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PRESSURE DEPENDENCE OF DEGENERATE FOUR-WAVE MIXING IN SO_2: EFFECT OF THE THERMAL GRATINGS

SHIMING SHI, DEYING CHEN, QIKE ZHENG,
MARIA PERSON and QIZONG QIN*

Institute of Laser Chemistry, Fudan University, Shanghai 200433, China

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The degenerate four wave mixing (DFWM) spectrum of the $A(^1A_2) \leftarrow X(^1A_1)$ and $B(^1B_1) \leftarrow X(^1A_1)$ transitions of SO_2 in the 299.5–305 nm region is presented. It has been found that the DFWM signal intensities are proportional to the cube of laser intensity and the square of SO_2 pressure. The DFWM signal increases dramatically with the pressure of N_2 as a buffer gas. The enhancement of the DFWM signal can be mainly attributed to the thermal grating contribution.

Keywords: SO_2; Degenerate four-wave mixing; Laser spectroscopy; Buffer gas; Enhancement

INTRODUCTION

There has been increasing interest in degenerate four wave mixing (DFWM) as sensitive spectroscopic probes of molecules [1]. Degenerate four wave mixing involves the interaction of three input beams of identical frequency ω with a nonlinear medium to produce a fourth signal beam of the same frequency ω. The generated coherent signal beam, propagating in a unique and well defined direction, is spectrally

*Corresponding author. Tel.: +86 21 65102777, Fax: +86 21 65102777, e-mail: qzqin@fudan.ac.cn

bright and highly collimated. To date DFWM has been successfully used to monitoring atoms, molecules and free radicals in the gas phase. It is generally found that laser induced fluorescence (LIF) is a very sensitive detection technique, however, LIF suffers from collisional quenching which at worst can remove the signal completely. DFWM could prove more applicable in the high pressure regime or inhomogeneous mixtures. Mann *et al.* [2] and Ishii *et al.* [3] demonstrated that dramatic increase of the DFWM intensity could be achieved with the addition of buffer gas. Recently several groups [2, 4] have studied the collision effects on the DFWM signals and provided convincing results which showed that various mechanisms can contribute to the formation of laser-induced gratings.

In this paper, we choose SO_2 as the subject to study its DFWM because its spectroscopy has been extensively studied and SO_2 is a major air pollutant contributing to the formation of smog and acid rain. We observed the DFWM spectrum of SO_2 in the 299.5 – 305 nm range for the first time, which is characterized by broad vibronic bands from a complex interaction between the $A(^1A_2) \leftarrow X(^1A_1)$ and $B(^1B_1) \leftarrow X(^1A_1)$ transitions. The intensities of DFWM signals were measured as a function of SO_2 pressure, the laser intensity and nitrogen buffer gas pressure. A simple model proposed by Dahney [4] was employed to fit the experimental results, and the reason for the DFWM signal intensity enhancement is discussed.

EXPERIMENTAL

A schematic diagram of the experimental set-up is shown in Figure 1. The 532 nm frequency doubled output of a Nd : YAG laser (Spectra-Physics GCR-190) at 10 Hz pumps a PDL-2 dye laser with a bandwidth of $0.6\,cm^{-1}$ using a R-640 dye, and the output is frequency doubled with an associated wavelength extension (WEX-1C). The laser is scanned from 299 to 305 nm to obtain SO_2 spectrum. A length of 12 cm glass sample cell equipped with two silica windows is used. The laser beam, collimated to approximately 3 mm in diameter, is splitted into a strong forward pump beam and a weak probe beam. After passage through the interaction region in the cell, the strong beam is retroreflected by a mirror to form the backward pump beam.

