Perturbative Theory and Modeling of Electronic-Resonance-Enhanced Coherent Anti-Stokes Raman Scattering Spectroscopy of Nitric Oxide

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Abstract

A theory is developed for three-laser electronic-resonance-enhanced (ERE) coherent anti-Stokes Raman scattering (CARS) spectroscopy of nitric oxide (NO). A vibrational Q-branch Raman polarization is excited in the NO molecule by the frequency difference between visible Raman pump and Stokes beams. An ultraviolet probe beam is scattered from the induced Raman polarization to produce an ultraviolet ERE-CARS signal. The frequency of the ultraviolet probe beam is selected to be in electronic resonance with rotational transitions in the $A^2\Sigma^+ \leftarrow X^2\Pi (1,0)$ band of NO. This choice results in a resonance between the frequency of the ERE-CARS signal and transitions in the $(0,0)$ band. The theoretical model for ERE-CARS NO spectra has been developed in the perturbative limit. Comparisons to experimental spectra are presented where either the probe laser was scanned with fixed Stokes frequency or the Stokes laser was scanned with fixed probe frequency. At atmospheric pressure and an NO concentration of 100 ppm, good agreement is found between theoretical and experimental spectral peak locations and relative intensities for both types of spectra. Factors relating to saturation in the experiments are discussed, including implications for the theoretical predictions.

1 Introduction

Electronic-resonance-enhanced (ERE) coherent anti-Stokes Raman scattering (CARS) spectra of nitric oxide (NO) have been investigated theoretically and experimentally by employing a three-laser or dual-pump CARS method. This paper explores the details and capabilities of a developed theory for the ERE-CARS process. With increased attention on combustion emissions and pollutant formation and the use of NO tracers in flowfield mixing studies, the need has arisen for a diagnostic technique capable of probing low number density levels ($\sim 10$ ppm) of radical species such as NO. Moreover, strong interest exists in studying thermally generated NO in hypersonic flowfields, as knowledge of NO concentration at elevated temperature levels would provide insight into the reaction rates required for modeling these flowfields. Beyond the effects on the flowfield, NO formation has been
demonstrated as an excellent flowfield tracer in hypersonic flows. Finally, developments in the area of national security have prompted a need for techniques that not only can detect minor species, pollutants, and toxins, but that can do so rapidly, and ERE-CARS is a possible solution to this requirement.

Figure 1 represents the energy-level diagram for the three-laser process utilized in this CARS method. Visible Raman pump and Stokes beams induce a Raman transition through a virtual state that is far from resonance with the $A^2\Sigma^+ \leftarrow X^2\Pi$ electronic transition of NO. The third laser beam, termed the ultraviolet “probe” beam, has a frequency that probes the Raman resonance through the first excited electronic state of NO. Usually, this third beam is termed a “pump” beam. This nomenclature arose in the CARS literature because, in most CARS experiments, the $\omega_1$ and $\omega_3$ beams are produced from the same laser beam, i.e., $\omega_1 = \omega_3$, and each beam serves as a probe for the Raman polarization pumped by the other. However, for the case shown in Fig. 1, the $\omega_3$ beam does not participate in the generation of a Raman polarization in the medium and is thus referred to as the “probe” beam. In this manner, the CARS method employed in this study is a modified version of the dual-pump CARS process previously investigated for the simultaneous detection of two species.

Typically, the application of CARS for minor species detection and measurement is limited by coherent interference of the nonresonant background and the CARS signal from the Raman resonance of interest. The inherent nonresonant background susceptibility from major species, such as diatomic nitrogen ($N_2$), dominates the susceptibility when the Raman species is present in low concentration. This problem is magnified for molecules such as NO that possess relatively weak Raman cross-sections, resulting in an additional reduction in signal level compared to $N_2$. The use of polarization techniques to suppress the nonresonant background has been demonstrated; however, the application of such techniques results in a reduction in signal strength by at least a factor of 16. Therefore, polarization techniques are beneficial, but increases in the Raman resonant signal strength must be performed simultaneously.
Since the late 1970's, a few groups have investigated the potential of ERE-CARS for minor species measurements in flames or plasmas.\textsuperscript{12} The term electronic-resonance-enhanced is used to indicate that the frequency of the pump, probe, and/or Stokes beam is tuned near resonance with an electronic transition of the molecule. The electronic resonance can increase the resonant CARS signal considerably, minimizing concerns associated with the nonresonant background. The current technique differs from previous ERE-CARS investigations\textsuperscript{13–15} in that the frequency of the Raman pump ($\omega_1$) and ultraviolet probe ($\omega_3$) beams are well separated. As a result, the Raman process and electronic process are, in a sense, uncoupled.

In the past, the pump, Stokes, and probe beam frequencies were all in or near electronic resonance, a case termed “triple resonance.”\textsuperscript{16,17} Triple resonance spectra are difficult to interpret, because weaker double resonances appear near the major peaks.\textsuperscript{18} In almost all of these investigations, the intensity of any ultraviolet beam is restricted so as to maintain both Raman and electronic transitions within the perturbative regime; i.e, so that laser-induced population transfer is negligible for both the Raman and electronic transitions. However, the intensities of the visible pump and Stokes beams in this experiment are high enough that stimulated Raman pumping is expected to be a significant effect, and the Raman polarization that is established in the medium by the visible pump and Stokes beams is close to the maximum that can be attained without saturating the transition. The use of visible pump and Stokes beams simplifies the experimental implementation and theoretical treatment of ERE-CARS without sacrificing detection sensitivity. Additional benefits of Raman excitation with visible beams are that it permits easier interpretation of the features in the spectra and more transitions can be probed simultaneously.

