Electromagnetically induced gain in molecular systems

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We report electromagnetically induced gain in a highly degenerate two-level rotational vibrational molecular system. Using two photon (Raman-type) interaction with right and left circularly polarized pump and probe waves, the Zeeman coherence is established within the manifold of degenerate sublevels belonging to a rotational vibrational eigenstate. We analytically and numerically calculate the third-order nonlinear optical susceptibility for a Doppler-broadened molecular transition for an arbitrary high rotational angular momentum \((J\gg 20)\). It is shown that for a \(Q\)-type open transition, a weak probe will experience an electromagnetically induced gain in presence of a strong copropagating pump wave. The inversionless gain originates due to cancellation of absorption from the interference of the coupled \(\Lambda\)- and \(V\)-type excitation channels in an \(V\)-type configuration. A detailed analysis of the optical susceptibility as a function of Doppler detuning explains how the gain bands are generated in a narrow transparency window from the overlapping contributions of different velocity groups. It is shown that the orientation dependent coherent interaction in presence of a strong pump induces narrow resonances for the probe susceptibility. The locations, intensity, and sign (positive or negative susceptibility) of these resonances are decided by the frequency detuning of the Doppler group and the strength of the coupling field. The availability of high power tunable quantum cascade lasers covering a spectral region from about 4 to 12 \(\mu m\) opens up the possibility of investigating the molecular vibrational rotational transitions for a variety of coherent effects.

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I. INTRODUCTION

Light induced coherence and interference has led to many important physical phenomena including electromagnetically induced transparency, coherent population trapping, and lasing without inversion [1]. The coherence and interference effects are mostly observed in three level \(\Lambda\)- or \(V\)-type configurations. The \(\Lambda\)- and \(V\)-type level configurations can also be realized in two-level degenerate systems under certain polarization condition of the pump and probe waves. For example, with a right circularly polarized pump wave and left circularly polarized probe wave, a pair of Zeeman levels belonging to either ground or excited states of the two-level system can be coherently coupled to form \(\Lambda\)- or \(V\)-type configuration. Akulshin and co-workers [2] studied the light induced coherent phenomena in a quasidegenerate two-level atomic system and observed electromagnetically induced transparency (EIT) as well as the electromagnetically induced absorption (EIA) when the coherence is established between the Zeeman sublevels of the ground state atoms. Ye et al. [3] also studied the optically induced coherent effects in quasidegenerate rubidium transitions and showed that EIA results from the laser induced atomic multicoherence in the upper and lower states for both the closed and open transitions. Here we report electromagnetically induced gain (EIG) in highly degenerate two-level open molecular systems of limited coherence. Inversionless coherent gain, the key idea behind the laser without inversion, has been studied experimentally and theoretically by Scully and co-workers [4]. Boon et al. [5,6] studied the electromagnetically induced transparency and gain in Doppler-broadened systems using moderately intense continuous wave laser powers. Their study showed the possibility of an inversionless gain even in the case of mismatched pump and probe wavelengths. These studies, however, were mostly confined to a three level \(\Lambda\)- or \(V\)-type atomic system and to realize the inversionless gain, a third pump wave (incoherent excitation) was required to populate the upper level of the probe transmission. Kochovskaya et al. [7] considered the problem of inversionless amplification in a three level \(\Lambda\)-type atomic system driven by a field reservoir and a low frequency coherent pump. Recently Wu et al. [8] demonstrated lasing without inversion in hot rubidium vapor using a single coherent driving field. We show here that an inversionless coherent gain can be realized in a Doppler-broadened two-level degenerate rotational vibrational (RV) system using a moderately intense coupling wave without the need of a third incoherent pump wave.

The rotational vibrational eigenstates of molecules are degenerate in the projection of their rotational angular momentum. Therefore, the electromagnetically induced coherent effects observed in two-level degenerate atomic systems are expected to reproduce for two-level rotational vibrational molecular transitions. Recently, EIT and orientation dependent Autler-Townes splittings have been observed in three level \(\Lambda\)-type configurations involving the electronic transitions in molecules [9,10]. However, there are no such reports of EIT or EIG for two-level purely RV transitions in the ground electronic potential of a molecule.

