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Anil K. Patnaik

Wright State University - Main Campus, anil.patnaik@wright.edu

Sukesh Roy

James R. Gord

Robert P. Lucht

Thomas B. Settersten

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Effects of collisions on electronic-resonance-enhanced coherent anti-Stokes Raman scattering of nitric oxide

Anil K. Patnaik,^{1,2,a)} Suresh Roy,¹ James R. Gord,¹ Robert P. Lucht,³ and Thomas B. Settersten⁴

¹*Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson AFB, Ohio 45433, USA*

²*Department of Physics, Wright State University, Dayton, Ohio 45435, USA*

³*Department of Mechanical Engineering, Purdue University, West Lafayette, Indiana 47907, USA*

⁴*Combustion Research Facility, Sandia National Laboratories, Livermore, California 94551, USA*

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A six-level model is developed and used to study the effects of collisional energy transfer and dephasing on electronic-resonance-enhanced coherent anti-Stokes Raman scattering (ERE-CARS) in nitric oxide. The model includes the three levels that are coherently coupled by the three applied lasers as well as three additional bath levels that enable inclusion of the effects of electronic quenching and rotational energy transfer. The density-matrix equations that describe the evolution of the relevant populations and coherences are presented. The parametric dependencies of the ERE-CARS signal on collisional energy transfer and dephasing processes are described in terms of both a steady-state analytical solution and the numerical solutions to the governing equations. In the weak-field limit, the ERE-CARS signal scales inversely with the square of the dephasing rates for the electronic and Raman coherences. In accord with published experimental observations [Roy *et al.*, Appl. Phys. Lett. **89**, 104105 (2006)], the ERE-CARS signal is shown to be insensitive to the collisional quenching rate. Parametric dependencies on quenching, rotational energy transfer, and pure electronic dephasing are presented, demonstrating reduced collisional dependence for saturating laser fields. © 2009 American Institute of Physics. [DOI: [10.1063/1.3137106](https://doi.org/10.1063/1.3137106)]

I. INTRODUCTION

Growing concern over the environmental impact of combustion emissions has driven the demand for increased regulation of emissions in recent years. In response, engine manufacturers are designing combustors with greatly reduced emissions levels. In addition, the demand for high-performance, and ultracompact combustors has inspired revolutionary designs for which neither validated combustor models nor scaling laws are available. In light of these requirements, understanding the nitric oxide (NO) formation processes in practical combustors is essential for minimizing NO concentrations in engine exhausts. Accurate measurement of NO concentrations in high-pressure combustors, although very difficult, is critical for the minimization of pollutant emissions from new combustor systems.

A new spectroscopic technique, electronic-resonance-enhanced coherent anti-Stokes Raman scattering (ERE-CARS) with visible pump and Stokes beams and an ultraviolet probe beam, demonstrates significant potential for application in practical high-pressure combustion systems.^{1–8} In contrast with conventional CARS spectroscopy, in the ERE-CARS technique the probe beam is tuned to an electronic resonance of the target molecule, thereby providing a significant enhancement of the CARS signal by more than three orders of magnitude.⁸ In previous fully resonant CARS approaches, all of the applied laser beams are electronically resonant with molecular transitions,^{9,10} whereas in the

ERE-CARS approach the pump and Stokes beams are two-photon resonant with Raman transitions in the ground state but far off-resonant with single-photon transitions. The induced Raman coherence is probed by an electronically resonant laser beam to produce the electronic coherence in the anti-Stokes transition, which generates the ERE-CARS signal.

Our group pursued this ERE-CARS technique with visible pump and Stokes beams and an ultraviolet probe beam because of several unique features that are ideally suited for measurements in high-pressure turbulent reacting flows. (1) This technique has enhanced chemical selectivity because of the requirement of simultaneous Raman resonance and electronic resonance for the signal-generation process. (2) The double-resonance condition suppresses potential interference from other molecules such as CO₂, O₂, and polycyclic aromatic hydrocarbons. (3) The coherent nature of the signal beam is particularly advantageous in sooting environments.^{3,5} (4) ERE-CARS is insensitive to drastic changes in the quenching (electronic energy transfer) environment² and exhibits favorable scaling with pressure.^{4,6}

Although experimental results demonstrated insensitivity of the signal to the electronic quenching rate of NO, the need exists to develop a more comprehensive predictive capability for the performance of ERE-CARS under varying collisional conditions. Recently, several of the current authors developed a simple four-level mathematical model to explain the insensitivity to electronic quenching of ERE-CARS.¹¹ However, the effects of the other important NO-specific collisional processes—rotational energy transfer (RET) of the ex-

^{a)}Electronic mail: anil.patnaik@wpafb.af.mil.

FIG. 1. (Color online) Six-level model for ERE-CARS in NO.

cited electronic state and electronic dephasing—on the ERE-CARS signal were not investigated. Furthermore, the RET in the excited state cannot be accounted for in that four-level model. The objective of the current research effort is to develop a simple model that enables the investigation of all of the effects of the important collisional processes on the ERE-CARS signal of NO. To this end, a general six-level model has been developed, with three levels that directly participate in the coherent processes and three additional bath levels that are incoherently coupled to each other and the main levels through the relevant collisional processes. This model is used to explore collisional effects on the ground-state coherence and on the generated molecular polarization in the anti-Stokes transition.

In the following section, the six-level model for ERE-CARS in NO is described and the equations for the molecular dynamics are derived. A steady-state solution is presented in Sec. III to describe the general collisional dependence of the ERE-CARS signal. In Sec. IV, a set of non-perturbative simulations reproduces the conditions associated with published experimental results that demonstrate the relative insensitivity of the ERE-CARS signal to electronic quenching. Subsequently a series of numerical solutions to the model equations is presented to investigate the effects of the other important collisional processes on the Raman and electronic coherences, which ultimately generate the ERE-CARS signal. Concluding remarks are presented in Sec. V.

II. SIX-LEVEL MODEL FOR ERE-CARS IN NO

We consider the six-level model shown in Fig. 1 to study the population and coherence dynamics of the ERE-CARS process in the NO molecule. The unprimed levels correspond to single rotational states that directly participate in the coherent ERE-CARS process and the primed levels correspond to rotational baths that can influence the signal through collisional energy transfer. Levels $|a\rangle$ and $|a'\rangle$ comprise all of the rotational levels in $A^2\Sigma^+(v=0)$, $|b\rangle$ and $|b'\rangle$ comprise all of the rotational levels in $X^2\Pi(v=1)$, and $|c\rangle$ and $|c'\rangle$ comprise all of the rotational levels in $X^2\Pi(v=0)$.