Other techniques, such as laser-induced fluorescence (LIF), degenerate four-wave mixing (DFWM), and laser-induced polarization spectroscopy (PS) have proven useful for probing minor species; however, ERE-CARS has advantages over these techniques when the medium is at high pressure or when multiple species are present. For instance, to interpret an experimental LIF spectrum for concentration measurements, the collision partners must
be identified.\textsuperscript{2} DFWM can be independent of quenching rates,\textsuperscript{19} but it loses sensitivity compared to ERE-CARS at increased pressure levels.\textsuperscript{20} Similar to DFWM, PS can also be affected by collision rates.\textsuperscript{12} Hence, ERE-CARS is a preferable technique at high pressure or when quenching is problematic.

Additionally, at elevated temperatures and/or pressures, the LIF or DFWM spectra of various species can overlap, resulting in uncertainty as to which molecule is being probed.\textsuperscript{21,22} As implemented in these experiments, ERE-CARS has enhanced selectivity compared to LIF and DFWM because of the requirement for simultaneous Raman and electronic resonance for signal generation. This benefit in conjunction with minimized effects owing to pressure and varying collision partners make ERE-CARS a very attractive prospect.

2 Experimental System

The experimental system for NO ERE-CARS measurements is shown schematically in Fig. 2. A Q-switched Nd:YAG laser (Spectra-Physics GCR-4) with a repetition rate of 10 Hz and a pulse duration of approximately 7 ns was used to pump a narrowband, tunable dye laser (Lumonics), with Rhodamine 610 dye as the lasing medium. The dye laser output was centered near 590 nm with a frequency bandwidth of approximately 0.08 cm\textsuperscript{-1} and supplied the source for the Stokes beam (\(\omega_2\)). The 532-nm pump beam (\(\omega_1\)) for the CARS process was generated using a second injection-seeded, Q-switched Nd:YAG laser (Spectra-Physics 290-10). A narrowband dye laser (Continuum ND6000) was also pumped using this 532-nm output to produce tunable radiation in the vicinity of 704 nm; the laser dye used here was LDS 698. This radiation was mixed with the 355-nm third-harmonic output of the injection-seeded Nd:YAG laser to generate the probe beam (\(\omega_3\)) near 236 nm. A feedback-controlled frequency conversion system (INRAD Autotracker III) with a \(\beta\)-BBO nonlinear crystal was used for the sum-frequency-mixing process. The full-width at half-maximum (FWHM) frequency bandwidth of the single-axial-mode pump beam (\(\omega_1 = 532\) nm) was 0.003 cm\textsuperscript{-1} while the bandwidth of the ultraviolet probe beam (\(\omega_3 = 236\) nm) was approximately 0.1 cm\textsuperscript{-1}. 

5
A three-dimensional phase-matching scheme was employed to generate the ultraviolet, 226-nm ERE-CARS signal. The BOXCARS geometry$^{23}$ is slightly modified from the case of CARS performed with all visible beams. The patterns of the three laser beams on the focusing lens and of the laser beams and the CARS signal beam on the collimating lens are shown in Fig. 3. As a consequence of the large difference in momentum of the ultraviolet and visible photons interacting in the CARS process, the ultraviolet probe beam is much closer to the axis joining the centers of the input and output lenses than the visible pump and Stokes beams. The ultraviolet CARS signal beam is also generated much closer to this axis.

During a typical experiment, pulse energies of 5 mJ were used for the visible pump and Stokes beams. The maximum pulse energy of the ultraviolet probe beam was 0.25 mJ. The beams were focused at the probe volume and recollimated after interaction, along with the ERE-CARS signal, using a pair of 500-mm, focal-length lenses. At this point, beam dumps were used to capture the visible pump and Stokes beams. A joulemeter (Molectron J3-05) monitored the pulse energy of the ultraviolet probe beam after interaction. Four 215-nm dielectric mirrors, designed to be used at 45° incidence, and a set of apertures filtered the ERE-CARS signal. By utilizing the 215-nm mirrors at 0° incidence, a low-pass filter is formed that transmits 70% at 226 nm but only 1% at 236 nm, thereby significantly reducing background interference from the ultraviolet probe beam. The ERE-CARS signal was further isolated by a 1-m spectrometer (SPEX). The resulting signal intensity was collected using a solar-blind-photomultiplier tube (Hamamatsu R166) and oscilloscope (Tektronix TDS5054B). The joulemeter and photomultiplier output were recorded on a shot-by-shot basis during which time either the Stokes or the probe-beam frequency was scanned under computer control.