For the application of electromagnetically induced coherent effects, for example, in phase conjugation using middle infrared lasers, we are particularly interested in pure rotational vibrational transitions in the ground electronic potential of a molecule. Pure RV molecular systems even for fairly small size polyatomic molecules (NO\(_2\), SO\(_2\), etc.) are characteristically different from their atomic counterpart for the following reasons:

1. Contrary to the electronic excitations, the infrared spontaneous emission rates are significantly weaker (~100 Hz) than the decay rates (~100 kHz at ~30 mTorr pressure) of population due to state changing collisions. In such situations, the decay of the ground and excited state...
Zeeman coherences is dominated by the collision induced relaxation of rotational levels \[11\]. (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 ground and excited vibrational manifolds are comparable (a detailed discussion on collision induced decay of molecular coherences can be found in Ref. \[11\]). (4) It provides a two-level open system with very high degeneracy associated with the isotropic orientation of the rotational angular momentum.

With the above decay characteristics of rotational vibrational transitions, the excited state Zeeman coherence becomes appreciable compared to the ground state Zeeman coherence and significantly influences the quantum interference responsible for the EIT or EIG. For the application of electromagnetically induced coherent effects using middle infrared light sources, it is necessary to analyze the role of multilevel Zeeman coherence in shaping the optical nonlinearity of a rotational vibrational molecular system.

In this paper we show that the electromagnetically induced coherent effects in two-level molecular systems with high rotational angular momentum have distinctive characters, which do not have parallel in atomic systems. Using two photon (Raman-type) interaction with right and left circularly polarized pump and probe waves, the Zeeman coherence can be established within the manifold of degenerate sublevels belonging to a rotational vibrational eigenstate. It is shown that for a Q-type open transition, an electromagnetically induced gain can be observed for the weak probe in presence of a strong copropagating pump wave. The inversionless gain originates due to interference of the coupled \(\Lambda\) and \(V\) excitation channels in an N-type configuration.

In the following, we derive an analytical expression for the nonlinear optical susceptibility of a left circularly polarized probe wave for a pure rotational vibrational transition with an arbitrary angular momentum \(J\). The probe wave absorption for a Doppler-broadened \(Q(J)\) transition is then numerically calculated as a function of probe detuning. A detailed analysis of the optical susceptibility as a function of Doppler detuning explains how the gain bands are generated in a narrow transparency window from the overlapping contributions of different velocity groups. We show that the orientation dependent coupling of the pump and probe waves plays an important role in controlling the electromagnetically induced coherent effects in molecular transitions. Finally, we discuss how the predicted results can be verified in an actual experiment using the quantum cascade lasers (QCLs).

**II. NONLINEAR OPTICAL SUSCEPTIBILITY IN DEGENERATE MOLECULAR SYSTEM**

With combined right (\(\sigma^+\)) and left (\(\sigma^-\)) circularly polarized optical excitations, the degenerate Zeeman levels of the rotational vibrational transitions are coherently coupled to form two independently running \(N\) series with a \(\Lambda\) and or a \(V\) transition hanging at either end, as shown in Figs. 1(a) and 1(b), for a \(Q\)-type transition with an arbitrary angular momentum \(J\). In Fig. 1(b), \(M\) is the quantum number for the projection of the rotational angular momentum \(J\).

According to the dipole selection rules the \(\sigma^-\) circular waves induce transitions \(M_e \leftrightarrow M_g = M_e \pm 1\) between the ground and excited Zeeman sublevels. For such a system, the amplitude of the optical polarization at probe wave frequency \(\omega_p\) is given by

\[
P(\omega_p) = \sum_M \sigma_{\mid gM\rangle \mid eM\rangle}^\dagger(\omega_p)\mu_{\mid eM\rangle \mid gM}.
\]

The off diagonal density matrix element \(\sigma_{\mid gM\rangle \mid eM\rangle}^\dagger(\omega_p)\) describes the coherent superposition of ground \(\mid gM\rangle\) and excited \(\mid eM\rangle\) Zeeman sublevels. \(\mu_{\mid eM\rangle \mid gM}\) is the corresponding transition dipole matrix element. In order to calculate the probe susceptibility we solve the coupled density matrix equations for the degenerate two-level system in presence of a right circularly polarized pump wave and a left circularly polarized probe wave. Using a diagrammatic approach \[12\], the relevant steady state density matrix equations are derived for the three overlapping N-type transitions shown in Fig. 1(b).

\[
\sigma_{\mid eM\rangle \mid eM\rangle}^\dagger(\omega_p) = D_1\Omega^+_{\mid eM\rangle \mid eM\rangle}^\dagger(\omega_p)\mu_{\mid eM\rangle \mid eM}\] 

\[
\sigma_{\mid gM\rangle \mid eM\rangle}^\dagger(\omega_p) = D_1\Omega^+_{\mid gM\rangle \mid eM\rangle}^\dagger(-\delta)\mu_{\mid gM\rangle \mid eM}\] 

\[
\sigma_{\mid eM\rangle \mid gM}\] 