The electric fields of the three input pulses $\vec{E}_1$, $\vec{E}_2$, and $\vec{E}_3$ coherently drive a nonlinear polarization between $|a\rangle$ and $|c\rangle$ that results in the CARS signal field $\vec{E}_4$. The pump ($\vec{E}_1$) and the Stokes ($\vec{E}_2$) lasers are tuned to the two-photon Raman resonance $|b\rangle \leftrightarrow |c\rangle$. However, each of these lasers is far detuned from single-photon electronic resonances that couple the ground levels to either $|a\rangle$ or $|a'\rangle$. The detuning from these electronic resonances δ is larger than any relaxation parameter in the system. In practice, δ is of the order of 10^{15} s^{-1} .¹ The probe field ($\vec{E}_3$) is near resonant with the electronic transition $|a\rangle \leftrightarrow |b\rangle$, with a small detuning Δ . Note that the signal and all applied fields are assumed to be linearly polarized and parallel and their explicit couplings to magnetic sublevels of the rotational levels are not considered here. A comprehensive study of collisional effects for other possible polarization configurations is beyond the scope of this paper.

The current work focuses on a parametric study of the effects of collisions on the ERE-CARS process. Collisions cause not only transfer of population between energy levels but also dephasing of the coherent processes. The population transfer rate Γ_{ij} indicates the rate of incoherent transitions from level $|i\rangle$ to level $|j\rangle$ and the rate γ_{ij} is the dephasing rate for coherence between these levels. Although these rates include a contribution from spontaneous emission, the contribution is generally negligible compared to the relevant collision rates in the current system. The incoherent transitions considered in the current model are indicated by the dashed arrows in Fig. 1 and are discussed in the following section.

A. Relaxation model

In the current model, $\Gamma_{\alpha\alpha'}$ and $\Gamma_{\alpha'\alpha}$ ($\alpha=a, b, c$) are RET rates between each of the bath levels and the corresponding laser-coupled level. The RET rates are related by microscopic reversibility such that

$$\Gamma_{\alpha\alpha'} N_{\alpha'}^{\text{eq}} = \Gamma_{\alpha'\alpha} N_{\alpha}^{\text{eq}}, \quad (1)$$

where N_{α}^{eq} and $N_{\alpha'}^{\text{eq}}$ are the equilibrium number densities in levels $|\alpha\rangle$ and $|\alpha'\rangle$, respectively. In the current model, we assume $N_{\alpha}^{\text{eq}}/N_{\alpha'}^{\text{eq}}=0.1$. Furthermore, we define a single RET rate parameter R for the unprimed level in all three vibrational manifolds because ground-state^{12–14} and excited-state^{15,16} RET rates agree to within experimental uncertainty. Thus,

$$\Gamma_{\alpha\alpha'} = R, \quad (2)$$

$$\Gamma_{\alpha'\alpha} = 0.1R. \quad (3)$$

Rotational energy transfer is typically the most rapid inelastic collision process, causing only a change in the rotational energy of the molecule. For atmospheric-pressure systems, RET rates for NO^{12–16} are of the order of 10^{10} s^{-1} .

Although incoherent transitions between the ground-state vibrational levels are possible, they are not shown in Fig. 1. Such transitions, which are caused by vibrational energy transfer and spontaneous infrared emission between $v=1$ and $v=0$ in NO($X^2\Pi$) with a rate of 10^3 s^{-1} , are highly

improbable on the time scale of the current model.^{17–20} Therefore, these relaxation pathways are not included in the analysis.

The electronically excited state is incoherently coupled to the ground electronic states through spontaneous ultraviolet emission and collisional quenching. The incoherent transfer rates for transitions from excited level $|\alpha\rangle$ to ground level $|j\rangle$ are

$$\Gamma_{\alpha j} = A_{\alpha j} + Q_{\alpha j}, \quad (4)$$

where $A_{\alpha j}$ and $Q_{\alpha j}$ are the relevant spontaneous emission and collisional quenching rates, respectively, and $\alpha = a, a'$ and $j = b, b', c, c'$. The rates for endothermic transitions ($\Gamma_{j\alpha}$) are negligible at practical temperatures and only the downward relaxation rates are included in the model. For simplicity, we model the incoherent relaxation from $|a\rangle$ and $|a'\rangle$ to levels in $X^2\Pi(v=0, 1)$ solely through the pathways to bath levels $|b'\rangle$ and $|c'\rangle$. Although the direct pathways to levels $|b\rangle$ and $|c\rangle$ are ignored, the model still indirectly accounts for incoherent transfer from the electronically excited levels to $|b\rangle$ and $|c\rangle$ through RET with bath levels, which rapidly thermalizes the population distribution in each vibrational manifold.

To simplify the parametrization of the relaxation model, the electronic relaxation rates $\Gamma_{\alpha j}$ ($\alpha = a, a'$; $j = b', c'$) are defined in terms of the total quenching rate Q and the total spontaneous emission rate A for $A^2\Sigma^+(v=0)$. The rates are written as

$$\Gamma_{\alpha j} = q_{\alpha j}A + \beta Q, \quad (5)$$

where $q_{\alpha j}$ is a Franck–Condon factor and β is a branching ratio for quenching. The values for q_{ab} and q_{ac} are 0.26 and 0.17, respectively,²¹ and $A = 5 \times 10^6 \text{ s}^{-1}$.^{21–23} In Eq. (5), we further simplify the quenching model by assuming both vibrational manifolds in the ground electronic state are equally populated by quenching. The branching parameter β enables investigation of the potential effects of incoherent transfer to the ground-state vibrational manifolds. Contributions from these quenching pathways are maximized by setting $\beta = 0.5$ and eliminated by setting $\beta = 0$. Unlike RET rates, quenching rates are strongly dependent on the collision partner. For example, the quenching rate of NO $A^2\Sigma^+(v=0)$ caused by an atmosphere of N_2 at room temperature is approximately 10^6 s^{-1} .²³ In contrast, an atmosphere of CO_2 produces a rate of 10^{10} s^{-1} .²²

To ensure the model predicts the correct lifetime ($A + Q$)^{−1} of the $A^2\Sigma^+(v=0)$ manifold, an additional loss channel is introduced for $|a\rangle$ and $|a'\rangle$. The relaxation rate for this additional channel is

$$\begin{aligned} \Gamma_{a0} &= (1 - q_{ab'} - q_{ac'})A + (1 - 2\beta)Q \\ &= 0.57A + (1 - 2\beta)Q. \end{aligned} \quad (6)$$

This loss channel represents the incoherent transitions to all NO states that are not explicitly included in the model.

Three incoherent dephasing rates are important in the current model. Dephasing of the Raman coherence is given by the rate γ_{bc} , and γ_{ab} and γ_{ac} are the dephasing rates for

the probe and signal transitions, respectively. In general, the coherence dephasing rate for a transition between states $|i\rangle$ and $|j\rangle$ can be described as²⁴

$$\gamma_{ij} = \frac{1}{2}(\Gamma_i + \Gamma_j) + \gamma_{ij}^{\text{pd}}, \quad (7)$$

where Γ_i and Γ_j are the total population decay rates for the two states ($\Gamma_i = \sum_{k \neq i} \Gamma_{ik}$) and γ_{ij}^{pd} is the pure dephasing rate for the coherence between the states.