In addition to interference caused by scattered background from the ultraviolet probe beam, the ERE-CARS signal contained significant contributions from the nonresonant four-wave-mixing background signal, as discussed earlier. Therefore, once the ERE-CARS signal
was located and optimal system alignment obtained, a polarization technique was utilized to suppress the nonresonant background. This polarization arrangement is demonstrated in Fig. 4. The ultraviolet probe beam was vertically polarized, while the axes of the visible pump and Stokes beams were rotated $60^\circ$ to the vertical. This generates an almost vertically polarized ERE-CARS signal, and at the same time, caused the polarization of the nonresonant background to be rotated $30^\circ$ to the vertical. To take advantage of this technique, an $\alpha$-BBO analyzer was placed in the signal channel such that the transmission axis was perpendicular to the nonresonant background polarization. This significantly reduced the nonresonant background signal. While this diminishes the ERE-CARS signal as well, the overall effect is a considerable increase in signal-to-noise ratio (SNR).

3 Experimental Demonstration of Electronic Resonance Enhancement

The initial NO ERE-CARS experiments were performed with a room-temperature, sub-atmospheric mixture of 1% NO in a buffer gas of $N_2$ (10,000 ppm). The NO ERE-CARS spectrum shown in Fig. 5(a) was recorded by scanning the Stokes dye laser beam with a fixed ultraviolet probe-beam frequency $\omega_3$ of 42140.75 cm$^{-1}$ (237.3 nm). For this probe frequency, there is some electronic resonance enhancement, but the probe frequency is below the electronic transition frequency for the $(v_b = 1, v_d = 0)$ vibrational band. The spectrum shown in Fig. 5(b) was recorded by scanning the Stokes dye laser beam with a fixed ultraviolet probe-beam frequency closer to resonance (42194.09 cm$^{-1}$ or 237.0 nm). The enhancement upon electronic resonance is clearly evident.

The ERE-CARS signal frequency, $\omega_4$, is readily absorbed by 1% NO. Therefore, as the frequency $\omega_3$ is scanned further into electronic resonance, the NO concentration in the gas cell was decreased by a factor of ten to 1000 ppm. The results of this change are shown in Fig. 5(c), which represents a spectrum recorded for a fixed ultraviolet probe-beam frequency of 42337.00 cm$^{-1}$ (236.2 nm). The spectrum shown in Fig. 5(c) was acquired with all beams vertically polarized. The Stokes beam was blocked at the beginning of the scan for a Raman shift range of 1871.1 to 1871.6 cm$^{-1}$; hence, the increase in signal level at 1871.6 cm$^{-1}$ is
due to the nonresonant background. For subsequent recording of ERE-CARS spectra, the polarization scheme shown in Fig. 4 was used to suppress the nonresonant background. A typical spectrum recorded with polarization suppression is shown in Fig. 5(d) for 1000 ppm NO and a fixed probe-beam frequency of $42342.9 \text{ cm}^{-1}$.

4 Perturbative Theory for ERE-CARS

Theoretical studies of the third-order polarization susceptibility in the perturbative limit (low input laser powers) have been previously developed and tested for ERE-CARS.\textsuperscript{17,24–27} Bloembergen \textit{et al.}\textsuperscript{24} and Oudar and Shen\textsuperscript{25} both performed a perturbation expansion of the density matrix for the system. Eesley\textsuperscript{26} employed Hellwarth diagrams as a basis for the derivation, and Druet \textit{et al.}\textsuperscript{27} used a time-ordered diagrammatic approach. A review of these theories is found in Attal \textit{et al.}\textsuperscript{17} Line strength calculations for various Hund’s coupling cases for OH, C\textsubscript{2}, and CH\textsubscript{18} and for I\textsubscript{2}\textsuperscript{28} have also been performed. While significant work has been done to model the aforementioned molecular species, applying these models to NO requires some additional considerations. Because NO is closer to a pure Hund’s case (a), the satellite branches in the absorption spectrum are much stronger for higher values of the rotational quantum number, $J$, as opposed to OH.\textsuperscript{18} This introduces new transitions into the spectrum, which must be accounted for in the model.

The form of the polarization susceptibility modeled here is derived from the general third-order susceptibility given by Prior for all four-wave mixing processes.\textsuperscript{29} The double-sided Feynman diagrams concerning Raman resonances between levels $a$ and $b$ (see Fig. 1) are displayed in Fig. 6. These diagrams are similar to previous time-ordered diagrams,\textsuperscript{13} however, this presentation accounts for nondegenerate pump beams. In particular, Figs. 6(b), (d), (e), and (g) correspond to Fig. 1(a), 1(b), 2(a), and 2(b) in Attal \textit{et al.},\textsuperscript{13} respectively. Assuming levels $c$ and $d$ are initially unpopulated, the diagrams of Fig. 6 result in a reduction of the general form to the following (in units of $m^2/V^2$):
\[
\chi_{CARS}(\omega_4 : \omega_1, -\omega_2, \omega_3) = \chi_{NR} + \frac{N}{4\pi \varepsilon_0 h^3} \sum_{a,b} \left\{ \left( \frac{1}{\omega_{ba} - (\omega_1 - \omega_2) - i\Gamma_{ba}} \right) \times \sum_d \left( \frac{\mu_{4da}\mu_{3bd}}{\omega_{da} - \omega_4 - i\Gamma_{da}} + \frac{\mu_{3da}\mu_{4bd}}{\omega_{db} + \omega_1 + i\Gamma_{db}} \right) \times \left[ \sum_c \rho_{aa}^{(0)} \left( \frac{\mu_{1cb}\mu_{2ac}}{\omega_{ca} + \omega_2 - i\Gamma_{ca}} + \frac{\mu_{2cb}\mu_{1ac}}{\omega_{ca} - \omega_1 + i\Gamma_{ca}} \right) - \sum_c \rho_{bb}^{(0)} \left( \frac{\mu_{2cb}\mu_{1ac}}{\omega_{cb} + \omega_2 + i\Gamma_{cb}} + \frac{\mu_{1cb}\mu_{2ac}}{\omega_{cb} + \omega_1 - i\Gamma_{cb}} \right) \right] \right\} (1)
\]