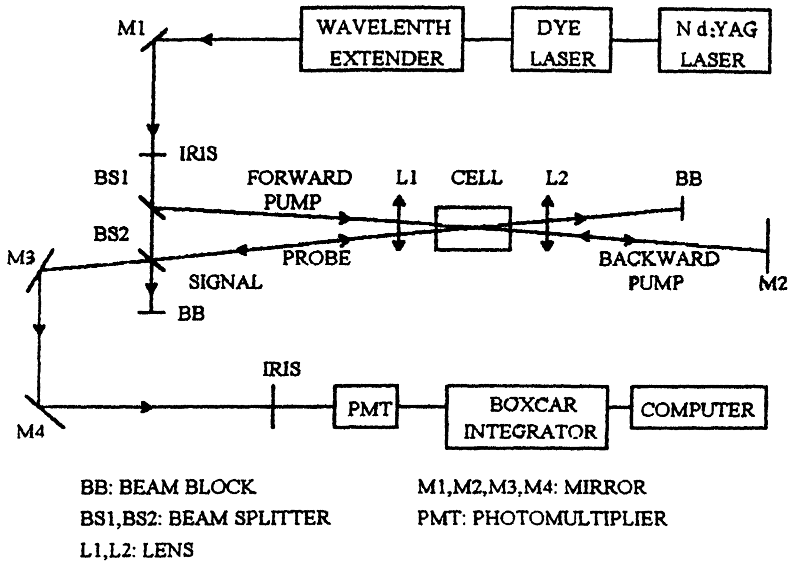

FIGURE 1 Schematic diagram of the experimental apparatus for DFWM.

These two pump beams are of approximately the same intensity. The probe beam is directed at an angle of about one degree against the forward pump beam to achieve a maximum spatial overlap with the pump beams. The DFWM signal of SO_2 is so bright that can be observed by naked eyes, and is extracted by one of the beam splitters and directed approximately 6 m away from the interaction region through several irises. The signal is detected with a photomultiplier tube and fed to a gated integrator (PAR 162 and 165 Boxcar) for processing. Data acquisition and storage are performed with a PC computer. The dependencies of the DFWM signal on the laser intensity and SO_2 pressure are measured by monitoring the signal intensity at 300 nm. The effect of added N_2 buffer gas on the DFWM signal is examined by monitoring the signal intensity as a function of total pressure of gas mixtures containing 1.0 Torr SO_2. The laser intensity is measured with energy ratiometer (RJ-7200), and kept constant during each scan. To compare with the DFWM spectrum, a linear absorption spectrum of SO_2 is also taken *via* the measurement of SO_2 absorption with the same laser beam.

RESULTS AND DISCUSSION

The DFWM and absorption spectra in the region of the $A(^1A_2) \leftarrow X(^1A_1)$ and $B(^1B_1) \leftarrow X(^1A_1)$ transitions of SO_2 are presented in Figure 2. The DFWM spectrum is taken with 1.0 Torr SO_2 and 206 μJ of pump laser beam energy. Because the relative absorption of 1.0 Torr SO_2 in a 12 cm cell is about 7 percent, which will attenuate the intensities of all the pumps, probe and signal beams. So we calibrate the measured DFWM signals with taking the SO_2 absorption into account. It can be seen that the overall features of the DFWM

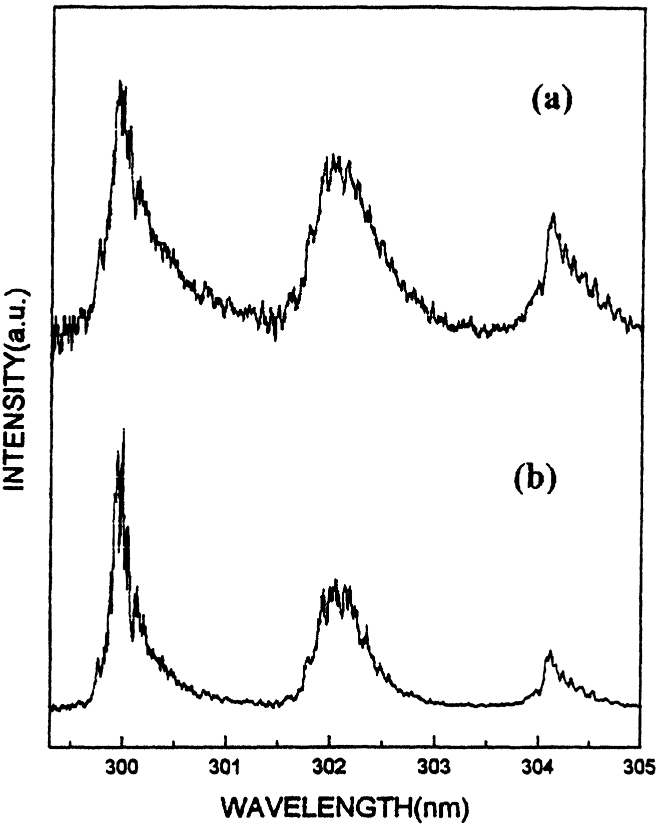

FIGURE 2 A Comparison of the absorption (a) and DFWM (b) spectra of $A(^1A_2) \leftarrow X(^1A_1)$ and $B(^1B_1) \leftarrow X(^1A_1)$ transitions of SO_2. Pump beam energy: 260 μJ; probe beam energy: 160 μJ.