The electronic dephasing rates for the probe and signal transitions are given by

$$\gamma_{aj} = \frac{1}{2}(2R + Q + A) + \gamma_{aj}^{\text{pd}}, \quad (8)$$

where $j = b, c$. We assume that pure electronic dephasing, which results from elastic collisions, is the same for both electronic transitions. Therefore, we subsequently drop the subscript on the pure electronic dephasing rate for convenience ($\gamma_{ab}^{\text{pd}} = \gamma_{ac}^{\text{pd}} \equiv \gamma^{\text{pd}}$). Room-temperature collisional linewidth measurements for broadening of NO(A -X) transitions by N_2 ,^{25,26} O_2 ,^{27,28} and CO_2 (Ref. 26) indicate that the coherence dephasing rate is of the order of $5 \times 10^{10} \text{ s}^{-1}$ at atmospheric pressure. Accounting for the contributions from RET and quenching, these measurements imply that the pure dephasing rate is $\sim 4 \times 10^{10} \text{ s}^{-1}$ or four times larger than the RET rate for all of these species.

The situation is different for dephasing of the Raman coherence, however, because the pure vibrational dephasing rate γ_{bc}^{pd} is negligible compared to the total ground-state RET rates. Recent linewidth measurements of infrared^{29,30} and microwave³¹ transitions confirm the coherence dephasing rate is approximately equal to the RET rate,^{12,13}

$$\gamma_{bc} = R. \quad (9)$$

Parametrization of the collisional model is, thus, reduced to four adjustable parameters: the RET rate R , the electronic quenching rate Q , the branching ratio β , and the pure electronic dephasing rate γ^{pd} . The spontaneous-emission coefficient A is a constant of the system; although it has little impact on modeling practical conditions, we use A as a normalization parameter.

B. Governing equations

1. Generation and propagation of the ERE-CARS field

The electric fields of the three applied laser pulses and of the generated signal pulse are represented by plane waves. To simplify the model to one spatial dimension, we assume a copropagating geometry with all four waves propagating along the z -direction. The electric field is

$$\vec{E}_j(z, t) = \hat{e}_j \mathcal{E}_j(z, t) e^{-i(\nu_j t - k_j z)} + \text{c.c.}, \quad (10)$$

where $\hat{e}_j$ is the unit polarization, $\mathcal{E}_j$ is the slowly varying envelope, ν_j is the angular frequency, and k_j is the propagation constant of the j th field. In general, $\mathcal{E}_j$ is a complex number. The nonlinear interaction of the applied laser fields with NO molecules in the sample generates a macroscopic polarization. The ERE-CARS signal field $\vec{E}_4$ is generated by the component $\vec{P}_4$ of the induced polarization that oscillates at the ERE-CARS signal frequency ν_4 . We assume $\vec{P}_4$ has the same phase dependence as $\vec{E}_4$, given by

$$\vec{P}_4 = \hat{e}_4 \mathcal{P}_4(z, t) e^{-i(\nu_4 t - k_4 z)} + \text{c.c.}, \quad (11)$$

where, $\mathcal{P}_4$ is the amplitude of the component of macroscopic polarization that oscillate at frequency ν_4 .

Assuming no transverse dependence, the propagation of the signal field is governed by the one-dimensional wave equation,

$$\frac{\partial^2 \vec{E}_4}{\partial z^2} - \frac{1}{c^2} \frac{\partial^2 \vec{E}_4}{\partial t^2} = \frac{1}{\epsilon_0 c^2} \frac{\partial^2 \vec{P}_4}{\partial t^2}, \quad (12)$$

where ϵ_0 and c are electrical permittivity and speed of light in free space, respectively. To reduce the second-order wave equation to a first-order partial differential equation, we substitute Eqs. (10) and (11) in Eq. (12) and impose the slowly varying envelope approximation. This approximation requires that variation of the field amplitudes in both t and z be small compared to the optical period (both space and time) of the radiation field.²⁴ Thus Eq. (12) reduces to

$$\frac{\partial \mathcal{E}_4}{\partial z} + \frac{1}{c} \frac{\partial \mathcal{E}_4}{\partial t} = i \frac{k_4}{2\epsilon_0} \mathcal{P}_4. \quad (13)$$

A further simplification results by invoking the retarded-time transformation $t \rightarrow t - z/c$. This change of variables reduces the above wave equation to a differential equation, with a single independent variable describing the growth of the signal field,

$$\frac{\partial \mathcal{E}_4}{\partial z} = i \frac{k_4}{2\epsilon_0} \mathcal{P}_4. \quad (14)$$

The macroscopic polarization is the ensemble average of the induced dipole moments of the molecules. The macroscopic polarization can be expressed in terms of the density-matrix and dipole-moment operators, ρ and $\vec{d}$, respectively,²⁴

$$\vec{P} = N \text{Tr}(\rho \vec{d}), \quad (15)$$

where Tr represents the trace of the matrix and N is the number density of the molecules. The amplitude $\mathcal{P}_4$, given in Eq. (11), is extracted from the total polarization and substituted into Eq. (14).

In the following section, we present the quantum-mechanical description of the system in terms of density-matrix equations that describe the microscopic response of the NO molecules to the external laser fields. Solution of these equations provides the density-matrix elements that are necessary for evaluation of Eq. (15). We assumed homogeneously broadened stationary NO molecules in the following calculation.

2. Density-matrix equations

The density matrix is composed of diagonal elements ρ_{jj} , which represent the probabilities that each level $|j\rangle$ is populated, and off-diagonal elements $\rho_{ij} = \rho_{ji}^*$ ($i \neq j$), which represent the coherences between levels $|i\rangle$ and $|j\rangle$. The equation of motion for the density matrix can be expressed as the quantum Liouville equation,

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} [\mathcal{H}_0 + \mathcal{H}_1, \rho] - \sum_j \left(\Gamma_j \rho_{jj} |j\rangle\langle j| - \sum_i \gamma_{ij} \{ |i\rangle\langle i|, \rho \}_+ \right), \quad (16)$$

where we express the total Hamiltonian of the system as a sum of the Hamiltonian of the unperturbed system $\mathcal{H}_0$ and an interaction Hamiltonian $\mathcal{H}_1$. The notation $\{ \}_+$ represents the anticommutator of the operators. In the current analysis, the interaction Hamiltonian is expressed in the electric-dipole approximation as $\mathcal{H}_1 = -\vec{d} \cdot \vec{E}$. Additionally, the relaxation processes are assumed to be Markovian and their associated rates Γ_i and γ_{ij} are described phenomenologically in the previous section. With these approximations, we can write the following equations for the diagonal and off-diagonal elements of the density matrix:

$$\frac{\partial \rho_{jj}}{\partial t} = -\Gamma_j \rho_{jj} + \sum_{k \neq j} \Gamma_{kj} \rho_{kk} + \frac{i}{\hbar} \sum_k (\vec{d}_{jk} \rho_{kj} - \rho_{jk} \vec{d}_{kj}) \cdot \vec{E}, \quad (17)$$

$$\frac{\partial \rho_{ij}}{\partial t} = -\rho_{ij}(i\omega_{ij} + \gamma_{ij}) + \frac{i}{\hbar} \sum_k (\vec{d}_{ik} \rho_{kj} - \rho_{ik} \vec{d}_{kj}) \cdot \vec{E},$$

where $\hbar\omega_{ij}$ is the energy difference between levels $|i\rangle$ and $|j\rangle$, and coherence matrix element $\rho_{ij} = \rho_{ji}^*$.

