Infrared Seeded Parametric Four-Wave Mixing for Sensitive Detection of Molecules

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We have developed a sensitive resonant four-wave mixing technique based on two-photon parametric four-wave mixing with the addition of a phase matched "seeder" field. Generation of the seeder field via the same four-wave mixing process in a high pressure cell enables automatic phase matching to be achieved in a low pressure sample cell. This arrangement facilitates sensitive detection of complex molecular spectra by simply tuning the pump laser. We demonstrate the technique with the detection of nitric oxide down to concentrations more than 4 orders of magnitude below the capability of parametric four-wave mixing alone, with an estimated detection threshold of 10^{12} molecules/cm^3. [S0031-9007(97)03996-3]

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Trace species detection using electronic transitions in the visible and ultraviolet is advantageous due to the strong resonance enhancement of the interaction cross section. Detection of molecules in the ultraviolet can be achieved with many different techniques, the suitability of which is application dependent. Pulsed lasers offer a great deal of versatility, providing broad tunability over the visible and ultraviolet as well as high spectral intensities suitable for nonlinear techniques. Resonance enhanced degenerate four-wave mixing is one such technique which has received much attention due to its high sensitivity and highly collimated coherent signal output [1]. Coherent techniques are particularly applicable to remote sensing applications where there are restrictions to optical access. Currently all nonlinear diagnostic techniques that generate a coherent signal beam require the use of multiple beams satisfying complicated phase matching geometries, and many are susceptible to spectral interference from other molecular species.

In this Letter we demonstrate a new resonance enhanced nonlinear technique useful for detecting molecular species in trace amounts, which only requires a single beam, is automatically phase matched, and provides excellent species discrimination. The technique, named seeded parametric four-wave mixing (SPFWM), is based on two-photon resonant parametric four-wave mixing (PFWM) [2,3], with the addition of an extra "seeder" field. Both techniques generate coherent signals at wavelengths different from that of the pump, uniquely determined by the interacting species (see Fig. 1) and which travel collinearly with the pump beam. The addition of a phase matched seeder field to the PFWM process serves to increase the sensitivity by many orders of magnitude. The seeder field is simply provided by PFWM in a high gain (high pressure) cell containing the molecule of interest; the signal fields travel collinearly with the pump, and the unwanted component is removed using a filter. Therefore, SPFWM will automatically provide a phase matched seeder field over the entire extent of a molecular spectrum and so is suitable for use with tunable pulsed dye lasers for detecting complex molecular spectra. We demonstrate the potential of SPFWM using a recently reported PFWM transition in nitric oxide [4]. The two-photon $C^2\Pi\,(v = 0) \leftarrow X^2\Pi\,(v = 0)$ spectrum at a NO partial pressure of 1 μbar is detected. This corresponds to a detection threshold more than 4 orders of magnitude below that using PFWM alone and indicates a sensitivity far greater than is achievable with alternative coherent two-photon resonant techniques such as two-photon degenerate four-wave mixing [5–7]. Furthermore, we show that SPFWM can be understood in terms of established PFWM theory [8,9].
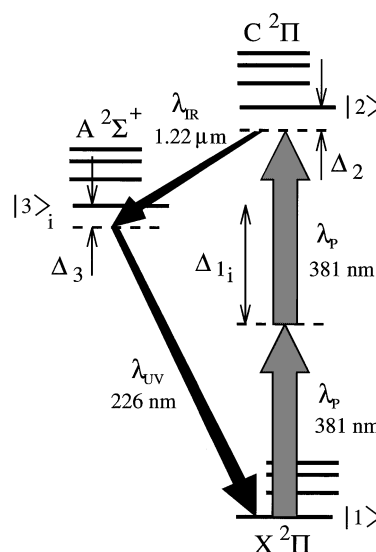

FIG. 1. The nitric oxide level scheme used for PFWM. The ground state, $X^2\Pi$, the excited state, $C^2\Pi$, and the intermediate state, $A^2\Sigma^+$, manifolds are indicated with four-wave mixing occurring among the $v = 0$ vibronic levels. The relevant detunings are also indicated, with the pump detuning, Δ_{1_i}, indicating a sum over the intermediate state manifold.

The use of an external field to improve the efficiency of nonlinear frequency conversion has been considered previously [10–14], with Czarnetzki and Döbele [12] studying the PFWM process in molecular hydrogen. All experimental studies were conducted with a fixed pump frequency and were not concerned with broadband tunability or trace species detection. To our knowledge, the results presented here constitute the first report of a fully tunable and suitably sensitive four-wave mixing process of this type.