spectrum are quite similar to the absorption spectrum. The three bands can be assigned to G, F, E bands, respectively, proposed by D. J. Brassington [5]. However, the bandwidth of the DFWM spectrum is narrower than that of the absorption spectrum. This result can be explained as it is known that the spectral intensities obtained by DFWM are proportional to the squared modulus of the complex third-order susceptibility tensor $|\chi^{(3)}|^2$, while perturbation in the index of the refraction and absorption coefficient correspond to resonances in $\chi^{(3)}$. Thus, the DFWM spectrum often resembles the square of the absorption spectrum. In the case of unsaturation, the DFWM profile is narrower than the absorption band by roughly a factor of 2.

We have measured the dependences of the DFWM signal intensity on the laser intensity and the SO_2 pressure. When both the laser intensity and SO_2 pressure are low and no buffer gas is added, the DFWM signal generation can mainly attribute to an optical absorption induced population grating. According to the theoretical analysis of the formation of the population grating, an approximate expression describing the pressure and laser intensity dependences of the DFWM signal is derived by Danehy *et al.* [4] in the form:

$$I_{\mathrm{PG}} = \tau I^3 \left(\frac{\sigma \Delta N_0 L}{I_{\mathrm{sat}}} \right)^2 \frac{1}{(1 + 4I/I_{\mathrm{sat}})^3} \tag{1}$$

where I_{PG} is the intensity of the DFWM signal originating from the population grating, τ is the pulse duration, σ is the peak (line-center) absorption cross section, ΔN_0 is the unperturbed population difference between ground and excited states, L is the interaction length, I is the laser intensity (assumed equal for each laser beam) and I_{sat} is the saturated intensity defined by Abrams *et al.* [6] with pressure (P) and temperature (T) dependences. In the case of $I \ll I_{\mathrm{sat}}$, Eq. (1) can be simplified and the DFWM signal intensity is proportional to the cube of the laser intensity and the square of the gas pressure of SO_2.

Figure 3 represents the DFWM signal intensity as a function of the laser intensity in a log-log plot. An $I^{2.9}$ dependence is obtained with the pump beam energy (E_p) in the range of 160 to 330 μJ, while an $I^{0.7}$ is observed at E_p above 330 μJ, indicating that the DFWM signal of SO_2 has been saturated above 330 μJ. Our result for a multilevel system of SO_2 is consistent with the results of a single rovibronic

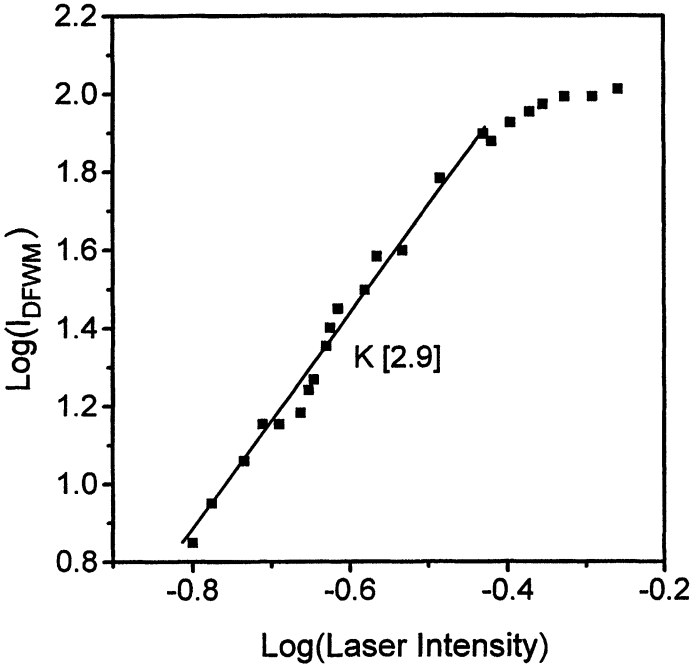

FIGURE 3 Log-Log plot of the DFWM signal intensity *versus* the laser intensity.