Because of incoherent coupling of all six levels through the relaxation model, all six equations for the diagonal elements of the density matrix must be considered. However, the density-matrix equations for only six of the off-diagonal elements are nontrivial because we assume the laser fields interact only with the three unprimed levels. Considering the four coherent transitions shown in Fig. 1, we assume the only nonzero interaction energies are $\vec{d}_{ac} \cdot \vec{E}_1$, $\vec{d}_{ab} \cdot \vec{E}_2$, $\vec{d}_{ab} \cdot \vec{E}_3$, and $\vec{d}_{ac} \cdot \vec{E}_4$. The three coherences oscillate at the frequencies of the relevant driving fields and can be written explicitly as³²

$$\begin{aligned} \rho_{ac} &= \sigma_{ac} e^{-i\nu_1 t} + \eta_{ac} e^{-i\nu_4 t}, \\ \rho_{ab} &= \sigma_{ab} e^{-i\nu_2 t} + \eta_{ab} e^{-i\nu_3 t}, \\ \rho_{bc} &= \tilde{\rho}_{bc} e^{-i(\nu_1 - \nu_2)t}, \end{aligned} \quad (18)$$

where σ_{aj} , η_{aj} , and $\tilde{\rho}_{bc}$ represent slowly varying amplitudes. Here, σ_{ac} and σ_{ab} correspond to the off-resonant coherence terms generated by the pump and Stokes interactions, respectively, and $\tilde{\rho}_{bc}$ is the resulting Raman coherence. Similarly, η_{ab} and η_{ac} represent the resonant coherences corresponding to the probe and signal interactions, respectively. The diagonal elements of the density matrix remain invariant in the transformed space because they are slowly varying with respect to optical frequencies.

We write the density-matrix equations in terms of the slowly varying envelopes by substituting Eqs. (18) into Eqs. (17) and use the rotating-wave approximation to eliminate the terms that oscillate at optical frequencies. The equations are explicitly written as

$$\begin{aligned}
\frac{\partial \sigma_{ab}}{\partial t} &= -(\gamma_{ab} + i\delta)\sigma_{ab} + i\Omega_2(\rho_{bb} - \rho_{aa}) + i\Omega_1\tilde{\rho}_{bc}^*, \\
\frac{\partial \eta_{ab}}{\partial t} &= -(\gamma_{ab} + i\Delta)\eta_{ab} + i\Omega_3(\rho_{bb} - \rho_{aa}) + i\Omega_4\tilde{\rho}_{bc}^*, \\
\frac{\partial \sigma_{ac}}{\partial t} &= -(\gamma_{ac} + i\delta)\sigma_{ac} + i\Omega_1(\rho_{cc} - \rho_{aa}) + i\Omega_2\tilde{\rho}_{bc}, \\
\frac{\partial \eta_{ac}}{\partial t} &= -(\gamma_{ac} + i\Delta)\eta_{ac} + i\Omega_4(\rho_{cc} - \rho_{aa}) + i\Omega_3\tilde{\rho}_{bc}, \\
\frac{\partial \tilde{\rho}_{bc}}{\partial t} &= -\gamma_{bc}\tilde{\rho}_{bc} + i(\Omega_2^*\sigma_{ac} + \Omega_3^*\eta_{ac}) - i(\Omega_1\sigma_{ab}^* + \Omega_4\eta_{ab}^*), \\
\frac{\partial \rho_{aa}}{\partial t} &= -\Gamma_{a'aa} + \Gamma_{a'a} \rho_{a'a'} + i(\Omega_1\sigma_{ac}^* + \Omega_4\eta_{ac}^*) \\
&\quad - i(\Omega_1^*\sigma_{ac} + \Omega_4^*\eta_{ac}) + i(\Omega_2\sigma_{ab}^* + \Omega_3\eta_{ab}^*) \\
&\quad - i(\Omega_2^*\sigma_{ab} + \Omega_3^*\eta_{ab}), \\
\frac{\partial \rho_{bb}}{\partial t} &= -\Gamma_{bb'} \rho_{bb} + \Gamma_{b'b} \rho_{b'b'} - i(\Omega_2\sigma_{ba} + \Omega_3\eta_{ba}) \\
&\quad + i(\Omega_2^*\sigma_{ab} + \Omega_3^*\eta_{ab}), \\
\frac{\partial \rho_{cc}}{\partial t} &= -\Gamma_{cc'} \rho_{cc} + \Gamma_{c'c} \rho_{c'c'} - i(\Omega_1\sigma_{ac}^* + \Omega_4\eta_{ac}^*) \\
&\quad + i(\Omega_1^*\sigma_{ac} + \Omega_4^*\eta_{ac}), \\
\frac{\partial \rho_{a'a'}}{\partial t} &= -\Gamma_{a'a} \rho_{a'a'} + \Gamma_{aa'} \rho_{aa}, \\
\frac{\partial \rho_{b'b'}}{\partial t} &= -\Gamma_{b'b} \rho_{b'b'} + \Gamma_{ab'} \rho_{aa} + \Gamma_{a'b'} \rho_{a'a'} + \Gamma_{bb'} \rho_{bb}, \\
\frac{\partial \rho_{c'c'}}{\partial t} &= -\Gamma_{c'c} \rho_{c'c'} + \Gamma_{ac'} \rho_{aa} + \Gamma_{a'c'} \rho_{a'a'} + \Gamma_{cc'} \rho_{cc}.
\end{aligned} \tag{19}$$

The above equations are expressed in terms of the time-varying Rabi frequencies for each of the laser interactions,

$$\begin{aligned}
\Omega_1 &= \vec{d}_{ac} \cdot \hat{e}_1 \mathcal{E}_1(t)/\hbar, \\
\Omega_2 &= \vec{d}_{ab} \cdot \hat{e}_2 \mathcal{E}_2(t)/\hbar, \\
\Omega_3 &= \vec{d}_{ab} \cdot \hat{e}_3 \mathcal{E}_3(t)/\hbar, \\
\Omega_4 &= \vec{d}_{ac} \cdot \hat{e}_4 \mathcal{E}_4(t)/\hbar.
\end{aligned} \tag{20}$$