We treat the four-wave mixing process using perturbation theory, assuming the fields do not strongly effect the states of the system. In this approximation we write the nonlinear polarization in terms of powers of the electric field and subsequently describe the field evolution in terms of the slowly varying envelope equations [8,9]. The PFWM scheme for nitric oxide is depicted in Fig. 1, where nitric oxide is considered as a three level system. Only one state is selected from each manifold, apart from the sum over the entire $A^2\Sigma^+$ ($v = 0$) manifold used for the two-photon transition [15]. When ignoring pump depletion and considering the case of perfect phase matching, $\Delta k = 0$, we obtain

$$\frac{dA_{\mathrm{UV}}}{dz} = \frac{2\pi\omega_{\mathrm{UV}}^2}{k_{\mathrm{UV}}\,c^2}(|\chi_{\mathrm{FWM}}^{(3)}|A_{\mathrm{IR}}A_P^2 - \mathrm{Im}\,\chi_{\mathrm{TPA}}^{(3)}A_{\mathrm{IR}}^2 A_{\mathrm{UV}}$$
$$- \mathrm{Im}\,\chi(\omega_{\mathrm{UV}})A_{\mathrm{UV}}), \quad (1a)$$

$$\frac{dA_{\mathrm{IR}}}{dz} = \frac{2\pi\omega_{\mathrm{IR}}^2}{k_{\mathrm{IR}}\,c^2}(|\chi_{\mathrm{FWM}}^{(3)}|A_{\mathrm{UV}}A_P^2 - \mathrm{Im}\,\chi_{\mathrm{TPA}}^{(3)}A_{\mathrm{IR}}A_{\mathrm{UV}}^2), \quad (1b)$$

where ω_{UV}, ω_{IR}, k_{UV}, and k_{IR} correspond to the angular frequencies and associated wave vectors of the two parametric fields, indicated in Fig. 1, and c represents the vacuum speed of light. A_P, A_{UV}, and A_{IR} represent the real pump, ultraviolet, and infrared field amplitudes, respectively, $\chi_{\mathrm{FWM}}^{(3)}$ is the third order nonlinear susceptibility representing the four-wave mixing process, $\chi_{\mathrm{TPA}}^{(3)}$ is the nonlinear susceptibility corresponding to two-photon absorption, and $\mathrm{Im}\,\chi(\omega_{\mathrm{UV}})$ represents absorption of the UV field by the ground state. The susceptibilities are directly proportional to the rotational state dependent molecular density, N_J, and are readily determined using perturbation theory [16]. In order to derive Eq. (1), we have used the asymptotic solution to the associated phase equation [8].

In the absence of absorption of the UV field, where the last term in Eq. (1a) is neglected, the fields grow to a steady state characterized by

$$\left(A_P^2 - \frac{\mathrm{Im}\,\chi_{\mathrm{TPA}}^{(3)}}{|\chi_{\mathrm{FWM}}^{(3)}|}A_{\mathrm{IR}}A_{\mathrm{UV}}\right) = 0. \quad (2)$$

This is termed the two-photon cancellation regime and corresponds to the existence of two competing excitation paths which exactly cancel such that population of the upper state is inhibited [8,17]. When absorption is present, this simple steady state cannot actually be achieved, but for small absorption it provides an effective limit to field

growth where the infrared field is enhanced as the ultraviolet field is reduced such that Eq. (2) is satisfied.

PFWM behavior in the small signal regime can be derived from the coupled equations (1), giving

$$A_{\mathrm{UV}}(z) \approx A_{\mathrm{UV}}(0)\exp\left(\frac{2\pi\omega_{\mathrm{IR}}^2}{k_{\mathrm{IR}}c^2}|\chi_{\mathrm{FWM}}^{(3)}|A_P^2\,z\right). \quad (3)$$

It is the presence of the vanishingly small initial field amplitude, $A_{\mathrm{UV}}(0)$, which limits the sensitivity of PFWM. Consequently, we were unable to detect NO below a partial pressure of 5 mbar using PFWM.

If one of the field amplitudes were to be initially very large, then the coupled equations, (1), become decoupled in the small signal limit and are solved to yield

$$A_{\mathrm{UV}}(z) \approx \frac{2\pi\omega_{\mathrm{UV}}^2}{k_{\mathrm{UV}}c^2}|\chi_{\mathrm{FWM}}^{(3)}|A_{\mathrm{IR}}(0)A_P^2\,z. \quad (4)$$

The behavior of Eq. (4) is significantly different from that of Eq. (3) and corresponds to seeding the PFWM process with a strong parametric field, $A_{\mathrm{IR}}(0)$, generated externally. The difference in initial gain can be characterized by the ratio of the initial seeder field amplitude to the initial PFWM amplitude, $A_{\mathrm{IR}}(0)/A_{\mathrm{UV}}(0)$, which can be a very large number. Therefore it is reasonable to expect a large gain in sensitivity using SPFWM.

