

Safe Detection of Hazardous Substances Using Resonance Raman LIDAR

Masakazu Ogita ^(a), Sachiyo Sugimoto ^(a), Yuji Ichikawa ^(a), Ayako Hoshino ^(a), Nozomi Yamashita ^(a), Shuzo Eto ^(b), Toshihiro Somekawa ^(c), Haik Chosrowjan ^(c), Seiji Taniguchi ^(c),
Ippei Asahi ^(a)

^(a) *Shikoku Research Institute Inc.*

2109-8 Yashima-nishimachi, Takamatsu-shi, Kagawa-ken 761-0192, Japan

^(b) *Central Research Institute of Electric Power Industry*

2-6-1 Nagasaka, Yokosuka-shi, Kanagawa-ken 240-0196, Japan

^(c) *Institute for Laser Technology*

3-11-20 Nakouji, Amagasaki-shi, Hyogo-ken 661-0794, Japan

m-ogita@ssken.co.jp

Abstract: New technologies to measure hazardous substances quickly and safely are always required in a wide range of fields. However, the physical properties and the physical states of hazardous substances generated by such as: air pollution, volcanic activity, CBRNE disasters are assumed to vary. For this reason, there is still no device can measure hazardous substances comprehensively. To solve this problem, we have been focusing on the research and development of remote sensing device that is highly sensitive and applicable to various hazardous substances by using resonance Raman effect. We selected air pollutants sulfur dioxide and ammonia as target gases for remote sensing. Three sigma limits for sulfur dioxide and ammonia in this measurement were 3 ppb and 15 ppb at 100 m.

1. Introduction

The development of new remote sensing technology of hazardous substance is required in a wide range of fields, regardless of industry. Numerous air pollutants and toxic chemicals are hazardous to humans at low concentrations. In order to ensure safety, it is extremely important to establish a technology for remote sensing of these trace components. We have previously conducted research and development on Raman LIDAR as a non-contact measurement technique for industrial applications [1-3]. The Raman effect is a useful phenomenon that can be applied to many substances. Conversely, the cross-section is very small compared to other light-matter interactions [4]. This is a issue in the development of the trace substance remote sensing device. The Raman effect is a type of inelastic scattering of light by molecules. This is a phenomenon in which light with a wavelength different from that of the incident light is scattered due to energy exchange between light and molecules that make up matter. The amount of wavelength shift of scattering light relative to incident light is unique for each substance, and scattering light with a changed wavelength is called Raman

scattering light, and the amount of shift is called Raman shift. Since the wavelength of the Raman scattering light is determined by the wavelength of the excitation light, it is possible to identify the substance by focusing on the Raman scattering wavelength even in situations where multiple substances coexist. Furthermore, since the Raman shift and scattering wavelength are unique for each substance, spectroscopic measurements of multiple substances are possible. In this way, the Raman effect has a high advantage over various measurement methods including spectroscopic measurement. In contrast, the fact that the Raman effects are extremely small compared to other light-matter interactions is a major disadvantage in trace component measurement and remote sensing. The cross-section of Raman scattering is approximately 1/1000 or less compared to other light-matter interactions. This shows that the measurement of Raman scattering light is greatly affected by the optical conditions of the observation environment. If the weak Raman scattered light could be enhanced, this problem would be solved.

To solve this problem, we have conducted research and development of LIDAR system using the resonance Raman effect that can

significantly enhance Raman effect with the aim of establishing a remote sensing techniques applicable to many trace hazardous substances. We selected air pollutants sulfur dioxide and ammonia as target gases and conducted remote sensing. Three sigma limits for sulfur dioxide and ammonia in this measurement were 3 ppb and 15 ppb at 100 m.

2. Methodology

Resonance Raman effect is a phenomenon in which the Raman scattering light corresponding to conjugated vibrational mode is significantly enhanced when a target substance is excited with light of a wavelength corresponding to the electron absorption band of the target substance. Energy level diagram of Raman effect is shown in figure 1.

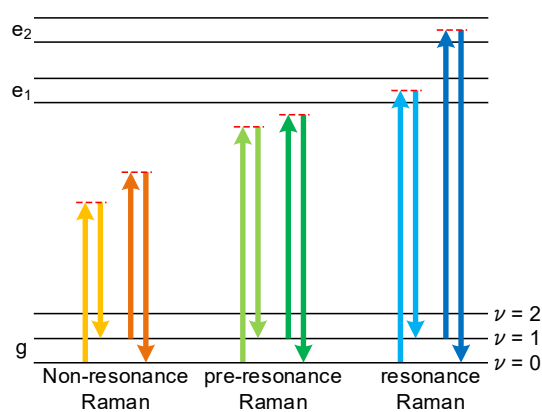


Figure 1. Energy level diagram of Raman effect.