The amplitude $\mathcal{P}_4$ of the macroscopic polarization can now be written in terms of the slowly varying coherence amplitude by isolating the term in Eq. (15) that oscillates at frequency ν_4 . According to the definition of coherence oscillation in Eq. (18), we write

$$\mathcal{P}_4 = N(\vec{d}_{ca} \cdot \hat{e}_4) \eta_{ac}. \tag{21}$$

This result can be directly substituted into Eq. (14) to describe the growth of the ERE-CARS signal field. Assuming η_{ac} does not change along the interaction length L , integration of Eq. (14) is trivial, and we can write the ERE-CARS signal intensity as

$$I_{\text{CARS}}(t) = \frac{\epsilon_0 c |\mathcal{E}_4(t, L)|^2}{2} \propto N^2 L^2 d_{ac}^2 |\eta_{ac}(t)|^2. \tag{22}$$

Equation (22) demonstrates the expected quadratic dependencies on number density, interaction length, and transition dipole moment. In laboratory experiments, the ERE-CARS signal is typically time integrated. Therefore, the recorded signal S_{CARS} is proportional to the integral of the squared coherence amplitude

$$S_{\text{CARS}} \propto \int |\eta_{ac}(t)|^2 dt. \tag{23}$$

Solutions for the electronic coherence η_{ac} can be obtained either by approximate analytical calculation or by direct-numerical integration³² of the density-matrix Eq. (19), as presented in the following sections.

III. STEADY-STATE SOLUTION IN WEAK-FIELD REGIME

In this section we present an analytical steady-state solution for η_{ac} in the regime of weak laser fields, i.e., $|\Omega_i| < \gamma_{ac}(=\gamma_{ab}), \gamma_{bc}$. In the steady-state limit, all time derivatives in Eq. (19) are set to zero. In this limit we adopt a new notation for density-matrix elements $\mathcal{R}_{\alpha\beta} \rightarrow \mathcal{R}_{\alpha\beta}^{\text{ss}}$, where $\mathcal{R}$ can correspond to ρ , σ , or η matrix elements. The calculation and results are briefly outlined in the following.

To simplify the solution, we set the probe detuning Δ equal to zero; assuming the pump and Stokes detuning δ is much larger than any other relevant frequencies in the solution. For a weak signal field, such that $\Omega_4(\rho_{cc}^{\text{ss}} - \rho_{aa}^{\text{ss}}) \ll \Omega_3 \rho_{bc}$, the steady-state solution for the electronic coherence is obtained as

$$\eta_{ac}^{\text{ss}} = i \frac{\Omega_3 \tilde{\rho}_{bc}^{\text{ss}}}{\gamma_{ac}}. \tag{24}$$

As expected, the form of Eq. (24) demonstrates the coherence responsible for generating the ERE-CARS signal is primarily the result of the interaction of the probe field with the Raman coherence. The magnitude of the resulting coherence is inversely proportional to the dephasing rate of the electronic coherence.

Solving the density-matrix equations for the steady-state Raman coherence, we obtain

$$\begin{aligned}
\tilde{\rho}_{bc}^{\text{ss}} &= -\frac{1}{\zeta} \left[\Omega_1 \Omega_2^* \left\{ \frac{\rho_{cc}^{\text{ss}} - \rho_{aa}^{\text{ss}}}{\gamma + i\delta} + \frac{\rho_{bb}^{\text{ss}} - \rho_{aa}^{\text{ss}}}{\gamma - i\delta} \right\} \right. \\
&\quad \left. + \frac{\Omega_3^* \Omega_4}{\gamma} (\rho_{cc}^{\text{ss}} + \rho_{bb}^{\text{ss}} - 2\rho_{aa}^{\text{ss}}) \right],
\end{aligned} \tag{25}$$

where

$$\zeta = \gamma_{bc} + \frac{|\Omega_1|^2}{\gamma - i\delta} + \frac{|\Omega_2|^2}{\gamma + i\delta} + \frac{|\Omega_3|^2 + |\Omega_4|^2}{\gamma}. \quad (26)$$

Here we assumed $\gamma_{ab} = \gamma_{ac} = \gamma$. To simplify the above solution for the Raman coherence in Eq. (25), we use the following approximations:

$$\delta \gg \gamma, \quad (27a)$$

$$|\Omega_3|^2 \gg \left(\frac{\gamma}{\delta}\right)|\Omega_1|^2, \left(\frac{\gamma}{\delta}\right)|\Omega_2|^2, |\Omega_4|^2, \left(\frac{\gamma}{\delta}\right)\gamma\gamma_{bc}, \quad (27b)$$

$$|\Omega_3| \ll \left(\frac{\gamma}{\delta}\right) \frac{|\Omega_1||\Omega_2|}{|\Omega_4|} \frac{(\rho_{cc}^{ss} - \rho_{bb}^{ss})}{(\rho_{cc}^{ss} + \rho_{bb}^{ss} - 2\rho_{aa}^{ss})}. \quad (27c)$$

In the limit $|\Omega_4| \rightarrow 0$, the approximation (27c) becomes trivial. The above conditions are within the range of typical experimental conditions. For example, in Ref. 2, $\gamma/\delta \sim 10^{-5}$ and $|\Omega_3|^2$ is only one order of magnitude weaker than $|\Omega_1|^2$ and $|\Omega_2|^2$. With the above approximations in Eq. (27), the steady-state Raman coherence is obtained as

$$|\tilde{\rho}_{bc}^{ss}| = \frac{|\Omega_1||\Omega_2|}{\delta\gamma_{bc} \left[1 + \frac{|\Omega_3|^2}{\gamma\gamma_{bc}}\right]} (\rho_{cc}^{ss} - \rho_{bb}^{ss}). \quad (28)$$

The probe Rabi frequency in the denominator of Eq. (28) indicates that the resonant probe interaction can decrease the Raman coherence in the ERE-CARS configuration. This effect is described in more detail in the numerical simulations presented in Sec. IV B. In the weak-field limit, however, $|\Omega_3|$ is significantly smaller than both dephasing rates and this term is negligible. The effects of probe intensity on Raman coherence in an ERE-CARS configuration are discussed in Ref. 11.

Neglecting the probe-intensity-dependent term in Eq. (28), we can rewrite the expression for the squared Raman coherence in terms of the electric-field amplitudes and transition dipole moments as follows:

$$|\tilde{\rho}_{bc}^{ss}|^2 = \left[\frac{d_{ac}^2 d_{ab}^2}{\hbar^2 \delta^2} \right] \frac{|\mathcal{E}_1|^2 |\mathcal{E}_2|^2}{\gamma_{bc}^2} (\rho_{cc}^{ss} - \rho_{bb}^{ss})^2. \quad (29)$$

The squared coherence term scales as the product of the pump and Stokes intensities and inversely as the square of the Raman dephasing rate. The term in brackets approximates the Raman cross section and the appearance in the denominator of the very large detuning δ of the pump and Stokes lasers from electronic resonance is a manifestation of their correspondingly weak electronic-dipole interactions. Although not implemented in the current work, Lucht and co-workers^{8,32} outlined a convenient means for appropriately adjusting the dipole-moment elements for the pump and Stokes interactions to approximate an empirically determined Raman cross section.