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\[ \sigma_{(gM-2)eM-1}(\omega) = D_2 \Omega^+_{(gM-2)eM-1}(N_{M-1}^g - N_{M-2}^g) \]

\[ - D_2 \sigma_{(gM-2)eM}(\delta) \Omega^-_{(gM)eM-1} \]

\[ + D_2 \Omega^-_{(gM-2)eM-3}(\delta) \Omega^+_{(gM-3)eM-1)} , \]

(5)

\[ \sigma_{(gM)eM+1}(\omega) = D_2 \Omega^+_{(gM)eM+1}(N_{M+1}^e - N_M^e) \]

\[ - D_2 \sigma_{(gM)eM+2}(\delta) \Omega^-_{(gM+2)eM+1} \]

\[ + D_2 \Omega^-_{(gM)eM+1}(\delta) , \]

(6)

where

\[ \Omega^{\pm}_{(gM)eM} = \frac{\mu_{(gM)eM} E_\pm e^{iKZ}}{h} \]

is the Rabi frequency for the transition \( gM \rightarrow eM \pm 1 \) induced by the \( \sigma^\pm \) waves. \( E_\pm \) is the optical field amplitude and \( K \) is the corresponding propagation vector for the \( \sigma^\pm \) circular waves. The dipole matrix element \( \mu_{(gM)eM} \) is \( C^{gM}_{JM,1} \) where \( C^{JM}_{J'M',1} \) are the Clebsch–Gordan coefficients associated with the rotational vibrational (\( P, Q, \) or \( R \)) transition. Thus, the Rabi frequency, responsible for the non-linear coupling of the Zeeman levels, depends on the magnetic quantum number \( M \). This leads to the orientation dependent coherent effects and, as we shall see later, is responsible for the fundamental difference between the \( P, Q, \) and \( R \) transitions. \( \delta = \omega_\pm - \omega_e \) are the two photon detunings for the Raman transition between the magnetic sublevels belonging to the ground or excited state. \( \sigma_{(gM)eM\pm2}(\pm \delta) \) and \( \sigma_{(eM)eM\pm2}(\pm \delta) \) represent the ground state and excited state Zeeman coherences generated by two photon nonlinear couplings of the pump and probe waves. The resonant denominators are given by

\[ D_1 = \frac{1}{\Delta_1 - i \gamma} , \]

\[ D_2 = \frac{1}{\Delta_2 - i \gamma} , \]

\[ D_3 = \frac{1}{\delta - i \gamma_e} , \]

where \( \Delta_1 \) and \( \Delta_2 \) are the single photon detuning for the resonant interactions with \( \sigma^+ \) and \( \sigma^- \) waves, respectively. \( \gamma \) is the damping rate for the induced coherence between the ground and the excited states. \( \gamma_e \) and \( \gamma_e \) are the decay rates for the Zeeman coherences in the ground and excited states, respectively. As pointed out earlier in Sec. 1, that for pure rotational vibrational infrared transitions considered in our work (electronic excitations are excluded), the decay of the populations and induced coherence is dominated by the state changing collisions and in most cases, ground and excited state decay rates \( \gamma_e \) and \( \gamma_e \) are comparable.

\[ N_M^e \] and \( N_M^g \) represent the population of the ground and excited state Zeeman levels, respectively. The physics of electromagnetically induced coherent effects is contained in Eq. (2). The first term on the right-hand side (RHS) of Eq. (2) describes the single photon resonant saturable polarization at the probe frequency. The second term is the nonlinear contribution to the probe polarization, generated by the interaction of the pump with the ground state coherence \( \sigma_{(gM)eM-2} \). The third term originates from the nonlinear coupling of the pump and probe waves via the excited state Zeeman coherence \( \sigma_{(eM+1)eM-1} \). The interference of these three terms, shown schematically in Fig. 2, is responsible for the electromagnetically induced coherent effects in \( N \)-type systems. As a result of the interference, the probe absorption can be canceled and a net gain can be experienced by the probe wave.