transition of NO_2 which also obeyed an I^3 laser power dependence [2]. The DFWM signal intensity dependence on the pressure of pure SO_2 is shown in Figure 4. It can be seen that a linear relationship in a log-log plot gives a slope of 1.95 which is in good agreement with the expected value of 2 from Eq. (1).

In order to examine the enhancement of the DFWM signal intensity of SO_2 with added N_2 as buffer gas, the signal intensities are measured by varying the N_2 pressure for a fixed SO_2 pressure of 1.0 Torr. The result shows a 25 fold increase in the signal intensity at a total pressure of 760 Torr. This enhancement of DFWM signal intensity can be explained in term of the formation of collisionally induced thermal grating when the added buffer gas pressure is much higher than the pressure of SO_2. It has been suggested that collisions between the excited molecules and the surrounding buffer gas transfer their internal energy into translational motion of the buffer gas, thus producing a

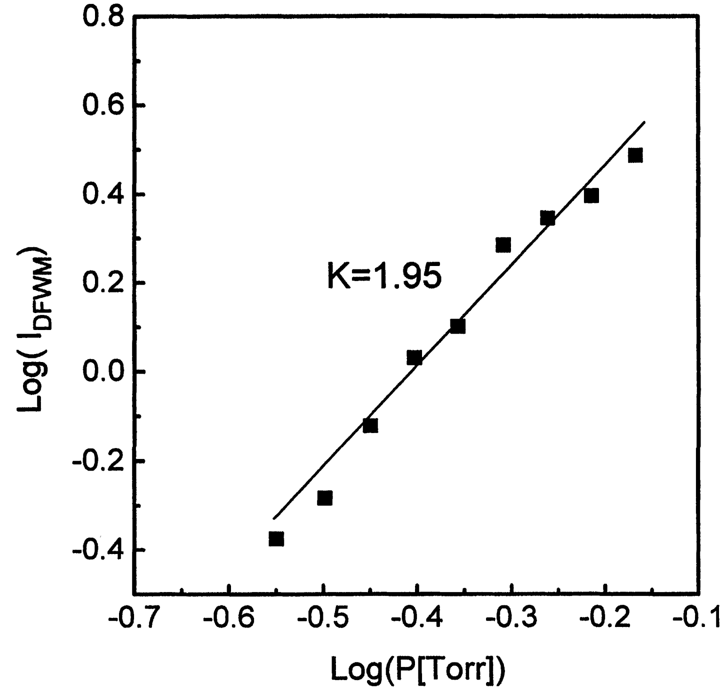

FIGURE 4 Log-Log plot of the DFWM signal intensity *versus* the pressure of SO_2.

spatial modulation of gas temperature and leading to the formation of thermal gratings [7]. An approximate expression for the thermal grating signal has been derived by Danehy *et al.* [4]. When $I/I_{sat} < 0.1$, the thermal grating signal intensity can be written as

$$I_{TG} = \frac{16\tau^3 I^3}{3}\left[\left(\frac{\Delta n_{buff}}{\Delta\rho}\right)_T\right]^2 \left(\frac{\pi\varepsilon\sigma\Delta N_0 L}{\lambda T C_p}\right)^2 \frac{1}{(1+4I/I_{sat})^2} \qquad (2)$$

where λ is the excitation wavelength, C_p is the specific heat of the buffer gas, ε is an empirical parameter that accounts for the fraction of absorbed energy converted to heat, Δn_{buff} is density-induced variations in the buffer-gas refractive index, $\Delta\rho$ is gas density variation, and the other parameters are the same as in Eq. (1).