Substituting the results of Eqs. (24) and (29) into Eq. (22) and assuming negligible vibrational excitation to the state $|b\rangle$, we obtain the following solution for the ERE-CARS signal:

$$I_{\text{CARS}} \propto (N\rho_{cc}^{ss})^2 L^2 \left[\frac{d_{ac}^2 d_{ab}^2}{\hbar^2 \delta^2} \right] \left[\frac{d_{ab}^2}{\hbar} \right] \left[\frac{d_{ac}^2}{\hbar} \right] \frac{|\mathcal{E}_1|^2 |\mathcal{E}_2|^2 |\mathcal{E}_3|^2}{\gamma^2 \gamma_{bc}^2}. \quad (30)$$

The ERE-CARS signal scales quadratically with $(N\rho_{cc})$, the number density of NO molecules in the ground level $|c\rangle$ that is directly addressed by the lasers. Unlike the signal in the case of laser-induced fluorescence, the ERE-CARS signal does not explicitly depend on the excited-state population. The signal scales as the product of the three applied laser pulse intensities and the terms in brackets are proportional to cross sections for the Raman, probe, and signal transitions.

The collisional dependence of the ERE-CARS signal enters through the electronic and Raman dephasing rates in the denominator of Eq. (30). Using Eqs. (8) and (9), we can explicitly write the collisional dependence for the signal in terms of RET, quenching, and pure electronic dephasing rates,

$$\gamma_{bc}^{-2} \gamma^{-2} = R^{-2} \left[\gamma^{\text{pd}} + R + \frac{Q+A}{2} \right]^{-2}. \quad (31)$$

For all practical purposes, spontaneous decay is negligible in the current expression. As discussed in Sec. II A, pure electronic dephasing is the fastest process, and RET is typically faster than or comparable to quenching. Thus we rewrite Eq. (31) as

$$\gamma_{bc}^{-2} \gamma^{-2} = R^{-2} (\gamma^{\text{pd}})^{-2} \left[1 + \frac{R}{\gamma^{\text{pd}}} + \frac{Q}{2\gamma^{\text{pd}}} \right]^{-2}. \quad (32)$$

Thus to the lowest order, the ERE-CARS signal scales inversely with the squares of the RET rate and the pure electronic dephasing rate of NO.

Because both R and γ^{pd} depend linearly on the total pressure p_{tot} and are generally only weakly dependent on the specific chemical composition of the NO gas mixture, the collision dependence in Eq. (32) is approximately proportional to $(p_{\text{tot}})^{-4}$. Although quenching is a strong function of the specific gas composition, its effect on the collisional dependence of the ERE-CARS signal is weak because the pure electronic dephasing rate is much faster than the quenching rate of NO. Thus, the experimentally observed insensitivity of ERE-CARS to quenching in Ref. 2 is explained in view of the current steady-state perturbation analysis. Expressing the number density of NO as the product of the NO mole fraction and the total pressure, one infers a $(p_{\text{tot}})^{-2}$ signal dependence when the gas composition is constant.

However, because we assumed weak laser fields in the above steady-state analysis, we cannot accurately predict collisional effects in the regime of strong nonlinear coupling between the levels. From a practical point of view, the use of stronger laser interactions is motivated both for increasing signal levels and for potentially reducing the collisional dependence.³³ In principle, at sufficiently high field strength, the effect of laser saturation on homogeneous broadening can overwhelm the effect of collisions and, thus, reduce the dependence of the ERE-CARS signal on the collision rate. The

TABLE I. Experimental mixture conditions from Ref. 2 and corresponding collision-model parameters used in simulations presented in Fig. 2. The bracketed values for the RET rates in mixtures containing CO₂ represent two limiting cases where the CO₂ RET rate is assumed to be either 15% less (Ref. 13) or 25% more (Ref. 15) than the N₂ RET rate.

Gas composition				Model parameters ($1 \times 10^{10} \text{ s}^{-1}$)		
X_{NO}	X_{N_2}	X_{O_2}	X_{CO_2}	R	γ_{aj}	Q
0.001	0.999	0	0	1.09	5.5	0.0007
0.001	0.799	0.20	0	1.06	5.4	0.086
0.001	0.499	0.50	0	1.02	5.3	0.21
0.001	0.199	0.80	0	0.98	5.1	0.34
0.001	0.799	0	0.20	{1.05–1.14}	5.6	0.20
0.001	0.499	0	0.50	{1.00–1.22}	5.6	0.50
0.001	0.199	0	0.80	{0.96–1.30}	5.7	0.81

exploration of the strong-interaction regime requires a numerical solution of the density-matrix equations, which is the subject of the following section.

IV. NUMERICAL RESULTS

In this section, nonperturbative numerical solutions to the density-matrix equations are presented. First, numerical solutions are used to simulate the ERE-CARS signals for the experimental conditions described in Ref. 2. Next, a series of results is used in a parametric study of the effects of quenching, RET, and pure electronic dephasing on the Raman coherence and the electronic coherence responsible for generating the ERE-CARS signal. Direct numerical integration of the density-matrix equations was performed using a fifth-order Runge–Kutta method. All computations used Gaussian applied laser fields with a full width at half maximum (FWHM) of 8 ns, which corresponds to a pulse-intensity FWHM of 5.7 ns. The Rabi frequencies of the pump and Stokes lasers were $\Omega_1 = \Omega_2 = 5 \times 10^{10} \text{ s}^{-1}$ ($=10^4 \text{ A}$), and the Rabi frequency of the probe field was $\Omega_3 = \Omega_1 / \sqrt{10}$. Unless otherwise noted, the quenching branching ratio β was set to 0.4. The detuning of the pump (and Stokes) field was $\delta = 5 \times 10^5 \text{ A}$. We observed that as long as δ was chosen to be larger than the maximum values of the decay and dephasing rates in the discussion, the behavior of the results presented below remained consistent.

A. Simulation of ERE-CARS in atmospheric-pressure flows

Here we present numerical results using parameters that represent the experimental conditions that were investigated in Ref. 2 in a study of effects of gas composition on the ERE-CARS signal. When the mixture composition of NO/N₂/O₂ or NO/N₂/CO₂ atmospheric-pressure jets was varied to produce quenching rates that spanned three decades, the authors observed only a minor (<30%) variation in signal. The experimental conditions are summarized in the first four columns of Table I.

