

Time Resolved Laser Excited Resonance Emission Spectra of SO₂ for Development of Resonance Raman LIDAR

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Abstract: Ns-scale time resolved laser excited resonance emission spectra of sulfur dioxide (SO₂) gas were acquired in two different deep UV wavelength regions. Both wavelength regions are in electronic resonance of SO₂ molecule but the temporal responses of the two emission spectra were different in ns time scale. When excited at 220.56 nm, the emission spectra were observed at almost the same time as the excitation laser and we conclude that the spectra were resonance Raman scattering. On the other hand, when excited at 279.60 nm, the emission spectra were observed approximately 5 ns after the excitation laser and we conclude that the spectra were resonance fluorescence. 5 ns difference in time is equivalent to 75 cm in distance measurement of ToF LIDAR, which is not negligible in short range or precision-needed situations.

1. Introduction

Remote and instant detection of hazardous materials is strongly needed for security issues such as homeland security and counterterrorism. However, most of the detection techniques commercialized to date don't work at a distance. Laser-based spectroscopies are one of the most promising candidates for the remote detection.

We have been engaged in development of remote detection techniques and systems utilizing resonance Raman spectroscopy in the deep ultraviolet (UV) spectral region [1]. UV excitation dramatically increases Raman scattering cross-sections of a variety of materials including toxic gases, explosives, and biological threats. Furthermore, in the deep UV spectral region, background interference signals from the sunlight is much less than in the visible spectral region. Due to these advantages, deep UV resonance Raman spectroscopy is an attractive tool for remote detection of hazardous materials [2]. In this paper, as a fundamental study for the development of resonance Raman LIDAR, time resolved laser excited emission spectra of SO₂ gas were acquired.

2. UV absorption of SO₂ gas

Raman spectroscopy is a versatile tool widely used in many fields of analytical sciences. However, because of quite small cross sections of spontaneous Raman scattering, sensitivity of

Raman spectroscopy is not high enough in remote or trace-level detection.

It is known that, when excited in the deep UV spectral region which corresponds to electronic resonances of target molecules, Raman scattering cross sections become as high as 10³ – 10⁵ times greater compared to those in the visible spectral region. This enhancement is advantageous for remote sensing of trace gases.

Figure 1 shows deep UV absorption spectra of SO₂ gas acquired in our laboratory. There are two distinct absorption bands, one is from 190 to 230 nm and the other is from 250 to 320 nm.

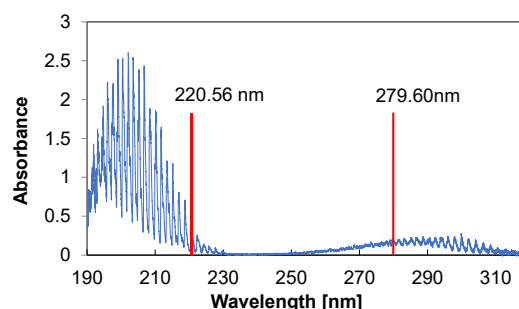


Figure 1. Absorption spectra of SO₂ in the deep UV region

We excited SO₂ gas at 220.56 nm in the first band and at 279.60 nm in the second band. Both excitation wavelengths are located at the apexes of the comb-like structures of the absorption spectra, which correspond to electronic resonance of SO₂ molecule.

3. Experimental Setup

The experiments were conducted in a 90° geometry. The excitation laser was a wavelength tunable dye laser (Sirah/Precision Scan) pumped by a ns frequency tripled Nd:YAG laser (Spectra-Physics/Quanta-Ray). SO₂ gas (1000 ppm, nitrogen base) was flowed in an 80 mm, cubic gas cell with four quartz glass side windows. The vertically polarized excitation laser irradiated the gas cell through the windows and emission spectra were collected and directed to a customized streak camera system (Hamamatsu/C13410-01A) through the other window.