A schematic representation of the essential elements of the SPFWM apparatus is shown in Fig. 2. The experiment was conducted with a pulsed dye laser system operating at about 763 nm. This output was doubled, producing 10 nsec pulses at around 381 nm with a linewidth of approximately 0.2 cm^{-1} and a maximum pulse energy of approximately 3 mJ. Each pulse consisted of many transverse modes producing an irregular mode pattern, and no attempt was made to improve the mode quality for this experiment. The beam is focused into the seeder cell, providing a maximum intensity in the focal region of approximately 5×10^8 W/cm^2 with a gain length of 1 cm, producing the 1.22 μm and 226 nm fields via two-photon parametric generation [4]. A BK7 glass exit window served as the filter, transmitting both the pump and the seeder fields at 381 nm and 1.2 μm, respectively, but completely absorbing the ultraviolet field at 226 nm. The recollimating lens, L2, was chosen to
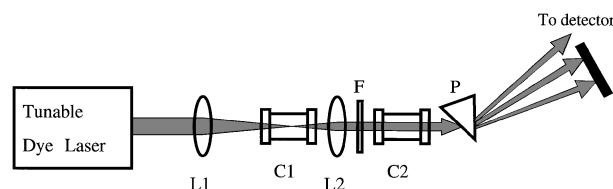

FIG. 2. The SPFWM experimental arrangement showing the high pressure seeder cell, C1, and low pressure sample cell, C2. The filter, F, consisted of a BK7 glass exit window in the seeder cell. A 200 mm focusing lens, L1, and 100 mm recollimating lens, L2, were used, with L2 positioned to produce a loose focus within the cell, C2. The prism, P, was used to separate the signal from the pump and seeder beams.

minimize the beam area and to loosely focus the beam in the sample area, providing a maximum intensity of approximately 5×10^7 W/cm^2 with a gain length of 3 cm. The copropagating signal beams were separated with a 45° quartz prism and the pump and 1.22 μm beams blocked. The signal was coupled into a 0.25 m monochromator, set to transmit 226 nm, and detected with a solar blind photomultiplier tube. The infrared seeder signal was sampled using a quartz plate beam splitter placed before the sample cell and detected with an InGaAs photodiode. Attenuators were used where necessary to ensure the linearity of the detectors. The signals were sent to a boxcar, digitized, and recorded.

In Fig. 3, we show the $C^2\Pi\,(v = 0) \leftarrow X^2\Pi\,(v = 0)$ spectrum of NO [15] obtained with the SPFWM apparatus (cf. Fig. 2) and using 10 shot averaging. The top spectrum, 3(a), was generated by monitoring the 226 nm signal obtained from a closed cell containing 1 μbar of NO buffered to 10 mbar with Ar. A maximum signal to noise ratio of approximately 100 scales [according to Eq. (4)] to a detection sensitivity of 0.1 μbar or 10^{12} molecules/cm^3. This places SPFWM within the realm of trace species detection [1] and is the essential result of the Letter.

The 1.22 μm seeder spectrum, obtained with 400 mbar of NO, is included for comparison in Fig. 3(b). It shows considerable broadening, indicating significant gain at this pressure, thus enabling detection of the detailed 226 nm signal spectrum in the low pressure cell, 3(a). We note that the high pressure seeder cell (cf. Fig. 2, C1) generates a strong UV signal in an otherwise optically thick medium. This indicates that phase matching is achieved with a considerable detuning, Δ_3, from the intermediate state [9].

In Fig. 4 we show the behavior of the signal and seeder field intensities with increasing pump energy. The seeder field behavior is approximately linear indicating that the PFWM is operating in the two-photon ca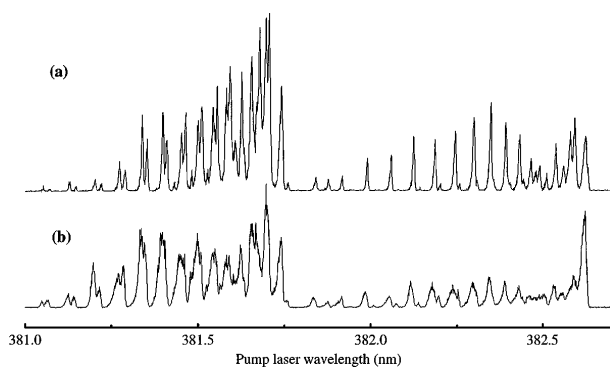ncellation regime. The 226 nm signal behavior is more com-plex, showing a cubic dependence in the small signal regime and then building to the threshold of the two-photon cancellation regime at a pump energy of approximately 1.5 mJ. The curve that traces the signal in Fig. 4(b) was generated by numerically integrating the coupled equations, (1), with a seeder field amplitude directly proportional to that of the pump, as observed. The linear absorption term was required to accommodate the isolated last datum. The dashed curve represents an independently scaled solution generated without the absorption term. The ratio of the linear absorption term to the four-wave mixing susceptibility, Im $\chi(\omega_{UV})/|\chi_{FWM}^{(3)}|$, was 0.5, indicating very little absorption, consistent with our observation. In Fig. 5 we show the pressure dependence of the signal along with a parabola of best fit. Thus we find both the pump intensity and density dependence consistent with the theory presented.