Species-specific rate constants were used to estimate the RET, quenching, and electronic dephasing rates for the seven gas mixtures in Table I. The calculated collision-rate parameters for the ERE-CARS model appear in the last three col-

umns of the table. The RET rate constants for N₂ ($14.3 \times 10^6 \text{ s}^{-1} \text{ Torr}^{-1}$) and O₂ ($12.5 \times 10^6 \text{ s}^{-1} \text{ Torr}^{-1}$) were taken from recent pressure-broadened lineshape measurements of pure rotational transitions in $X^2\Pi(v=0)$.³¹ These constants are consistent with those inferred from measurements of rovibrational line shapes.^{29,30} We are aware of only two investigations of NO RET caused by collisions with CO₂. Broida and Carrington¹⁵ studied RET in $A^2\Sigma^+(v=1)$ and reported that the NO RET rate constant for CO₂ is $\sim 25\%$ larger than that for N₂. On the other hand, Islam *et al.*¹³ reported that the NO RET rate constant in $X^2\Pi_{1/2}(v=2, J=6.5)$ for CO₂ is $\sim 15\%$ smaller than that for N₂. To bracket the value of the rate constant for CO₂, we scaled the rate constant for N₂ from Ref. 31 by the reported ratio of rate constants for CO₂ and N₂ in either Ref. 13 or Ref. 15. Room-temperature rate constants for electronic quenching of $A^2\Sigma^+(v=0)$ were taken from Refs. 22 and 23. The rate constants for quenching of NO by N₂, NO, O₂, and CO₂ are 0.001, 8.2, 5.6, and $13.3 \times 10^6 \text{ s}^{-1} \text{ Torr}^{-1}$, respectively. Total electronic dephasing rates were based on room-temperature collisional linewidth measurements for broadening of NO(A-X) transitions. The rate constants for electronic dephasing of NO by NO, N₂, O₂, and CO₂ are 6.8,²⁸ 7.3,²⁶ 6.6,²⁸ and $7.5 \times 10^7 \text{ s}^{-1} \text{ Torr}^{-1}$,²⁶ respectively.

Simulation results for the NO/N₂/O₂ mixtures are shown in Fig. 2(a) and those for the NO/N₂/CO₂ mixtures (using the smaller limiting values in Table I for R) are shown in Fig. 2(b). In accord with the experimental results,² only a weak dependence of $|\eta_{ac}|^2$ on the mixture composition is observed. Clearly, in both cases, changing the electronic quenching rate by a factor of up to 10^3 does not affect the signal significantly because the electronic dephasing rate, the fastest incoherent process, is similar in all mixtures.

Because both the Raman and electronic dephasing rates decrease slightly with increasing O₂ concentration, a corresponding increase in $|\eta_{ac}|^2$ is observed in the O₂ jet. The collision dependence in the steady-state solution, Eq. (32), predicts the signal in the 80% O₂ jet should be $\sim 45\%$ larger than that in the NO/N₂ jet. Similarly, the simulation results indicate a 30% change in the integrated signal. We ascertain that the high-field conditions slightly reduce the dependence on the electronic dephasing rate.

The electronic dephasing is approximately constant in

FIG. 2. (Color online) Squared electronic coherence amplitudes for the ERE-CARS signal transition in atmospheric-pressure flows of 1000 ppm NO in N_2 diluted with (a) O_2 and (b) CO_2 . The origin ($t=0$) of the time axis corresponds to the time when the peak of all applied pulses reaches the molecule. The relevant collisional parameters listed in Table I correspond to the experimental conditions investigated in Ref. 2.

the CO_2 jet, but the RET rate—and, thus, the Raman dephasing rate—decreases slightly with increasing CO_2 concentration. In accord with the steady-state solution, the simulations show a 15% increase in the signal when the CO_2 concentration is increased from 0% to 80%. Although not shown, when we used the larger limiting values in Table I for R in the CO_2 jet, a slight decrease in $|\eta_{ac}|^2$ was observed for increasing CO_2 concentration, in accord with expectations.

B. Parametric study

To isolate the individual effects of quenching, RET, and pure electronic dephasing on ERE-CARS signal generation, a parametric study was conducted. We considered variation of these three parameters around values that approximately correspond to conditions in an atmospheric-pressure mixture of 1000 ppm NO in 50% N_2 /50% CO_2 ($Q_0=10^3$ A, $R_0=2 \times 10^3$ A, and $\gamma_0^{pd}=10^4$ A). Numerical results for the evolution of Raman and electronic coherences are presented subsequently. Additionally, we simulated the parametric dependence of experimentally measured signals S_{CARS} by time integrating the square of the electronic coherence.

FIG. 3. (Color online) (a) Raman coherence and (b) squared electronic coherence for various values of the quenching rate, with the electronic dephasing rate and RET rate being fixed at the values γ_0^{pd} and R_0 , respectively. The dashed, solid, and dotted curves correspond to $Q=10^2$ A, 10^3 A, and 10^4 A, respectively. (c) Variation in the time-integrated signal for quenching branching ratios of 0.4 (solid) and 0 (dot-dashed).

1. Electronic quenching

The electronic quenching rate can change significantly if the quenching partners of NO change.²² Here, we consider results for quenching rates of $Q=10^2$ A, 10^3 A, and 10^4 A, with the electronic dephasing rate and RET rate being fixed at the values γ_0^{pd} and R_0 , respectively. Figure 3 presents the time evolution of the amplitude of the Raman coherence $|\tilde{\rho}_{bc}|$ and the square of the amplitude of the electronic coherence $|\eta_{ac}|^2$ that depicts the behavior of the signal intensity.

As shown in Fig. 3(a), the Raman coherence is insensitive to the quenching rate for $Q \leq \gamma_{bc} = R_0$. Interestingly, however, when the quenching rate exceeds the dephasing rate of the Raman coherence, $|\tilde{\rho}_{bc}|$ increases slightly. This increase can be explained by the following two phenomena: (1) population increases in the ground-state energy levels that result from rapid quenching and subsequent rapid rotational thermalization; then the quenched population is re-pumped by the strong coherent excitations via the pump and Stokes field to increase $|\tilde{\rho}_{bc}|$,¹¹ and (2) increased quenching also increases electronic dephasing in the probe transition and, thus, reduces the effective probe perturbation on Raman coherence such that ρ_{bc} approaches its enhanced unperturbed value. Note that while the above phenomenon (1) significantly contributes in the continuous-wave or long-pulse laser regime, phenomenon (2) is more prominent in a relatively short-pulse regime. Furthermore, even as the Raman coherence increases slightly because of the increased population transfer at the highest quenching rate, $|\eta_{ac}(t)|^2$ decreases by 35% because of the increased electronic dephasing.