To find the third-order nonlinear optical susceptibility, Eqs. (2)-(6) are solved for \( \sigma_{(gM)eM-1}(\omega) \) within the first order of the weak probe field and second order of the pump field. After substituting the solution for \( \sigma_{(gM)eM-1}(\omega) \) in Eq. (1) we arrive at the following expression for the third-order nonlinear optical susceptibility at the probe frequency \( \omega_p \):

\[ \chi(\omega_p) = \sum_{-j}^{j} \chi_M , \]

(7)

\[ \chi_M = \frac{Z_M}{N_M^e - N_M^g} \]

\[ + \frac{Z_M}{N_M^g} \frac{D_1}{D_2} \left| \Omega_{(gM)eM-1}^P \right|^2 (N_{M-1}^e - N_{M-2}^e) \]

\[ + \frac{Z_M}{N_M^e} \frac{D_1}{D_2} \left| \Omega_{(gM)eM+1}^P \right|^2 (N_{M+1}^e - N_M^e) , \]

(8)

\[ Z_M = 1 + D_1 D_2 \left| \Omega_{(gM)eM-2}^P \right|^2 + D_1 D_2 \left| \Omega_{(gM)eM+1}^P \right|^2 , \]

(9)

where \( \Omega_{(gM)eM-2}^P = \Omega_{(gM)eM+1}^P \) is the Rabi frequency for \( M \rightarrow M+1 \) transitions due to \( \sigma^+ \) pump wave.

The steady state populations are given by

\[ N_{M+1}^e - N_{M-2}^e = \frac{N_0}{G_{M-2}} , \]

(10)


\[ N_{M+1}^e - N_M^e = -\frac{N_0}{G_M}, \]

\[ N_{M-1}^e - N_M^e = -N_0 + \frac{\beta}{\gamma_e} |\Omega_{gM}|^2 (N_M^e - N_{M-2}^e) \]

\[ + \frac{\beta}{\gamma_g} |\Omega_{gM+1}|^2 (N_{M+1}^e - N_M^e), \]

where \( G_{M-1} = 1 - 2\tau_2 \beta |\Omega_{gM}|^2 \) and \( G_M = 1 - 2\tau_2 \beta |\Omega_{gM+1}|^2 \).

\[ \tau = \frac{\tau_e + \tau_g}{2}, \quad \tau_e = \gamma_e^{-1}, \quad \tau_g = \gamma_g^{-1}, \quad \beta = iD_2 + c.c., \]

and \( N_0 \) is the equilibrium population of a ground Zeeman level \( N_0 = N_j/(2J+1) \).

Equations (7)–(12) describe a nonlinear optical susceptibility generated by the coherent superposition of \( N \)-type transitions. Equation (8) shows that for each of these \( N \)-type transitions, there are three interfering terms contributing to the probe susceptibility. These terms originate from the three previously explained interfering terms in Eq. (2). The first term on the right-hand side of Eq. (8) describes the pump induced saturation of the probe susceptibility. As described before, the second term is the nonlinear contribution generated by the \( \Lambda \)-type Raman coupling of \( M \) and \( M-2 \) ground sublevels and the third term is due to a \( V \)-type Raman coupling of \( M+1 \) and \( M-1 \) excited sublevels.

III. NUMERICAL ANALYSIS

We numerically evaluate the optical susceptibility for a left circularly polarized probe wave as a function of probe detuning for a Doppler-broadened RV system. The right circularly polarized pump is copropagating and its frequency is held fixed at the line center. With this geometry of the pump and probe waves we have

\[ D_1 = \frac{1}{\Delta - \delta_D - i\gamma}, \]

\[ D_2 = \frac{1}{-\delta_D - i\gamma}, \]

\[ D = \frac{1}{-\Delta - i\gamma}, \]

\[ D_3 = \frac{1}{-\Delta - i\gamma_e}, \]

where \( \Delta \) is the single photon probe detuning and \( \delta_D \) is the Doppler shift of the molecular resonance for a certain velocity group. The probe absorption is determined by the Doppler averaged susceptibility, \( \langle \chi \rangle_D = \frac{1}{\Delta_0} \int_{-\infty}^{\infty} \chi_{\delta_D} \exp[-(\delta_D/\Delta_D)^2] d\delta_D \), where \( \Delta_0 \) is the \( 1/e \) width of the Doppler velocity distribution.