where \(N\) is the total population being probed, \(\varepsilon_0\) is the permittivity of free space, \(h\) is Planck’s constant, \(\rho_{ii}^{(0)}\) is the fractional population of the state \(i\), \(\omega_{ij}\) is defined as \((E_i - E_j)/h\) with \(E_i\) being the energy associated with state \(i\), \(\omega_k\) is the frequency of laser beam \(k\), \(\Gamma_{ij}\) is the dephasing rate for the electric dipole transition between states \(i\) and \(j\), and \(\mu_{kij}\) is defined as:

\[
\mu_{kij} = \mathbf{\hat{e}}_k \cdot \mathbf{\mu}_{ij} \quad (2)
\]

where \(\mathbf{\mu}_{ij}\) is the dipole matrix element for the transition \(i \rightarrow j\), and \(\mathbf{\hat{e}}_k\) is the normalized polarization vector for laser beam \(k\). The form of Eq. 1 is in agreement with others in the literature.\(^{17}\) The remaining susceptibility terms not shown in Eq. 1 arise from Raman resonances between levels other than \(a\) and \(b\) and one- and two-photon transitions. These excluded terms are small in magnitude, largely frequency-independent as compared to the terms shown, and can be accounted for in \(\chi_{NR}\), the nonresonant susceptibility.\(^{27}\)

Considering the case shown in Fig. 1, it is evident that \(\omega_{cb} \approx \omega_{ca} - \omega_1 + \omega_2\) and \(\omega_{ca}, \omega_{cb} \gg \omega_1, \omega_2\). Therefore, Eq. 1 can be reduced to:

\[
\chi_{CARS}(\omega_4 : \omega_1, -\omega_2, \omega_3) = \chi_{NR} + \frac{N}{4\pi \varepsilon_0 h^3} \sum_{a,b} \left\{ \left( \frac{1}{\omega_{ba} - (\omega_1 - \omega_2) - i\Gamma_{ba}} \right) \times \sum_d \left( \frac{\mu_{4da}\mu_{3bd}}{\omega_{da} - \omega_4 - i\Gamma_{da}} + \frac{\mu_{3da}\mu_{4bd}}{\omega_{db} + \omega_1 + i\Gamma_{db}} \right) \times \left[ \sum_c \left( \rho_{aa}^{(0)} - \rho_{bb}^{(0)} \right) \left( \frac{\mu_{1cb}\mu_{2ac}}{\omega_{cb} + \omega_1 + \omega_{ca} - \omega_1} \right) \right] \right\} (3)
\]
The final summation in brackets has the form of a spontaneous Raman cross-section (in units of m²/sr) for excitation at $\omega_1$:  
\[
\left( \frac{\partial \alpha}{\partial \Omega} \right)_{ab} = \frac{\omega_1^2}{(4\pi \varepsilon_0)^2 e^4} \left| \sum_c \left( \frac{\mu_{1cb} \mu_{2ac}}{\hbar (\omega_{cb} + \omega_1)} + \frac{\mu_{2cb} \mu_{1ac}}{\hbar (\omega_{ca} - \omega_1)} \right) \right|^2 
\]  
Eq. 3 can then be recast as:
\[
\chi_{CARS}(\omega_4 : \omega_1, -\omega_2, \omega_3) = \chi_{NR} + \frac{Nc^2}{4\pi \varepsilon_0 \hbar^3} \sum_{a,b,d} \left\{ \frac{1}{\omega_{ba} - (\omega_1 - \omega_2) - i\Gamma_{ba}} \right\} 
\times \sum_{d} \left( \frac{\mu_{4da} \mu_{3bd}}{\omega_{da} - \omega_4 - i\Gamma_{da}} + \frac{\mu_{3da} \mu_{4bd}}{\omega_{db} + \omega_4 + i\Gamma_{db}} \right) \right\} \times \left[ (\rho^{(0)}_{aa} - \rho^{(0)}_{bb}) \sqrt{\frac{(4\pi \varepsilon_0)^2 \hbar^2 e^4}{\omega_2^4}} \left( \frac{\partial \alpha}{\partial \Omega} \right)_{ab} \right] \]  
where $c$ is the speed of light. Observing for the electronic resonance case in Fig. 1 that $\omega_{da} \approx \omega_4$, the second term in the second line of Eq. 5 is nonresonant and can be absorbed into $\chi_{NR}$. Rearranging, Eq. 5 now becomes:
\[
\chi_{CARS}(\omega_4 : \omega_1, -\omega_2, \omega_3) = \chi_{NR} + \frac{Nc^2}{\hbar^2 \omega_2} \sum_{a,b,d} \left\{ \left( \frac{\partial \alpha}{\partial \Omega} \right)_{ab} \right\}^{1/2} \left( \frac{\rho^{(0)}_{ba} - \rho^{(0)}_{bb}}{\omega_{ba} - (\omega_1 - \omega_2) - i\Gamma_{ba}} \right) \times \left( \frac{\mu_{4da} \mu_{3bd}}{\omega_{da} - \omega_4 - i\Gamma_{da}} \right) \]  
This equation is employed in modeling the ERE-CARS spectra presented herein. To compare the theoretical spectra with the acquired data, convolutions must be performed to account for the finite laser linewidths used in the experiment. Three convolutions were conducted: one each for the pump, the Stokes, and the probe beams. Gaussian profiles were assumed for each laser beam. The third convolution is unique to this ERE-CARS process, and has not been applied in previous models, in which a convolution for the Stokes beam is typically applied. Once the convolutions are completed, the magnitude of the complex susceptibility can be compared to the data.