Since the DFWM signal mainly originates from the population grating and thermal gratings, total signal intensity obtained in the added buffer gas can be given by

$$I_{DFWM} = I_{PG} + I_{TG} \tag{3}$$

Using Eqs. (1), (2) and (3), the DFWM signal intensity can be simulated as a function of the pressure of N_2 buffer gas. In Eqs. (1) and (2), I_{sat} is buffer gas pressure dependent, give by $\Gamma_0\gamma_{12}\sigma_0^{-1}$ [4] when the pressure of SO_2 is fixed. Here σ_0 is the line-integrated absorption cross section, Γ_0 and γ_{12} are the population and coherence decay rates. In a situation where collision dominates lifetimes, they are both proportional to pressure P_{buff}. This lead to $I_{sat} \propto P^2$, but this relationship is not in good agreement with experimental observations [7, 8, 9]. The N_2 pressure dependence of DFWM signal of 1.0 Torr of SO_2 at $E_f =$ 300 mJ and the simulation results along with the contributions of population grating and thermal gratings are shown in Figure 5. Our

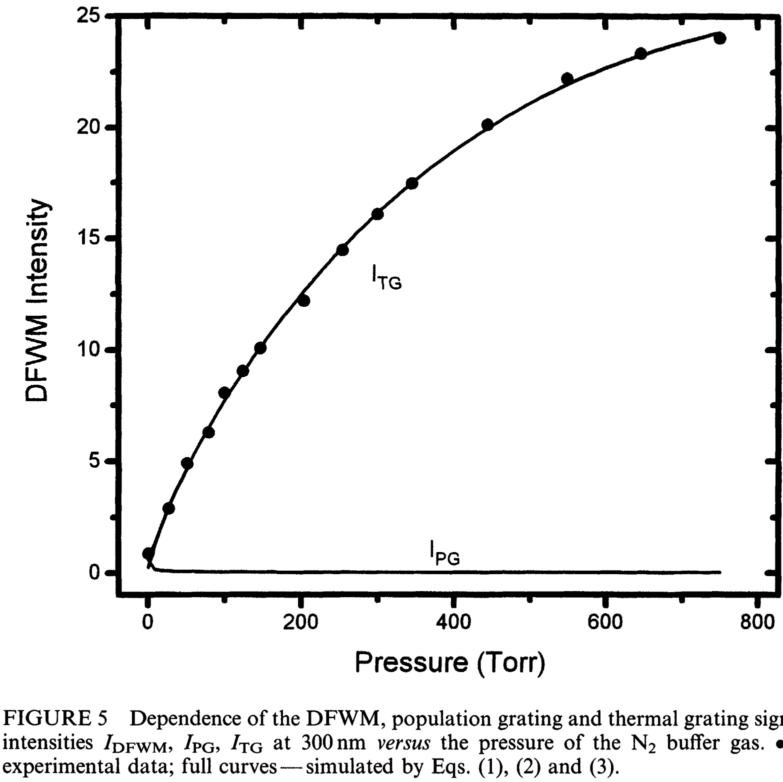

FIGURE 5 Dependence of the DFWM, population grating and thermal grating signal intensities I_{DFWM}, I_{PG}, I_{TG} at 300 nm *versus* the pressure of the N_2 buffer gas. •— experimental data; full curves — simulated by Eqs. (1), (2) and (3).

results show that the above equations are satisfactorily used to describe the dependence of the DFWM signal upon the N_2 pressure with $I_{sat} \propto P^{1.4}$. It can be seen that the intensity of the DFWM signal originating solely from a population grating I_{PG} almost drops to zero in the presence of buffer gas N_2. Different from I_{PG}, the contribution of the thermal gratings increases dramatically with the pressure of N_2. It is evident that collisionally induced thermal grating is dominant in the higher N_2 pressure region, and plays a major role in the enhancement of the DFWM signal intensity.

CONCLUSION

An excitation spectrum of the $A(^1A_2) \leftarrow X(^1A_1)$ and $B(^1B_1) \leftarrow X(^1A_1)$ transitions of SO_2 is observed by using the DFWM technique for the first time. The dependences of the DFWM signal on the laser intensity and the SO_2 pressure are in good agreement with the prediction from the population grating signal equation deviated by Danehy *et al.* [4]. The addition of N_2 buffer gas can enhance the DFWM signal significantly and it can be attributed to the contribution of the collisionally induced thermal gratings at high buffer gas pressure.

Acknowledgement

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