In Fig. 3 the dark solid line shows the numerically calculated transmission of a left circularly polarized probe wave as a function of probe detuning \( \Delta \) for a Doppler-broadened \( Q(20) \) transition. For this simulation we assumed a Doppler width at half maximum of 800 \( \gamma \), a reasonable Doppler width for small size molecules such as NO2, SO2, etc., at a gas pressure of 30–50 mtorr. We have also assumed \( \gamma_e = \gamma_g = \gamma \), which is generally true for pure rotational vibrational transitions [11]. A small unsaturated optical density \( \alpha_0 = 0.5 \) was assumed for the numerical analysis and the propagation effects of the pump and probe waves were neglected. For a two-level degenerate system, the probe transparency arises from a combined effect of EIT and pump induced absorption saturation (an incoherent process). In order to see the contribution of EIT, we disregarded the ground and excited state Zeeman coherence represented by \( \sigma_{gM} \) and \( \sigma_{gM+1} \) in Eq. (2) and calculated the optical susceptibility under pump induced saturation. The dashed curve shows the transparency due to saturation in absence of Zeeman coherence. The solid line shows that coherent coupling of the Zeeman levels in presence of a strong pump enhances the transparency of the weak probe (EIT). The enhancement of transparency due to electromagnetically induced coherent effects in presence of incoherent pump induced saturation was pointed out previously by Weiss et al. and later by Fulton et al. for the “V-type” rubidium atom [13,14].

Figure 4 shows the probe transmission at an elevated pump intensity with a Rabi frequency \( \Omega_p = 40\gamma \). A probe amplification or gain appears at two Rabi-like sidebands spaced symmetrically about the line center. The dashed curve in Fig. 4 shows the pump induced saturated absorption in absence of Zeeman coherence. Our calculations show that the gain peaks appear for \( \Omega_p \approx 2\gamma \) and grows with the pump power until it saturates at a value close to 40\( \gamma \). With small pump power \( \Omega_p \approx 3\gamma \) a single EIT peak appears at the line center. With increasing pump power, the EIG peak splits into Rabi-like sidebands and is broadened. Similar splitting of an inversionless gain was predicted by Boon et al. [5] for a V-type three level atomic system. Figure 5 shows that at higher pump intensity \( \Omega_p = 400\gamma \), the EIG peaks appearing at \( \Delta \)
= ±400γ are broadened significantly. The broadening of the EIG peaks for an “N-type” molecular system is closely related to the velocity and orientation (M) dependent resonances of the susceptibility.

Within the framework of third-order nonlinearity considered in this work, the inversionless gain in a two-level degenerate system could arise from the interference of the Δ- and V-type excitation channels within the N-type configuration shown in Fig. 2. It was pointed out by Scully and co-workers [4] in their work on laser without inversion that coherent gain may be realized when the absorption cancels due to destructive interference between various excitation channels resulting in a net emission or gain. For our two-level degenerate system, the interference between the single photon resonant excitation [the first term on the RHS of Eq. (8)] and two photon resonant channels involving the Zeeman coherence (second and third terms) would result in a cancellation of absorption (EIT) and a net gain for the probe wave.

To see how this gain arises let us consider a molecule at rest, i.e., δP=0, and in addition let us have the probe tuned to the resonance, i.e., Δ=0. To realize gain, we must have Im χ(ωp) = ΣM Im χM > 0.

Using the above resonance condition in Eqs. (8) and (9) we have

\[ Z_M = 1 + \frac{|\Omega^{P}_{\text{g}(M-2)(cM-1)}|^2}{\gamma \gamma_e} + \frac{|\Omega^{P}_{\text{g}(M)cM+1})|^2}{\gamma \gamma_e}. \]

Then, Im χM > 0 would imply

\[ \frac{|\Omega^{P}_{\text{g}(M-2)(cM-1)}|^2}{\gamma \gamma_e} (N_M^{c} - N_{M-1}^{c}) + \frac{|\Omega^{P}_{\text{g}(M)cM+1})|^2}{\gamma \gamma_e} (N_M^{c} - N_{M+1}^{c}) - (N_M^{c} - N_{M-1}^{c}) > 0. \]

A certain threshold pump intensity |ΩP|2 would be required to satisfy the above gain condition for N<sub>M</sub>−N<sub>M−1</sub> > 0. Solving the population Eqs. (10)–(13) for the resonant pump and probe waves and using Eq. (14), we can show that

\[ (\tau_c + 2\tau) \frac{\gamma S_{M-2}}{1 + 4\tau \gamma S_{M-2}} + (\tau_e + 2\tau) \frac{\gamma S_M}{1 + 4\tau \gamma S_M} > 1, \]

where

\[ S_M = \left| \frac{\Omega^{P}_{\text{g}(M)cM+1})}{\gamma} \right|^2 \]

and

\[ S_{M-2} = \left| \frac{\Omega^{P}_{\text{g}(M-2)(cM-1)}^{\gamma}}{\gamma} \right|^2. \]