As seen from Fig. 1, if $\omega_3$ is tuned into resonance with $\omega_{bd}$, then $\omega_4$ will be resonant with $\omega_{da}$. The enhancement resulting from this electronic resonance enables detection of weak Raman transitions of molecules such as NO, even at low concentrations. Improvements in
the detection limit on the order of $10^2$ to $10^8$ can be achieved.\textsuperscript{27} In addition, species selectivity for the CARS process is strengthened by this electronic resonance. For the standard CARS process, the Raman resonance criterion is:

\[ \omega_1 - \omega_2 = \omega_{ba} \]  \hspace{1cm} (7)

For the ERE-CARS process under consideration in this study, the electronic resonance criterion is:

\[ \omega_4 = \omega_{da} \]  \hspace{1cm} (8)

The extra selectivity provided by two resonance requirements can eliminate interferences from overlapping spectra of molecules, such as the $A \leftarrow X$ fluorescence band of NO with the Schumann-Runge system of O\textsubscript{2}.\textsuperscript{21}

Equation 6 is now considered in light of the specific energy-level diagram for the $\Pi_{3/2}$ ground state of NO shown in Fig. 7. A similar schematic could be presented for the $X^{2}\Pi_{1/2}$ state. Only the Raman Q-branch was probed during the experiments; therefore, the S- and O-branches are not included in the diagram. For the case under consideration in Fig. 7, $v_d = 0$. In accordance with the selection rules for Raman transitions, two distinct Raman Q-branch transitions can occur, corresponding to either parity of the lower rotational levels. To distinguish between parity levels, the transitions starting from negative parity ground states are shown with solid lines, whereas those that originate from positive parity states are shown with dashed lines. The Raman transition occurs through a virtual state, as only the ultraviolet probe beam is in electronic resonance. Once the molecule is excited to its first vibrational level ($v_b = 1, J_b$), three electronic transitions can couple the molecule to the $A^2\Sigma$ state for a specific rotational level and parity. Each of the electronic transitions is matched with a corresponding electronic transition that returns the molecule to the ground state. The large difference in frequency between the pump and probe beams separates the Raman process from the electronic process; thus, the enhancement of the Raman process is well defined, which assists in reducing the complexity of the model.
To apply the model, the Raman cross-section was calculated from values provided by Schrötter and Klöckner. The same cross-section was used for both electronic ground states of NO, as a previous study of NO CARS determined the values to be essentially the same. Resonance effects between $\omega_4$ and $\omega_{da}$ were evaluated using the dipole matrix elements $\mu_{3bd}$ and $\mu_{4da}$. These matrix elements were calculated following the formulae in Hilborn incorporating spectroscopic data from LIFBASE. The spontaneous emission coefficient $A_{21}$, used to calculate the matrix elements, was divided by a factor of three to account for isotropic emission and the fact that the Zeeman effect was not explicitly taken into account, as used previously by Siegman. The Raman shift ($\omega_{ba}$) was based on the constants of Huber and Herzberg and of Laane and Kiefer. The electronic transition frequencies, $\omega_{da}$, were taken from LIFBASE.

The Raman linewidths (cm$^{-1}$), $\Gamma_{ba}$ (FWHM), were obtained from Doerk et al. as follows:

$$\Gamma_{ba} = 0.12 \left( \frac{T_{\text{ref}}}{T} \right) \left( \frac{P}{P_{\text{ref}}} \right)$$

where $T_{\text{ref}} = 298$ K, and $P_{\text{ref}} = 1$ atm. The electronic transition linewidth, $\Gamma_{da}$, was calculated from a combination of the Doppler and collisional widths. The collisional width was approximated as:

$$\Gamma_{da,c} = 0.6P$$

where $\Gamma_{da,c}$ has units of cm$^{-1}$ and $P$ has units of atm. The above relation is an approximation to the work of Chang et al. and is in agreement with other studies in the literature. The Doppler width for the electronic resonance transitions is based on standard theory and at room temperature is approximately $\Gamma_{da,D} = 0.1$ cm$^{-1}$. The total linewidth was then approximated by:

$$\Gamma_{da} = \sqrt{\Gamma_{da,c}^2 + \Gamma_{da,D}^2}$$

5 Definition of an Effective Intermediate Raman Level

To address the contribution to the susceptibility in Eq. 6 from the numerous excited electronic states of NO, we define an effective electronic level for the calculations. We use
the general transition polarizability to determine the characteristics of the effective electronic level. The transition polarizability can be related to the Raman cross-section of Eq. 4 by:

\[
\frac{\partial \alpha}{\partial \Omega}_{ab} = \frac{\omega^4}{(4\pi\varepsilon_0)^2c^4} (\alpha_{zz})_{ab}^{2}
\]

