Saturated polarization spectroscopy with a picosecond laser for quantitative concentration measurements

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Abstract: The collisional dependence of saturated polarization spectroscopy with a picosecond laser is investigated by probing hydroxyl in a flow cell.

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OCIS Codes: (120.1740) Combustion diagnostics; (300.6420) Spectroscopy, nonlinear

While nanosecond lasers have been used often for nonlinear diagnostic measurements of flame composition, picosecond lasers provide a potentially superior source for such techniques. Compared to a nanosecond laser, picosecond lasers produce significantly greater peak power for the same pulse energy, and this could improve the signal strength of multi-photon techniques such as degenerate four-wave mixing (DFWM) and polarization spectroscopy (PS). The spectral bandwidth of a transform-limited, 50-150 ps pulsewidth laser [1] is sufficiently narrow to couple effectively with the molecules, and thus such lasers have been successfully used for laser-induced fluorescence (LIF) concentration measurements [2,3]. Such pulse widths are on the order of the characteristic collisional time in an atmospheric combustion environment. It has been suggested that the signal produced by such lasers would be less dependent on the collisional environment because the behavior of the molecular system probed by short-pulse lasers is governed more by the spectral width of the laser and the Doppler effect [4]. To investigate the collisional dependence of the polarization spectroscopy signal generated with a picosecond laser, we probe the $A^2\Sigma^+ - X^2\Pi(0,0)$ band of OH in a flow cell. In this well-controlled environment, we monitor the change in signal strength as we vary the buffer gas pressure by a factor of 50.

In PS two beams, a high-power pump and a low-power probe, are crossed at the measurement location. The probe beam is passed through two orthogonally oriented linear polarizers positioned on opposite sides of the measurement location. The pump beam is either circularly polarized or linearly polarized 45° with respect to the polarization of the probe beam. When the pump beam is tuned to a resonance of the interaction medium, it induces a change in both the real and imaginary parts of the refractive index. This causes the polarization of the probe beam to rotate as it passes through the medium, and the PS signal is observed as leakage of the probe beam through the second polarizer.

The experimental setup is pictured in Fig. 1. The laser source is the frequency-doubled output of a distributed feedback dye laser (DFDL) with motorized tuning and active wavelength stabilization. The energy of the doubled output is controlled by a polarizer preceded by a quarter-wave plate (to compensate for the slightly elliptical polarization of the beam) and half-wave plate (to rotate the polarization of the beam). The beam is down-collimated and directed toward an uncoated UV 3° wedge. The front surface reflection from the wedge forms the probe beam while the back surface reflection is sent to two photodiodes (Thorlabs DET 110 and DET 210) to monitor the beam energy. The portion of the beam that passes through the wedge forms the pump beam. The pump and probe beams are sent through separate delay lines. Before passing through the vertically-oriented polarizer, the probe beam is directed through a half-wave plate rotated to maintain the probe beam energy at 0.5% of the pump beam energy. A quarter wave plate is placed in the pump beam path to change the vertically polarized pump beam to a circular polarization.

Hydroxyl (OH) is created by photolysis of hydrogen peroxide (H_2O_2) using the softly focussed 266-nm output of a Continuum PL9020 Nd:YAG laser. Hydrogen peroxide is obtained by flowing 8 standard $cm^3 s^{-1}$ argon through a bubbler containing 95 wt. % aqueous H_2O_2 . Further details of the photolysis system are

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given by Kliner and Farrow [1]. The 266-nm beam crosses the pump and probe beams inside the cell in front of the LIF detection optics. The crossing angle between the pump and probe beams (both 900 μm in diameter) is 0.6° , resulting in an interaction length of 25 cm. The fluorescence signal is captured by an $f/2$ lens and focused with another $f/2$ lens onto the entrance slit of a 0.25-m monochromator (Oriel 77250) with a 1200 groove/mm grating (Oriel 77296). The fluorescence is attenuated with neutral density filters before detection by a photomultiplier tube (PMT, Hamamatsu R955).

Fig. 1. Schematic diagram of PS experiment. $\lambda/4$ – quarter-wave plate, $\lambda/2$ – half-wave plate, pol – polarizer, bd – beam dump, nd – neutral density filter, sf – spectral filter, dif – diffuser, PMT – photomultiplier tube.