In conclusion, we have shown SPFWM to be a readily implementable nonlinear technique capable of detecting trace quantities of nitric oxide in a cell. It displays the simplicity of single beam operation, excellent discrimination against other interfering species, and high sensitivity, characteristics that have been demonstrated elsewhere as being advantageous for the detection of NO generated in an air-acetylene flame [18], where it is apparent that phase matching is achieved even in extreme environments. Our results compare favorably with detection using degenerate four-wave mixing [1,19] and other
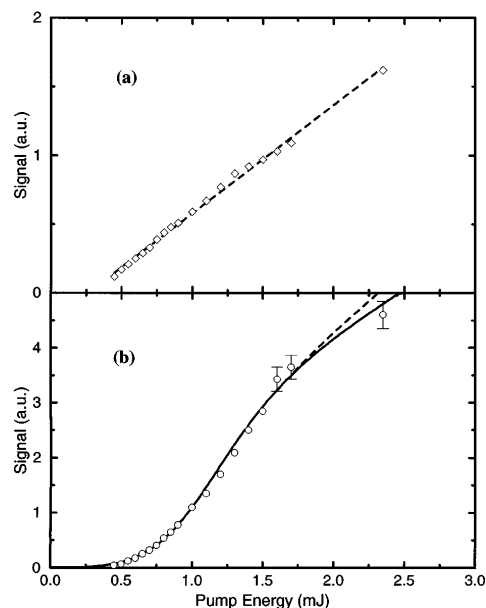

FIG. 4. The pulse energy dependence of the 1.22 μm seeder signal; (a) using 400 mbar of NO and the 226 nm signal; (b) obtained from 20 μbar of NO buffered to 10 mbar with Ar. A straight line is fit to the seeder data, while a curve generated by numerically integrating Eqs. (1) has been fit to the signal data. The dashed curve in (b) corresponds to the best fit obtained without the direct absorption term in Eq. (1a). The data were obtained from the relatively isolated $T_Z \leftarrow X^2\Pi_{3/2}\,Q(10.5)$ transition near 382.3 nm [15].

FIG. 3. SPFWM spectra of the NO $C^2\Pi\,(v = 0) \leftarrow X^2\Pi\,(v = 0)$ transition. The upper trace (a) is that of the 226 nm signal obtained from 1 μbar of NO buffered with Ar to 10 mbar. The lower trace (b) is that of the 1.22 μm seeder field obtained with a pressure of 400 mbar of NO.
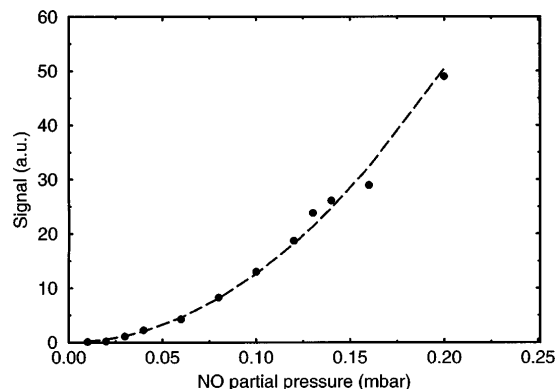
FIG. 5. The pressure dependence of the 226 nm signal field energy indicating square law behavior. The data were obtained from the $T_Z \leftarrow X^2\Pi_{3/2}\, Q(10.5)$ transition, using a 300 mbar seeder cell and buffering the sample to 100 mbar with Ar.

resonance enhanced nonlinear techniques. In the case of SPFWM, a greater pump power is required to achieve a comparable sensitivity. However, the technique has advantages due to the simplicity of single beam operation, species selectivity, and the ability to operate at high pump powers without saturation. Further enhancements, including optimization of the seeder cell pressure and focal geometry, are likely to further increase the sensitivity. We note that the high species selectivity offers the potential to detect larger molecules, which otherwise have broad, indistinct spectra. Therefore we offer SPFWM as another tool in the repertoire of molecular diagnostics possessing a unique set of characteristics which complement other existing techniques.

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