Therefore, the transition polarizability is found to be:

\[
(\alpha_{zz})_{ab}^2 = \sum_c \left( \frac{\mu_{1cb}\mu_{2ac}}{\hbar(\omega_{cb} + \omega_1)} + \frac{\mu_{2cb}\mu_{1ac}}{\hbar(\omega_{ca} - \omega_1)} \right)^2
\]

The summation over \(c\) includes only the possible intermediate states that have single-photon allowed transitions with both states \(a\) and \(b\). The polarizability for a transition between an initial rotational level \(A\) and final rotational level \(B\) is found by summing over all possible Zeeman states \(a\) and \(b\):

\[
(\alpha_{zz})_{AB}^2 = \frac{1}{(2J_A + 1)} \sum_{a,b} \sum_c \left( \frac{\mu_{1cb}\mu_{2ac}}{\hbar(\omega_{cb} + \omega_1)} + \frac{\mu_{2cb}\mu_{1ac}}{\hbar(\omega_{ca} - \omega_1)} \right)^2
\]

In general, the Raman cross-section or transition polarizability can not be calculated directly, especially for molecules such as NO which possesses numerous excited levels that are connected with the \(X^2\Pi\) ground state through single-photon transitions. In addition, many vibrational levels in each of these electronic levels are connected with the \(v'' = 0\) and \(v'' = 1\) vibrational levels in the \(X^2\Pi\) state by transitions with significant oscillator strengths. Beyond the sheer number of transitions that would have to be accounted for, the oscillator strengths for most of these transitions are not well known. This is especially the case for electronic levels above the \(E^2\Sigma^+\) level of NO.

Consequently, we chose one effective electronic level (\(C^2\Pi\)), aside from the \(A^2\Sigma^+\) state, to act as an intermediate level in the Raman transition by representing all of the nonresonant excited electronic levels. The oscillator strengths, and thus the dipole matrix elements, of the (0,0) and (0,1) bands in the \(C^2\Pi \leftarrow X^2\Pi\) electronic manifold were artificially enhanced so as to obtain the literature value\(^{10}\) of the transition polarizability for the fundamental (1,0) band of the Q-branch of NO in the \(X^2\Pi\) state. In particular, the values of the dipole matrix elements for this band were increased by a factor of 2.2 from the values of Luque and
The calculation for Eq. 14 was performed by summing only over states \( c \) in the \( v = 0 \) vibration-rotation bands of the \( A^2\Sigma^+ \) and \( C^2\Sigma^+ \) levels.

6 Enhancement Factor

Because a primary advantage of employing ERE-CARS over CARS is the enhancement in signal level, a parameter that quantifies this increase was developed as part of the study. The resulting enhancement factor, or \( \delta(\omega_4) \), is defined as:

\[
\delta(\omega_4) = \frac{\chi_{CARS}(\omega_4 : \omega_1, -\omega_2, \omega_3)}{\chi_{CARS}((2\omega_1 - \omega_2) : \omega_1, -\omega_2, \omega_1)}
\] (15)

where the denominator represents the degenerate pump-beam case, \( \omega_1 = \omega_3 \). The enhancement factor is used to evaluate the reduction in detection limit resulting from electronic-resonance enhancement. This factor is proportional to the increase in CARS susceptibility and thus inversely proportional to the NO detection limit. The CARS signal is proportional to the square of the enhancement factor.

7 Results

During the experiments, either the Stokes or the ultraviolet probe-beam frequency was scanned to produce a CARS spectrum. These two spectrum types were acquired experimentally and theoretically modeled and are referred to as “Stokes scans” or “probe scans” to indicate which laser beam was tuned across the spectrum. Because the spectral features of these scan types differ, the results will be covered in separate sections.

For clarity, a notation is introduced here, similar to that found in the literature,\(^{17}\) to denote the overall ERE-CARS transition. The notation begins by listing the Raman transition with a subscript (1 for \( \Pi_{1/2} \) and 2 for \( \Pi_{3/2} \))\(^{41}\) to indicate the \( \Pi \) state of molecule. The final electronic transition is identified next following the notation of Mavrodineanu and Boiteux.\(^ {42}\) The value of \( J_a \) in the ground state is then listed in parentheses. Therefore, processes involving transitions on the far right and second from far right in Fig. 7 would be denoted by \( Q_2R_2(2.5) \) and \( Q_2^PQ_{12}(2.5) \), respectively.
7.1 Results for Probe Scans

Figure 8 shows comparisons between theoretical and experimental spectra for six atmospheric probe-scan cases. For these scans, the probe frequency was tuned over the approximate range of 42280 to 42400 cm\(^{-1}\) (236.5 to 237.0 nm). The spectra encompass fixed Stokes frequencies that correlate to Raman shifts between 1872.74 and 1875.95 cm\(^{-1}\). The data were acquired at room temperature using a concentration of 100 ppm NO in N\(_2\).

As shown in Fig. 8, good agreement exists between the theoretical and experimental spectra for all fixed Raman shifts. Spectral peak locations and relative intensities are well represented. While a good match generally occurs in linewidths, we should note that the theoretical spectra were generated using Stokes and probe linewidths of 0.08 cm\(^{-1}\) and 1.0 cm\(^{-1}\), respectively. This probe linewidth is wider than that estimated experimentally. The enhanced linewidth indicates the presence of saturation in the electronic process \(b \rightarrow d\) (see Fig. 7) and highlights the necessity of a triple convolution in generating the theoretical spectra. These results confirm that the model is capable of calculating theoretical spectra in good agreement with experimental spectra, and, more importantly, that the essential physics of the ERE-CARS process are captured by the model.

