal for the optimum efficiency of the PC reflectivity shown in Fig. 10(a).
IV. CONCLUSION

A comprehensive theoretical analysis is presented for the vectorial phase conjugation of middle infrared waves using FWM with the rotational vibrational molecular transitions. With orthogonal circularly polarized pump and probe waves the Zeeman coherence is established within the manifold of degenerate magnetic sublevels of rotational vibrational eigenstates. It is shown that the Zeeman coherence not only introduces the EIT type transparency for the probe and the signal waves it also shapes the FWM polarization responsible for the generation of the phase conjugate reflected wave. With a detailed numerical analysis which takes into account the Doppler broadening, the dynamic level shifts and saturation we show that a destructive interference between the contributions due to Zeeman coherence and population grating degrades the PC reflectivity. Using an optical density $aL = 1$ at a low gas pressure ($\sim$100 mTorr), our numerical analysis shows that at a relatively low pump intensity ($\frac{I}{I_c} \leq 0.5$) the Zeeman coherence dominates and a maximum PC reflection of $\sim5\%$ is obtained at the line center. At larger pump intensity, an equally strong population contribution almost cancels the FWM polarization due to Zeeman coherence reducing the net gain and the PC reflectivity ($R \sim 0.25\%$) by more than an order of magnitude. We show that it is possible to significantly improve the PC reflectivity by adjusting the relative phase of the population and the Zeeman term. The phase alignment is accomplished by introducing a small detuning of the pump frequency from the line center. For a pump detuning of 3.3 MHz ($\sim10\gamma$), 20% PC reflectivity is achieved with a normalized intensity of $\frac{I}{I_c} = 80$ for the $Q(10)$ transition belonging to the $v_3$ vibrational band of NO$_2$ molecule (6 μm mid-infrared wave). The narrow bandwidth ($\sim4$ MHz) single mode external cavity MIR quantum cascade lasers are ideally suited to match the bandwidth ($\sim5$ MHz) of the PC reflection and provide the pump power density necessary for the optimum reflectivity.

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APPENDIX

We show here how the phase conjugate polarization, generated via successive scattering processes, can be found using a graphical expansion of the relevant density matrix. For the demonstration of the graphical technique in the following we consider two examples: (A) scattering of the backward pump $E_B$ from the Zeeman coherence described in section (b) of the main text; (B) Graphical expansion of the population modulation appearing in Eq. (3) of section (a).

(A) Scattering of $E_B$ from Zeeman coherence is described graphically in Fig. 11:

The phase conjugate polarization $\sigma_{[ε_M]|ε_{M+1}}(ω_S)$ is generated by two equally probable time ordered interactions connecting the initial state $|ε_M⟩$ with the final state $|ε_{M+1}⟩$. Following Ref. [21], the Zeeman coherence contribution to $\sigma_{[ε_M]|ε_{M+1}}(ω_S)$ can be written using the above diagrams as follows:

$$\sigma_{[ε_M]|ε_{M+1}}(ω_S) = D_3[\mu_{[ε_M]|ε_{M+1}}E_F^*\sigma_{[ε_{M-1}|ε_{M+1}}(ω_F) - \sigma_{[ε_{M-1}|ε_{M+1}}(ω_F)] E_F$$

$$D_3D_F^*\mu_{[ε_{M-1}|ε_{M+1}}E_F^*(N^e_{M-1} - N^g_{M-1}) E_F$$

(A1)

Similarly the graphical expansion in Fig. 13 can be used to get an expression for the Fourier component of the ground state Zeeman coherence $\sigma_{[ε_M]|ε_{M+1}}(ω_F - ω_p)$ as

$$\sigma_{[ε_M]|ε_{M+1}}(ω_F - ω_p) =$$

FIG. 11. (Color online) Graphical description of scattering of the backward pump EB from the ground and excited state Zeeman coherence.

FIG. 12. (Color online) Graphical expansion of the excited state Zeeman coherence $\sigma_{[ε_M]|ε_{M+1}}(ω_F - ω_p)$.
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\[ \sigma_{\text{FM}}(\omega_F - \omega_P) = \]

\[ \sigma_{\text{FM}}(\omega_m + 2\omega_F - \omega_{\text{pump}}) \]

\[ + \sigma_{\text{FM}}(\omega_m + \omega_F + \omega_P) \]

FIG. 13. (Color online) Graphical expansion of the ground state Zeeman coherence \( \sigma_{\text{FM}}(\omega_F - \omega_P) \).

follows:

\[
\sigma_{\text{FM}}(\omega_F - \omega_P) = D_1 [\mu_{\text{FM}}(\omega_{\text{pump}} + \omega_P)] E_F \sigma_{\text{FM}}(\omega_F - \omega_P) \\
- \sigma_{\text{FM}}(\omega_F - \omega_P) [\mu_{\text{FM}}(\omega_{\text{pump}} + \omega_P)] E^*_F \\
= D_1 [\mu_{\text{FM}}(\omega_{\text{pump}} + \omega_P)] E_F D_P \mu_{\text{FM}}(\omega_{\text{pump}} + \omega_P) \sigma_{\text{FM}}(\omega_F - \omega_P) \\
- D_1 D_P \mu_{\text{FM}}(\omega_{\text{pump}} + \omega_P) E_F N_{\text{FM}}^P - N_{\text{FM}}^P E_F \sigma_{\text{FM}}(\omega_F - \omega_P) \\
= D_1 D_P \mu_{\text{FM}}(\omega_{\text{pump}} + \omega_P) E_F N_{\text{FM}}^P - N_{\text{FM}}^P E_F \sigma_{\text{FM}}(\omega_F - \omega_P)
\]

(A3)

Substituting \( \sigma_{\text{FM}}(\omega_{\text{pump}} + \omega_P) \) from Eq. (A2) and \( \sigma_{\text{FM}}(\omega_{\text{pump}} + \omega_P) \) from Eq. (A1), we get the Zeeman coherence contribution to the PC polarization given by Eq. (6) in item (b) of the main text. Figure 2(b) provides a comprehensive picture of the scattering process which we have elaborated above graphically with all intermediate steps.

Following the graphical techniques of Ref. [21], we can write

\[
N_{\text{FM}}^P(\omega_F - \omega_P) = D_2 [\mu_{\text{FM}}(\omega_{\text{pump}} + \omega_P)] E_B \sigma_{\text{FM}}(\omega_{\text{pump}} + \omega_P) \\
- \sigma_{\text{FM}}(\omega_{\text{pump}} + \omega_P) \mu_{\text{FM}}(\omega_{\text{pump}} + \omega_P) E^*_B
\]

(A4)

where

\[
D_2^{-1} = \omega_F - \omega_P - i \gamma_F
\]

\[
\sigma_{\text{FM}}(\omega_{\text{pump}} + \omega_P) = D_2 \sigma_{\text{FM}}(\omega_{\text{pump}} + \omega_P) E^*_B N_{\text{FM}}^P - N_{\text{FM}}^P E^*_B
\]

(A5)

Using the density matrix expressions of Eq. (A5) in Eq. (A4) we get the final expression for the population modulation \( N_{\text{FM}}^P(\omega_F - \omega_P) \) generated by the interference of the backward pump \( E_B \) and the probe wave \( E_P \). For a more detailed description of the graphical method see Ref. [21].