Generally, non-resonance Raman is not limited by the wavelength of the incident light. Resonance Raman scattering greatly enhances Raman scattering light when the wavelength of excitation light is matched to the electronic transition energy of the target substance. The case where Raman scattering light is enhanced by light near the resonance wavelength is called pre-resonance Raman. The incident light wavelength completely matches the resonance wavelength and the enhancement is maximum, it is called resonance Raman. Pre-resonance Raman and resonance Raman differ for each substance. Besides, Raman scattering light follows the fourth-power law of frequency, which is a characteristic of scattering light in general. Since the scattering light intensity increases in proportion to the fourth power of the excitation light energy, further enhancement of Raman scattering cross-section can be expected in this wavelength region.

In the case of actual measurement, the pattern of the UV-VIS absorption spectrum, which indicates the electronic transition energy of the target substance, is an indicator of the applicability of the resonance Raman effect. If the electronic transition energy of the target substance exists in the wavelength region that can be oscillated by laser technology, there is a prospect of application of the resonance Raman effect. Sulfur dioxide and ammonia have light absorption near the DUV wavelength region [5], therefore, resonance Raman effect can be applied.

Sulfur dioxide has two UV absorption bands at 180-235 nm and 260-340 nm. Ammonia has an UV absorption band at 170-217 nm. Also, according to literature values, there is an absorption band at 140-169 nm [6]. In this research and development, the resonance Raman excitation profiles of sulfur dioxide and ammonia were obtained in the range of 196-220 nm and 200-218 nm. The wavelengths below 280 nm can be measured outdoors during the daytime. This wavelength range is known as the solar-blind area, where almost no sunlight reaches the earth's surface due to light absorption by atmospheric components. Being able to suppress the effects of sunlight, which is a significant disturbance, is extremely useful for during daylight hours measurements using LIDAR. The measured resonance Raman excitation profiles and UV absorption of sulfur dioxide and ammonia are shown in figure 2 and 3.

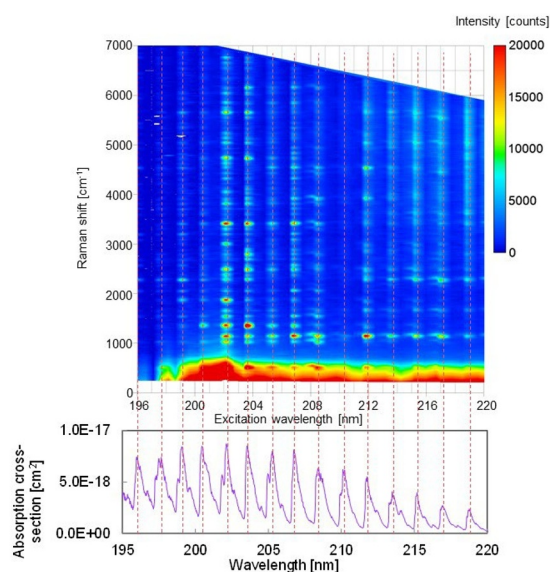


Figure 2. Resonance Raman excitation profile and UV absorption of sulfur dioxide.

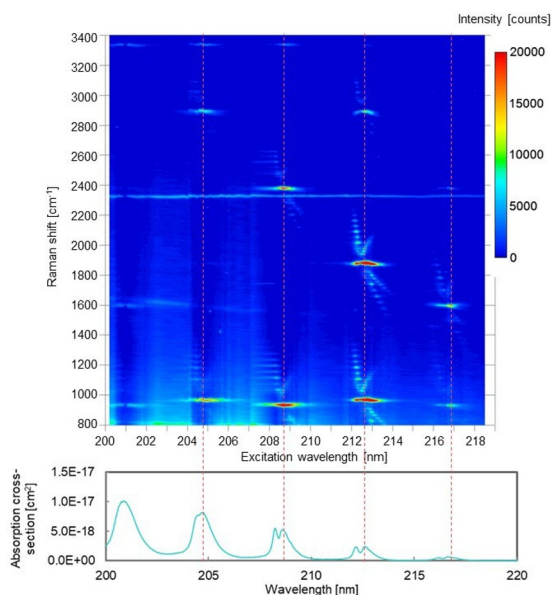


Figure 3. Resonance Raman excitation profile and UV absorption of ammonia.