Figure 9 displays three probe-scan cases over an extended probe-frequency range. These three cases correspond to those shown in Fig. 8(a), (b), and (d). By expanding the scale, the spectra now encompass resonances in the \(\Pi_{3/2}\) ground state. The amplitude variation between the spectra of Figs. 8 and 9 occurs because the frequency difference \(\omega_1 - \omega_2\) is in resonance with different rotational levels. For the expanded spectra, the \(\Pi_{1/2}\) transitions correspond to the peaks on the righthand side of each spectrum and the \(\Pi_{3/2}\) transitions are on the lefthand side. As an example, the major peaks in Fig. 9(a) are marked and correspond to the following transitions from left to right: \(Q_2P_2(1.5) + Q_2PQ_1(1.5), Q_1Q_1(2.5) + Q_1QP_2(2.5),\) and \(Q_1R_1(2.5) + Q_1RQ_2(2.5)\). Similar transitions occur in Figs. 9(b) and 9(c), with the transition \(Q_1P_1\) appearing in Fig. 9(c) for \(J_1 = 7.5\).
The relative intensities within a given Π state are generally predicted with good accuracy. However, the relative intensities between Π states, i.e., on the right and left sides of the spectra, are not in complete agreement with the experimental spectra. This is primarily due to a decrease in probe-beam power during the scan, which arises from the short lifetime of the LDS698 laser dye employed in the experiments. The experimental spectra were normalized by dividing by the measured probe-beam power, but this procedure might not be the most accurate normalization approach if the electronic resonance were saturated. In addition, the two Π states may not have the same Raman cross-section, as assumed for our calculations.

The enhancement factor associated with each spectrum in Fig. 8 is shown in Fig. 10. Because of the isolated electronic resonances that dominate each spectrum, the spectral behavior of the enhancement factor is very similar to its corresponding spectrum. As can be seen from Fig. 10, the electronic resonance for the ERE-CARS process provides an enhancement in signal strength by a factor of approximately 1000 compared to a typical CARS process. This significant enhancement permits the CARS signal to be detected above the nonresonant background.

### 7.2 Results for Stokes Scans

Figure 11 displays comparisons between theoretical and experimental spectra for three atmospheric Stokes-scan cases. The experimental spectra were acquired by scanning the Stokes frequency over a Raman shift range of 1872.5 to 1877.5 cm$^{-1}$ for three different fixed ultraviolet probe-beam frequencies. The experimental spectra were obtained for the same diagnostic conditions as for the probe-scan spectra shown in Fig. 8 (1.0 atm and 100 ppm NO). The theoretical spectra were generated using a smaller probe-beam linewidth (0.08 cm$^{-1}$) and an identical Stokes-beam linewidth. This behavior indicates that the effects of saturation occurring in the electronic process are not significant for Stokes-scan spectra. As the probe-beam frequency is fixed, the convolution with the Stokes beam linewidth becomes the dominant factor in determining the shape of the Stokes-scan spectra.
The theoretical spectra in Fig. 11 are in good agreement with the experimental results. Because of the numerous Q-branch transitions probed and the three possible electronic transitions at or near resonance for each case (see Fig. 7), the Stokes scans include a greater number of enhanced transitions as compared to the probe scans. These transitions overlap and interfere, and thus appear as a single wide peak. This merging results from the frequency spacing of the NO Q-branch Raman lines, which is far less than the frequency spacing of the electronic transitions, and the use of visible pump and Stokes beams. Similar to the probe scans, the spectral shape of the experimental Stokes scans changes as the ultraviolet probe-beam frequency is varied. The modeled spectra capture these spectral changes well for all cases.

The behavior of the Stokes-scan spectra can be explained by considering the dominant transitions as the probe frequency is changed for each scan. Only transitions arising from the $\Pi_{1/2}$ state are probed using these diagnostic parameters. Starting with Fig. 11(a), the ERE-CARS process is in strong resonance with the $Q_1Q_1$ and the $Q_1^P P_{21}$ transitions for $J = 1.5 - 5.5$, with the dominant peak occurring for $J = 4.5$. As the probe beam is shifted to higher frequencies, these resonances move to higher values of $J$, with a maximum intensity occurring at $J = 7.5$ and a shift to the left of the dominant peak, as shown in Fig. 11(b). Simultaneously, a new set of resonances appears on the righthand side of the spectrum, corresponding to $Q_1R_1$ and $Q_1^R Q_{21}$ for $J = 1.5 - 2.5$. These two sets of resonances continue to shift to the left as the probe frequency rises, as displayed in Fig. 11(c), with the maximum intensity occurring for $J = 10.5$ and $J = 4.5$ for the left and right peaks, respectively.