4. Results

Figure 2 shows time resolved emission spectra of SO₂ gas when excited at 220.56 nm and figure 3 shows spectra excited at 279.60 nm.

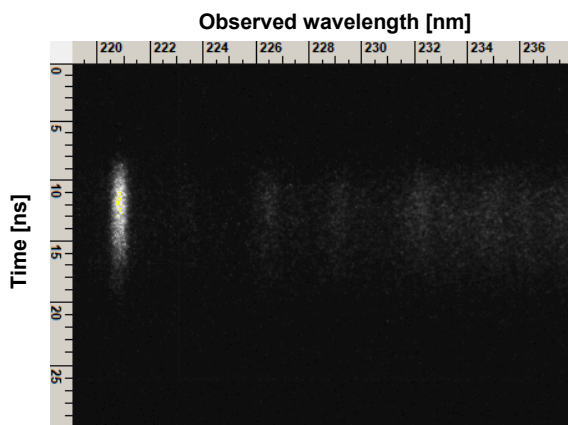


Figure 2. Time resolved emission spectra of SO₂ gas (excitation wavelength: 220.56 nm)

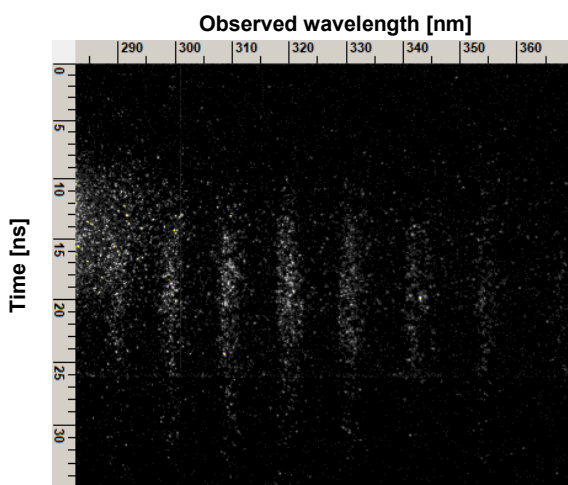


Figure 3. Time resolved emission spectra of SO₂ gas (excitation wavelength: 279.60 nm)

The vertical axis represents time in ns and the horizontal axis represents observed wavelength in nm.

In figure 2, the bright spot in the upper left is spectra of the excitation laser (Rayleigh scattering). Emission spectra of SO₂ were observed at the same vertical position as the laser, which means the emission was observed instantaneously after the excitation.

However, in figure 3, excitation laser and emission spectra of SO₂ were not observed at the same time. In figure 3, Rayleigh scattering spectra of the laser is out of the observed range but the vertical position was the same as that in figure 2. In this case, comparing their intensity peak positions, the emission spectra of SO₂ were observed approximately 5 ns after the excitation.

5. Discussion

The results shown in figure 2 and 3 imply that the two spectra are different types of resonance emissions. We conducted further experiments in which the excitation laser wavelengths were slightly changed in the vicinity of 220.56 nm and 279.60 nm, respectively. When excited at around 220.56 nm, positions of the spectral peaks moved according to the change of the laser wavelength but the shift in wavenumbers from the excitation laser remained the same. On the contrary, when excited at around 279.60 nm, positions of the spectral peaks didn't move and were not affected by the change of the excitation laser wavelength. We believe that the former type of resonance emission is resonance Raman scattering and the latter is resonance fluorescence, but the difference of the two has been the subject of considerable interest and controversy [3, 4].

This study revealed that there is a 5 ns temporal difference between the two resonance emissions of SO₂ gas. 5 ns corresponds to 75 cm in distance measurement of time-of-flight (ToF) LIDAR. This difference is not negligible in short range or precision-needed measurements. Besides, some other target substances may have different and much longer response time of resonance emissions. For the development of resonance Raman LIDAR, we will further study on time-resolved resonance emission spectra of target substances other than SO₂ gas.

6. Acknowledgments

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7. References

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