For a large value of the rotational angular momentum \( J \gg 1 \), \( S_{M-2} \approx S_M \) and the condition for gain becomes

\[ |\Omega^{P}_{\text{g}(M)cM+1})| > \sqrt{\frac{\gamma}{2\tau^2}}, \]

with \( \gamma_c = \gamma_e = \gamma \), true for most molecular systems, we get

\[ |\Omega^{P}_{\text{g}(M)cM+1})| > \frac{\gamma}{\sqrt{2}}. \]

In general, however, to fulfill the above gain condition for all molecular orientation and for all velocity groups of a Doppler-broadened distribution, we would require stronger pump intensity. Depending on the Doppler shift, at stronger pump intensity, the probe resonance would be Stark shifted. The Stark shift will also depend on the molecular orientation. As a result, the gain becomes a sensitive function of the pump intensity and probe detuning. In Fig. 6 we plot the peak gain (=Im χ(ωp)>0) versus the pump field Rabi frequency for various Doppler groups. As explained in the following paragraphs, with a certain pump intensity the gain maximum for a given Doppler group is found at the Stark shifted resonance. The requirement of a threshold pump intensity is clearly seen in the plots of Fig. 6. With increasing pump intensities the gain diminishes due to saturation.

For a given pump intensity and probe detuning, the net gain or absorption is due to contributions from all velocity groups of the Doppler distribution. To understand how each velocity group contributes to the probe gain or absorption, in Fig. 7 we have plotted the imaginary part of probe susceptibility as a function of Doppler shift \( \delta_0 \) for a few fixed probe detunings. For these plots the pump intensity corresponds to \( \Omega_p = 40\gamma \), and the positive value of the optical susceptibility

FIG. 4. EIG (dark solid line) for Q(20) transition with pump intensity corresponding to \( \Omega_p = 40\gamma \). The EIG peak splits into Rabi-like side bands spaced symmetrically about the line center near \( \Delta = ±30\gamma \). An optical density \( a_{01}L = 0.5 \) was used for the calculation. Field free Doppler profile (\( \Omega_p = 0 \)) and saturated absorption (SA) due to optical pumping in absence of Zeeman coherence are also shown for comparison.

FIG. 5. Broadening of EIG peaks at higher pump intensity.
implies gain for the probe wave. For the zero detuning of the probe wave, there is a narrow Doppler group about the line center contributing to a small positive susceptibility or gain. With increasing detuning, two separate bands of positive and negative molecular velocities asymmetrically placed about the line center (or zero velocity group) contribute to the optical susceptibility with opposite signs. As a result, depending on the detuning there will be a net gain or absorption for the probe wave. Figure 7 shows that the net gain maximizes for the probe detuning $\Delta = 30\gamma$. For $\Delta > 30\gamma$, the net gain is reduced as the absorption increases for a wider group of positive velocities. For $\Delta = 60\gamma$, there is no gain and the negative susceptibility indicates absorption for a Doppler velocity group in the range of $60\gamma \leq \delta_0 > 0$. The small wiggles present in the susceptibility are due to the superposition of orientation dependent contributions, as explained later in this paper. For $\Delta > 200\gamma$ only linear absorption can be seen for the single photon resonant Doppler group. By repeating these calculations for the negative probe detuning ($\Delta < 0$) it can be shown that the susceptibility versus Doppler shift has symmetrical behavior yielding a gain peak around $\Delta = -30\gamma$. The above analysis shows that the pump field, corresponding to a Rabi frequency $\Omega_p = 40\gamma$, strongly modifies the optical susceptibility of a small velocity group within a window of $|\delta_0| \approx 100\gamma$ about the line center. In Fig. 8 we plot the imaginary part of the probe susceptibility as a function of probe detuning $\Delta$ for a few significant Doppler groups contributing to the gain. Each Doppler group produces dispersion like gain curve in a certain spectral window. Figure 8 shows how the gain bands are created in a narrow transparency window as a result of the superposition of positive and negative contributions from different Doppler groups. As mentioned earlier, the small wiggles in the susceptibility curves of Figs. 7 and 8 are related to the orientation dependent dynamic Stark shift of the probe resonance. The orientation dependent or $M$ dependent Rabi frequency associated with the pump field induces narrow resonances for an $N$-type molecular system. The locations of these pump induced resonances (similar to Autler-Townes) depend sensitively both on the molecular orientation and Doppler detunings. To understand the orientation dependent gain, in Fig. 9 we plotted the imaginary part of the probe susceptibility for a single Doppler group for a few selected molecular orientation ($M$ values).