The spectral response of NO is clearly detectable over the nonresonant background even at this low concentration and the model is capable of predicting the spectrum for these thermodynamic conditions for both types of scans. The SNR for the spectra shown in Fig. 8 and Fig. 11 is approximately 10, and as such, the detection limit is estimated to be less than 10 ppm. In comparison, using polarization CARS, Pott et al.\textsuperscript{43} report a detection limit of 200 ppm with a SNR of approximately unity.
Figure 12 displays the enhancement factors corresponding to the Stokes scan spectra shown in Fig. 11. As with the probe scans, the spectral shape of the enhancement factor is similar to the corresponding spectrum. Moreover, the enhancement magnitude is similar to that of the probe scans, near a factor of 1000.

8 Conclusions

In conclusion, the ERE-CARS process has been demonstrated both experimentally and theoretically for NO. The good agreement between the experimental and theoretical spectra for both the probe and Stokes scans highlights the capabilities of the theoretical model developed and described in this paper. The predicted line positions match closely with those of the transitions in the experimental spectra. The relative intensities corresponding to each Π state are approximately correct, and good comparisons occurred between spectra encompassing both Π states. This theory complements the sensitivity of the experimental setup, which was able to obtain NO spectra for a concentration of 100 ppm at a SNR of 10. This low detection limit makes the technique viable for many practical applications. In addition, the enhancement factor illustrates the advantages of employing ERE-CARS over the degenerate pump-beam case.

Another advantage of ERE-CARS is increased species selectivity. This feature can be demonstrated from the results presented for both the probe and Stokes scans. As shown in Fig. 8, only a few dominant transitions occur for each configuration of probe and Stokes frequencies. While an increased number of transitions occur for the Stokes-scan spectra (Fig. 11), it is clear from all cases that not all Raman Q-branch transitions can be probed and enhanced simultaneously. Therefore, if the entire range of transitions for one molecule can not be satisfied completely, it is very unlikely that the probe and Stokes frequencies chosen will satisfy the selection criteria for two molecules simultaneously. This benefit of ERE-CARS is just as important as the enhancement in signal strength, because a strong signal arising from multiple species can be just as difficult to analyze as a weak, indiscernible signal.
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References


Figure 1: CARS energy-level diagram including electronic resonances
Figure 2: Experimental system for the NO ERE-CARS system
Figure 3: Phase-matching geometry employed in the NO ERE-CARS system
Figure 4: Polarization arrangement for ERE-CARS detection
Figure 5: Experimental NO ERE-CARS spectra demonstrating electronic resonance enhancement at room temperature and subatmospheric pressure for the following conditions (a) $\omega_3 = 42140.75$ cm$^{-1}$ and 1% NO, (b) $\omega_3 = 42194.09$ cm$^{-1}$ and 1% NO, (c) $\omega_3 = 42337.00$ cm$^{-1}$ and 1000 ppm NO, and (d) $\omega_3 = 42342.92$ cm$^{-1}$ and 1000 ppm NO.
Figure 6: Double-sided Feynman diagrams for the ERE-CARS process corresponding to the following terms in Prior:\textsuperscript{29} (a) 3, (b) 4, (c) 21, (d) 24, (e) 9, (f) 10, (g) 39, and (h) 42.
Figure 7: Energy-level diagram of the ERE-CARS process for the $X^2\Pi_{3/2}$ ground electronic state of NO
Figure 8: Comparison of theoretical (black line) and experimental (red line) ERE-CARS spectra generated for a pressure of 1.0 atm, a concentration of 100 ppm NO, and for Raman shifts and Raman transitions of (a) 1875.95 cm\(^{-1}\), \(Q_1(2.5)\); (b) 1875.82 cm\(^{-1}\), \(Q_1(3.5)\); (c) 1875.66 cm\(^{-1}\), \(Q_1(4.5)\); (d) 1875.00 cm\(^{-1}\), \(Q_1(7.5)\); (e) 1874.02 cm\(^{-1}\), \(Q_1(10.5)\); and (f) 1872.74 cm\(^{-1}\), \(Q_1(13.5)\)
Figure 9: Comparison of theoretical (black line) and experimental (red line) ERE-CARS spectra generated for a pressure of 1.0 atm, a concentration of 100 ppm NO, and for Raman shifts and Raman transitions of (a) 1875.95 cm\(^{-1}\), \(Q_1(2.5)/Q_2(1.5)\); (b) 1875.82 cm\(^{-1}\), \(Q_1(3.5)/Q_2(1.5)\); and (c) 1875.00 cm\(^{-1}\), \(Q_1(7.5)/Q_2(6.5)\)
Figure 10: Enhancement factor for a pressure of 1.0 atm, a concentration of 100 ppm NO, and for Raman shifts of (a) 1875.95 cm$^{-1}$, (b) 1875.82 cm$^{-1}$, (c) 1875.66 cm$^{-1}$, (d) 1875.00 cm$^{-1}$, (e) 1874.02 cm$^{-1}$, and (f) 1872.74 cm$^{-1}$
Figure 11: Comparison of theoretical (black line) and experimental (red line) ERE-CARS spectra for a pressure of 1.0 atm, a concentration of 100 ppm, and probe frequencies of (a) 42322.61 cm$^{-1}$, (b) 42330.41 cm$^{-1}$, and (c) 42343.00 cm$^{-1}$
Figure 12: Enhancement factor for a pressure of 1.0 atm, a concentration of 100 ppm, and probe frequencies of (a) 42322.61 cm\(^{-1}\), (b) 42330.41 cm\(^{-1}\), and (c) 42343.00 cm\(^{-1}\)