In Fig. 3(c), the integrated signal is plotted as a function of the quenching rate. The solid curve corresponds to the results shown in the main plot, where we assume significant branching of quenched molecules to the ground levels occurs ($\beta=0.4$). The dot-dashed curve corresponds to the case where no transfer of quenched population to the ground levels occurs ($\beta=0$). Here, it is clear that the population transfer to the ground state for $Q > R_0$ can slightly offset (of the order 1% or less) the loss in signal caused by increased electronic dephasing of the probe and signal transitions. Thus, the dominant effect of quenching on the ERE-CARS signal is dephasing and the final states of the quenching process are of only minor importance.

2. Rotational energy transfer

Rotational energy transfer enables rotational thermalization within each vibrational manifold, completely accounts for the dephasing of the Raman coherence, and contributes to the electronic dephasing. Here we consider results for RET rates of 2×10^2 A, 2×10^3 A, and 2×10^4 A, with the pure electronic dephasing rate and quenching rate being fixed at the values γ_0^{pd} and Q_0 , respectively. Figure 4 presents the time evolution of $|\tilde{\rho}_{bc}|$ and $|\eta_{ac}|^2$.

Because saturation of the Raman coherence scales inversely with the dephasing rate ($\gamma_{bc}=R$) and because the Rabi frequency associated with the pump and Stokes fields is 10^4 A, strong saturation of $|\tilde{\rho}_{bc}|$ is evident for $R=2 \times 10^2$ A. Although the slow RET has a considerable effect on saturation of the Raman coherence, its effect on dephasing of the electronic interactions of the probe and signal pulses is negligible for $R=2 \times 10^2$ A.

The integrated signal is shown as a function of the RET rate in Fig. 4(c). In the steady-state limit, Eq. (32) predicts that the signal scales as R^{-2} when $R \ll \gamma^{\text{pd}} + Q/2$ and that it scales as R^{-4} when $R \gg \gamma^{\text{pd}} + Q/2$. Because of the strong saturation of the Raman transition for $R=2 \times 10^2$ A, the integrated signal displays a very weak collisional dependence of

FIG. 4. (Color online) (a) Raman coherence and (b) squared electronic coherence for various values of the RET rate, with the electronic dephasing rate and quenching rate being fixed at the values γ_0^{pd} and Q_0 , respectively. The dashed, solid, and dotted curves correspond to $R=2 \times 10^2$ A, 2×10^3 A, and 2×10^4 A, respectively. (c) Variation in the time-integrated signal as a function of RET rate.

$\sim R^{-0.3}$, which is far less than the expected R^{-2} dependence. The sensitivity of the signal to the collision rate, however, does increase with R because of the reduced saturation of the Raman transition and the additional detrimental effect of increased electronic dephasing. At the largest value of R in Fig. 4, saturation is significantly reduced and the sensitivity of the simulated signal is in accord with the predicted $R^{-3.5}$ dependence from Eq. (32).

FIG. 5. (Color online) (a) Raman coherence and (b) squared electronic coherence for various values of the pure dephasing rate, with the RET rate and quenching rate being fixed at the values R_0 and Q_0 , respectively. The dashed, solid, and dotted curves correspond to $\gamma^{pd}=10^3 A$, $10^4 A$, and $10^5 A$, respectively. (c) Variation in the time-integrated signal as a function of the pure dephasing in the electronic transition.

3. Pure electronic dephasing

In NO, pure electronic dephasing is the most rapid collisional process relevant to ERE-CARS signal generation. Here, we consider numerical results for pure electronic dephasing rates of $10^3 A$, $10^4 A$, and $10^5 A$, with RET and quenching rates being fixed at values R_0 and Q_0 , respectively. Figure 5 presents the time evolution of $|\tilde{\rho}_{bc}|$ and $|\eta_{ac}|^2$ for these conditions.

Pure electronic dephasing directly affects saturation of

the probe and signal transitions and its effect on the pump and Stokes transitions is negligible because of the very large detuning of these fields from electronic resonance. Therefore, the Raman coherence is sensitive to the vibrational—not the electronic—dephasing. However, Fig. 5(a) shows both the shape and the amplitude of the Raman coherence depend on γ^{pd} . Although this effect is nonintuitive upon first consideration, we can explain this behavior in terms of the higher-order interaction of the probe laser with the Raman transition. Although in a strict sense not valid for the current conditions, Eq. (28) can be used to describe the numerical results qualitatively. If population is pumped out of $|b\rangle$, a strong resonant probe interaction can decrease the Raman coherence. At $\gamma^{pd}=10^5 A$, dephasing is sufficiently rapid that the effect of the probe interaction is weak, and the Raman coherence is relatively unperturbed by the probe. At the slower dephasing rates, however, the probe interaction becomes more significant. For $\gamma^{pd}=10^4 A$, the ratio $|\Omega_3|^2/\gamma_{ac}\gamma_{bc}=0.4$ and the probe interaction causes slight temporal broadening and reduction in the maximum of the Raman coherence. This effect is more dramatic for $\gamma^{pd}=10^3 A$, where $|\Omega_3|^2/\gamma_{ac}\gamma_{bc}=1.4$ and the saturated probe transition causes significant temporal broadening as well as a 45% reduction in the maximum of the Raman coherence.

The time evolution of $|\eta_{ac}|^2$ is shown in Fig. 5(b). In this case a strong negative dependence on the pure dephasing rate is observed, in accord with expectations. Figure 5(c) shows the integrated signal as a function of the pure dephasing rate. Here, it is clear the detrimental effect of dephasing of the electronic coherence overwhelms the relatively small effects on the Raman coherence.

V. CONCLUSION

A six-level model is used to describe the coherent-excitation and collisional incoherent-relaxation processes that are relevant to ERE-CARS in NO. A semiclassical description of the ERE-CARS signal is presented using the density-matrix formalism. An approximate steady-state solution to the density-matrix equations predicts an inverse squared dependence on the Raman and electronic dephasing rates for the ERE-CARS signal in the weak-field limit. Because the total electronic dephasing rate of NO is largely determined by pure electronic (elastic) dephasing, only a weak dependence on electronic quenching is observed.

Direct numerical integration of the density-matrix equations provides a nonperturbative solution for the coherences. Numerical simulations of ERE-CARS signals for experimental conditions representative of those used in Ref. 2 to study the effects of gas composition on the signal agree with experimental results, demonstrating relative insensitivity to collisional quenching. A detailed parametric study of the effects of quenching, RET, and pure electronic dephasing rates on the Raman and electronic coherences is presented. The parametric studies reveal weak dependencies of the Raman coherence on the electronic quenching and electronic (elastic) dephasing rates but a very strong dependence on the RET rate. Furthermore, the square of electronic coherence in the CARS transition, and, hence, the ERE-CARS signal, has a

very strong dependence on both RET and electronic (elastic) dephasing and has a much weaker dependence on quenching. The results also indicate that strong saturation by the applied lasers not only enhances the signal strength but also reduces the effective dependence of the signal on the decay and dephasing rates.

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