FIG. 6. (Color) The maximum gain $\text{Im} \chi > 0$ is plotted as a function of coupling field Rabi frequency for a few selected Doppler groups. For a given Doppler group a certain threshold pump intensity is required to satisfy the gain condition $\text{Im} \chi > 0$.

FIG. 7. Imaginary part of the probe susceptibility as a function of the probe detuning $\Delta$ for a few selected Doppler groups: $\delta_0 = \pm 10, \pm 30, \pm 50, \pm 70\gamma$. Each colored graph representing a particular Doppler group shows a dispersive susceptibility as a function of the probe detuning $\Delta$. Gain bands are generated in narrow spectral windows around $\Delta = \pm 30\gamma$ as a result of the contributions from various Doppler groups. The pump intensity corresponds to $\Omega_p = 40\gamma$.

FIG. 8. (Color) Imaginary part of the probe susceptibility versus probe detuning $\Delta$ for a few significant Doppler groups: $\delta_0 = \pm 10, \pm 30, \pm 50, \pm 70\gamma$. Each colored graph representing a particular Doppler group shows a dispersive susceptibility as a function of the probe detuning $\Delta$. Gain bands are generated in narrow spectral windows around $\Delta = \pm 30\gamma$ as a result of the contributions from various Doppler groups. The pump intensity corresponds to $\Omega_p = 40\gamma$.

FIG. 9. (Color) Narrow resonances for the orientation dependent susceptibility of the Doppler group with $\delta_0 = 30\gamma$. The pump intensity corresponds to $\Omega_p = 40\gamma$. The net susceptibility is the coherent superposition of overlapping orientation or $M$ dependent resonances.
FIG. 10. Orientation or $M$-dependent Rabi frequency $\Omega^\pm$ for $P$- and $Q$-type transitions. $\Omega^+$ and $\Omega^-$ represent the Rabi frequency for the right ($\sigma^+$) and left ($\sigma^-$) circularly polarized waves, respectively. Stronger coupling between the $\sigma^+$ and $\sigma^-$ waves is evidenced for $Q$-type transition.

FIG. 11. Schematic of a proposed experiment to measure EIG in $Q$-type transition. AOM1 and AOM2, acousto-optic modulators; $P$, polarizer; $\lambda/2$, half wave plate; $\lambda/4$, quarter wave plate, and M1, M2, and M3, mirrors.

Molecular orientation there are two sharp resonances on both sides of the line center $\Delta = 0$. The coherent gain maximizes for $M = 0$ corresponding to the angular momentum orientation perpendicular to the optical beam, whereas the gain disappears for $M = \pm J$ corresponding to orientation parallel to optical axis. As shown later, this is consistent with a coupling Rabi frequency $\Omega_M$ for a "$Q$-type" transition being a symmetric function of $M$ with a maximum at $M = 0$. The superposition of these orientation dependent resonant contributions produces the small oscillations in the net susceptibility seen in the plots of Figs. 7 and 8. As the coupling Rabi frequency increases with stronger pump intensity, the orientation dependent resonances are further separated in frequency increasing the effective bandwidth of their resultant contribution. This explains the broadening of the gain bandwidth at higher pump intensity ($\Omega_P = 400 \gamma$) seen in Fig. 5.

Our calculations show that EIG increases with the rotational angular momentum $J$ until it saturates for $J \geq 20$. Similar calculations performed for the $P$- and $R$-type transitions show the coherent enhancement of transmission (EIT); however, the EIT peak height is significantly reduced compared to an equivalent $Q$-type transition. In addition, for the $P$- and $R$-type transitions, no EIG can be observed for any value of the rotational angular momentum $J$. The difference between the coherent effects for $P$, $Q$, and $R$ transitions is due to the orientation dependent two photon coupling of the pump and probe waves. For the $P$- or $R$-type transition, the Rabi frequency $\Omega^\pm$ associated with the $\sigma^+$ and $\sigma^-$ waves has asymmetric $M$ dependence. Figure 10 compares the $M$ dependence of $\Omega^\pm$ for $P$- and $Q$-type transitions. As a result of the asymmetric $M$ dependence for a $P$- (or $R$-) type transition, the Zeeman levels are weakly coupled by the two photon interaction of the $\sigma^+$ and $\sigma^-$ waves, resulting in a weaker EIT and no EIG. Figure 10 shows that the Rabi frequency, $\Omega^\pm(Q)$, in a $Q$-type transition is almost symmetric in $M$ for angular momentum $J = 20$. However, with decreasing values of $J$ in $Q$-type transitions, the Rabi frequencies for the $\sigma^\pm$ waves will no longer be symmetric, resulting in a weaker coupling and smaller EIG in agreement with the result of the numerical simulation. The maximum coupling of $\sigma^\pm$ waves near $M = 0$ in a $Q$-type transition is responsible for the coherent gain.