As shown in figure 2 and 3, the resonance Raman spectra of sulfur dioxide and ammonia tended to follow the pattern of the UV absorption spectrum of the substance. Based on this result, we made a resonance Raman LIDAR.

3. Device specifications

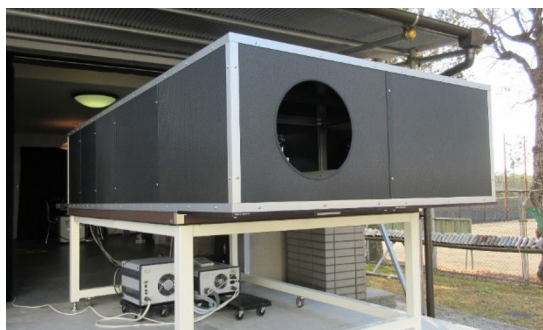


Figure 4. Equipment appearance of the resonance Raman LIDAR.

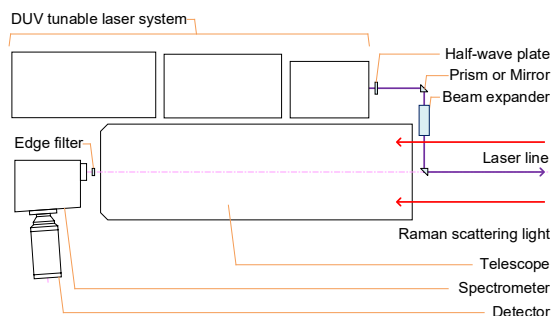


Figure 5. Device implemented in the resonance Raman LIDAR.

The LIDAR arrangement was a coaxial type. The light source for sulfur dioxide measurement

was a DUV tunable laser system with a tunable Ti:S laser (LS-2134N, Ti:S and LT-2211N-FP, HG-TF Unit, product of LOTIS TII, PRF 10 Hz, pulse energy 1.49 mJ at fourth harmonic generator). The DUV tunable laser system consists of: a nanosecond pulse laser for excitation, Ti:S for wavelength tuning and second harmonic generator, and third and fourth harmonic generator. The telescope used was a Classical Cassegrain telescope with an effective diameter of 300 mm. The telescope's focus shifts due to the operation of the secondary mirror. This makes it possible to measure a range of about 100 m from short distances with high sensitivity. The collected resonance Raman scattering light is detected by a spectrometer and photodetector (IsoPlane160, PI-MAX4:1024EMB, product of Teledyne Princeton Instruments) at the rear of the telescope.

4. Results

We conducted a remote sensing experiment of sulfur dioxide and ammonia using the resonance Raman LIDAR. The measurements were carried out outdoors during the daytime. The excitation wavelength of sulfur dioxide was set to 211.8 nm, which is one of the resonance wavelengths, and measurements were performed while changing the concentration stepwise from 1 ppm to 0.1 ppm. In the case of ammonia, the excitation wavelength was set to 212.8 nm and the concentration was measured at 20-1 ppm. The target gas was released into the atmosphere at a distance of 100 m from the LIDAR. The peaks 1551 cm^{-1} and 2330 cm^{-1} in figure 6 and 7 are the non-resonance Raman spectra of oxygen and nitrogen in the atmosphere.

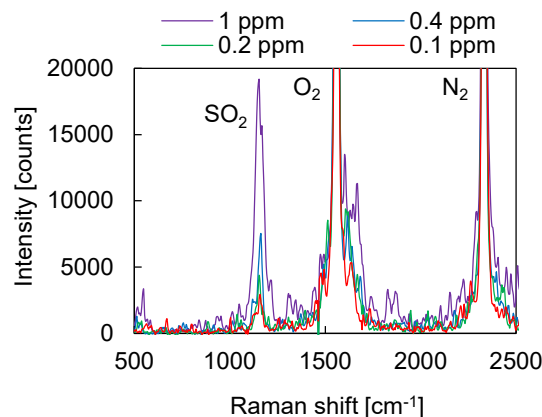


Figure 6. Resonance Raman spectrum of sulfur dioxide.