After exiting the cell, the probe beam is picked off with a mirror, sent through a horizontally-oriented polarizer, attenuated by neutral density filters, and passed through a spatial filter before being detected by another Hamamatsu R955 PMT. A Schott Glass UG-1 filter eliminates ambient light. The rejection ratio of the crossed polarizers is 10^{-7} , but because the windows on the cell are strained by the pressure differential they induce a polarization rotation of the probe beam that would interfere with the PS signal. A quarter-wave plate is placed between the probe beam polarizer and the cell to compensate partially for the birefringence of the cell windows. The resulting rejection ratio is 10^{-6} . The PS and LIF signals, as well as the photodiode output, are amplified and digitized using 12-bit A/D converters. For the results reported in this paper, the laser was tuned to the $P_1(2)$ transition.

Figure 2 displays saturation curves acquired by recording the LIF and PS line-center signal strengths with increasing laser energy. At low laser pulse energies the LIF and PS signals increase with increasing laser energy until the laser radiation significantly populates the upper molecular level of the transition, decreasing the efficiency of the signal generation. The LIF and PS signals experience saturation at a pump beam energy of $\sim 1 \mu\text{J}$, above which the LIF signal becomes nearly independent of laser power. However, the PS signal exhibits a plateau between 1 and $3 \mu\text{J}$ pump energy, then increases again until finally rolling over near $10 \mu\text{J}$. We have seen such saturation effects before in theoretical studies of DFWM using short-pulse lasers [4]. Further theoretical studies are underway to analyze these effects for PS, similar to the DFWM analysis but for a multistate molecular system.

Scans of the $P_1(2)$ transition were acquired at different pressures to investigate the collisional dependence of the PS signal. The cell pressure was adjusted with a needle valve on the gas flow output port. The same computer that recorded the digitized signals also incremented and recorded the DFDL wavelength. One hundred laser shots were averaged at each wavelength, and the visible wavelength step size was $7 \times 10^{-4} \text{ nm}$. The PS signals integrated over the spectral line shapes are plotted as a function of cell pressure in Fig. 3. The results are displayed for both an unsaturating pump beam and for a saturating pump beam. The PS signal is proportional to the square of the number density probed, and therefore has been normalized by the square of the OH concentration measured with unsaturated LIF. The LIF signals were corrected for quenching for each cell pressure by measuring the fluorescence decays with a 1-GHz digital oscilloscope (Tektronix TDS 680B). Varying the cell pressure between 10 and 500 torr, we found the unsaturated PS signal decreased by a factor of 15 while the saturated PS signal decreased by only a

factor of 3. This remarkable insensitivity to pressure would correspond to an error of only $\sqrt{3}$, or 70%, in the saturated concentration measurements if the effects of pressure were neglected in data analysis.

The quenching rate and collisional environment in the cell are dependent on the partial pressures of Ar, H_2O , and H_2O_2 in the cell. Because the vapor pressure for 95 wt. % aqueous H_2O_2 is only 1.8 torr, Ar is the major species in the cell for all pressures investigated. The overall collisional width is then expected to vary approximately linearly with cell pressure as $18.5 \times 10^{-5} \text{ cm}^2/\text{torr}$ given by Shirinzadeh et al. [5]. The quenching rate, on the other hand, is a strong function of the relative concentrations of H_2O and H_2O_2 . While Ar is a relatively weak quencher of OH, both H_2O and H_2O_2 are strong quenchers [6,7]. As the cell pressure was increased, the partial pressures of H_2O and H_2O_2 also increased. The quenching rate calculated from the acquired fluorescence decays increased by a factor of 5 from 0.013 ns^{-1} to 0.071 ns^{-1} . The saturated PS signal, which varied by only a factor of 3 over the pressure range, is therefore also quite insensitive to collisional quenching.

In conclusion, saturated PS with a picosecond laser is relatively insensitive to both the overall collisional rate and to collisional quenching. Nonlinear resonance techniques benefit from saturation, because saturating beam intensities both increase the signal intensity and decrease the dependence of the signal on the collisional environment. Saturation is easily achieved with the frequency-doubled DFDL, and the laser pulse energy had to be reduced by 3 orders of magnitude from its peak energy to avoid the effects of saturation even with relatively large beam diameters.

Acknowledgements

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division.

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Fig. 2. LIF (closed circles) and PS (open circles) saturation curves of the $P_1(2)$ transition. The cell pressure was 106 torr and the bubbler pressure was 129 torr. Arrows indicate the pump laser energy maintained for the measurements displayed in Fig. 3.

Fig. 3. PS signal (normalized by the square of the OH concentration) as a function of cell pressure. The results are displayed for both an unsaturating pump beam and for a saturating pump beam.