Even though the decay of coherences and the radiative coupling strengths in atomic systems are different from the

RV molecular systems, the recent experiment of Wu et al. [8] on lasing without inversion in hot rubidium atoms for the $F = 2 \rightarrow F' = 2$ transition has a noticeable similarity with the EIG in a degenerate two-level system considered in this work. For the RV molecular transitions, however, the predicted gain for $J = 2$ would be one order of magnitude smaller than that for large $J \geq 20$.

IV. PROPOSED EXPERIMENT

Figure 11 shows the schematic of a proposed experiment to measure the EIG for the $Q^9_5(9)$ parallel transition belonging to the $v_3$ band of NO$_2$ molecule. Using an optical density $= 0.7$, corresponding to $\sim 50\%$ linear absorption at the line center, an EIG of $\sim 10\%$ is numerically calculated with an input pump Rabi frequency $\Omega_P = 30 \gamma$. The phase locked circular pump and probe waves are derived from a single mode external cavity grating tuned QCL laser operating at the desired wavelength of $\sim 6.25 \mu$m. The QCL can be frequency locked to the line center of $Q^9_5(9)$ transition. The probe frequency is shifted from the pump laser using two acousto-optic modulators (AOMs) in series. The probe tuning is then accomplished by tuning the radio frequency (RF) of one of the AOMs. The oppositely handed circular waves are sent through a 1-m-long NO$_2$ gas cell at a pressure of $\sim 70$ mtorr, required to match the optical density of 0.7. At the exit end of the gas cell the $\sigma^+$ probe wave is filtered out using a combination of a quarter wave plate and a polarizer and detected with an HgCdTe detector. The transmission of the probe wave is recorded as a function of the probe detuning $\Delta$. Since the EIG resonances are sensitive function of the pump intensity, the propagation effects of the coupled pump and probe waves must be included for a complete description of the nonlinear transmission. Using the experimental parameters and taking into account of the pump attenuation, the EIG for $Q^9_5(9)$ transition is optimized for a probe detuning of $\pm 4.4$ MHz. At a pressure of 70 mtorr, the collisional dephasing $\gamma$ is $\sim 245$ kHz. For this experiment the transit time broadening is minimized using a QCL beam diameter of 4 mm. Using our recently measured vibrational dipole moment of 0.37 D
for the $v_3$ band of NO$_2$ molecule [15], we estimate a pump intensity of $\sim 2$ W/cm$^2$ to reach the Rabi frequency $\Omega_p = 30\gamma$ ($\sim 7.4$ MHz) for the $Q_{5/2}(9)$ transition. The required pump power level ($\sim 250$ mW) is readily available from the newly developed external grating cavity quantum cascade lasers [16].

V. CONCLUSION

In conclusion, we have shown that with copropagating right and left circularly polarized pump and probe waves electromagnetically induced transparency and gain can be observed in a degenerate two-level RV molecular system. The probe transparency for the degenerate two-level system arises from the interference of direct single photon excitation with the two photon resonant channel with the two photon resonant splitting. It is shown that the gain originates from the interference of direct single photon excitation channel with the two photon resonant $\Lambda$- and $V$-type Raman channels within an $N$-type configuration. A detailed analysis of the optical susceptibility as a function of Doppler detuning explains how the gain bands are generated in a narrow transparency window from the overlapping contributions of different velocity groups. Our analysis reveals that the orientation dependent coherent interaction with a strong pump induces narrow resonances similar to the Autler-Townes resonance. The locations and intensity of these resonances are decided by the frequency detuning of the Doppler group and the coupling strength $\Omega_M$. The net optical susceptibility of a Doppler group is determined by a coherent superposition of these overlapping resonances. With increasing intensity of the coupling field the orientation dependent resonances are further separated, widening the bandwidth of their resultant contribution. For the $P$- and $R$-type transitions the relatively weaker EIT and absence of EIG are due to weaker orientation dependent coupling of the right and left circularly polarized pump and probe waves.

To our knowledge, the electromagnetically induced gain has not been seen or predicted for a highly degenerate two-level rotational vibrational molecular system. We have presented a schematic of a simple experiment to measure the predicted EIG for a $Q$-type transition in NO$_2$ molecule using a single mode quantum cascade laser. The electromagnetically induced gain in molecular systems might find useful applications in optical phase conjugation using middle infrared laser sources.

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