As a result of the measurement, an extremely strong resonance Raman spectrum of sulfur dioxide was obtained. Resonance Raman spectrum of sub-ppm order for sulfur dioxide was measured in the same range as atmospheric components. The estimated enhancement ratio of resonance Raman effect of sulfur dioxide was 10000 times more.

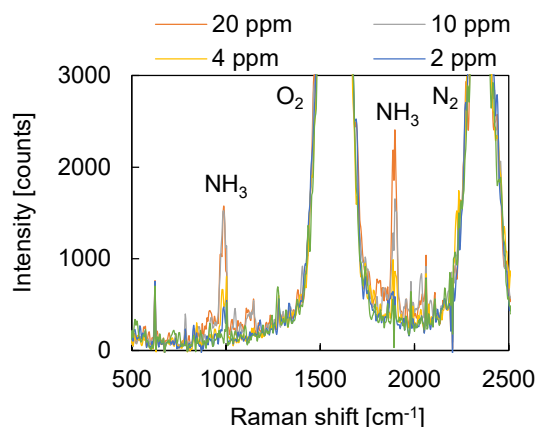


Figure 7. Resonance Raman spectrum of ammonia.

As shown in figure 7, the enhancement of Raman scattering light was also confirmed in the case of ammonia. The estimated enhancement ratio of resonance Raman effect of ammonia was about 10000 times.

The distance resolution of the LIDAR used in this case was 1.5 m. Assuming that sulfur dioxide and ammonia stagnating to the distance resolution of LIDAR, the three sigma limits were 3 ppb, 15 ppb at 100 m. The results of the study underscore the effectiveness of resonance Raman LIDAR in measuring trace amounts of hazardous substances.

DIAL is a useful remote sensing technology for air pollutants that has already been put into practical use [7]. However, since DIAL measures at two wavelengths, one for the absorption ON/OFF of the target substance, it is difficult to detect the substance or requires a long measurement time when the target substance is unknown. In addition, because the distance resolution of ranging has a trade-off relationship with sensitivity, in the case of trace component measurement that requires long optical path measurement, the ability to identify the position and the distance resolution deteriorate. Furthermore, the DIAL that is in practical use cannot be applied to solid. Considering the above points, resonance Raman

LIDAR has an advantage in terms of ability to identify substances, ranging, and range of applicable substances.

5. Acknowledgments

This work was supported by Innovative Science and Technology Initiative for Security Grant Number JPJ004596, ATLA, Japan.

6. References

- [1] H. Ninomiya, S. Yaeshima, K. Ichikawa and T. Fukuchi, "Raman lidar system for hydrogen gas detection," *Opt. Eng.*, (Vol.46, No.9, 094301, 2007)
- [2] I. Asahi and H. Ninomiya, "Measurement of concentration distribution of hydrogen gas flow by measuring the intensity of Raman scattering light," *IEEJ Trans EIS*, (Vol.131, No.7, 2011), pp. 1309-1314.
- [3] I. Asahi, S. Sugimoto, H. Ninomiya, F. Shimokawa, H. Takao, F. Oohira, Y. Tsutsui, H. Hayashi and T. Konno, "Compact optical multi-gas sensors using micromachining technology [II] : Characteristics of Raman scattering gas sensor and ultraviolet absorption spectroscopy gas sensor," *IEEJ Trans SM*, (Vol.133, No.9, 2013), pp. 260-266.
- [4] J.J. Laserna, "Modern techniques in Raman spectroscopy," (John Wiley & Sons, New York, 1996), p. 22.
- [5] The MPI-Mainz UV/VIS spectral atlas of gaseous molecules of atmospheric interest, http://satellite.mpic.de/spectral_atlas
- [6] B.M. Cheng, H.C. Lu, H.K. Chen, M. Bahou, Y.P. Lee, A.M. Mebel, L.C. Lee, M.C. Liang and Y.L. Yung, "Absorption cross sections of NH₃, NH₂D, NHD₂, and ND₃ in the spectral range 140-220 nm and implications for planetary isotopic fractionation," *The Astrophysical Journal*, (The Astrophysical Journal, Vol.647, No.2, 2006), pp. 1535-1542.
- [7] T. Fukuchi, N. Goto, T. Fujii, K. Nemoto, "Analysis of SO₂ measurement accuracy by multiwavelength DIAL," *T.IEE Japan*, (Vol.118-C, No.5, 1998), pp. 630-635.