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A laser spectroscopy based method for the detection of acidic compounds in solution

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Highlights

- A laser spectroscopy method to detect the presence of small amounts of acids down to 10 ppm is proposed.
- The method relies on the laser emission from a cuvette containing a pH sensitive dye stimulated by the irradiation with a pumping beam.
- The emitted laser wavelength shifts as a function of the acid molecules presence. From the emitted wavelength the amount of acid can be precisely determined.

This work presents a laser spectroscopy based method to detect very small amounts of acidic molecules in concentrations down to 10 ppm. The proposed method relies on the sensitivity to acids of a fluorescent dye, which is used as the active material in a stimulated laser emission experiment. Using a cuvette, that works as a resonator, laser emission from a dye doped mixture can be observed. When an acidic species is added to the mixture, due to the solvatochromic effect, the spectral position of fluorescence shifts and, consequently, a shift in the emitted laser wavelength is observed. From the analysis of the laser lines the presence of a specific acid species and its concentration can be determined.

Keywords: Laser spectroscopy, atmospheric pollutant, fluorescent dye, sensor

1. Introduction

According to World Health Organization, air pollution is one of the main avoidable causes of disease and death globally. About 4.3 million deaths each year, most in developing countries, are associated with exposure to household (indoor) air pollution. A further 3.7 million deaths a year are attributed to ambient (outdoor) air pollution [1]. An air pollutant is known as a substance in the air that can cause harm to humans and the environment. Pollutants can be in the form of solid particles, liquid droplets, or gases. In addition, they may be natural or manmade [2]. Acid Rain (AR) is one of the most dangerous and widespread forms of pollution. The burning of fossil fuels (coal and oil) by power-production companies and industries releases sulfur into the air that combines with oxygen to form sulfur dioxide (SO_2). Exhausts from cars cause the formation of nitrogen oxides in the air. From these gases, airborne sulfuric acid (H_2SO_4) and nitric acid (HNO_3) can be formed and be dissolved in water vapor in the air. Although AR gases may originate in urban areas, they are often carried for hundreds of miles in the atmosphere by winds into rural areas. The real-time detection of trace amounts of AR gases and pollutants in the atmosphere is of great interest to a wide range of fields, including environmental science, safety monitoring, air quality control [3], defense and homeland security [4], and medical diagnostics [5]. Atmospheric pollutant monitors use different technologies as: electrospray mass spectrometry [6] adaptive infrared imaging spectro-radiometry [7], millimeter wave technology [8], chemical agent monitoring [9], electro kinetic injection in capillary electrophoresis [10], surface acoustic wave chemical sensors [11]. Detectors of AR and toxic industrial chemicals have to be robust, portable, fast-acting, cheap, simple to operate, they have to be very sensitive and selective to the detected gases. Modern analytical chemistry has instruments that can detect single molecules [12,13]. Each, however, has drawbacks and limitations. In general, these are delicate, stationary, and expensive equipment demanding complex and time-consuming sample preparation.

Colorimetric indicators, commonly referred to as chemical detection papers [14,15], are the fastest, cheapest, lightest, and easiest type of detector to use. However, they suffer the high cross-sensitivity to smoke, acetone, gasoline and other interferents. Colorimetric tubes are applicable to both vapors and gases and provide a semi-quantitative indication of the amount of agent present in the environment. The drawbacks of this technique are the low speed of the responses to agents and the size of instrumentation.

Laser-based techniques for trace gas detection have many advantages over other techniques because of their ability to provide real-time monitoring capabilities with greater sensitivity and selectivity. They usually involve the detection and measurement of radiation of different wavelengths reflected or emitted from distant samples. All the techniques rely on optical phenomena as: absorption, fluorescence, resonance scattering, Raman scattering, Mie scattering, Rayleigh scattering. Up to

now, various diagnostic methods based on physical processes using laser light to detect environmental species have been developed [16-22]. Nevertheless, instruments that use the above mentioned operating principles are very robust but complicated and expensive. As an example, infrared spectrometers offer a limited level of standoff detection, they are expensive, complex and bulky. Further, Raman spectroscopy, that has successfully been employed for AR detection in laboratory conditions, is not applicable for identification of the agents in a real-world environment due to the lack of robustness.

In this work, we propose a novel method based on laser spectroscopy for the fast and accurate detection of acid pollutants. The method is based on monitoring the laser emission from a cuvette containing an organic dye in a common solvent. It is well known that some species of organic dyes change their optical properties following exposure to different chemical and biological substances [23,24]. In some cases, the changes consist in the shift of their absorption and emission band within a certain range of the optical spectrum.

In the last years, organic fluorescent dyes have been widely employed as a key component in mirror-less lasing [25]. Compared to gases and most solid state lasing media, they allow to obtain lasing on a much wider range of wavelengths.

A polarity and viscosity sensitive organic fluorescent dye, such as Nile Red (NR), can be used to probe the environmental properties in organized molecular assemblies of micelles, bilayer membranes, and biological complex systems. NR is an intensely fluorescent dye that acts as a hydrophobic probe, i.e. its fluorescence maxima vary depending on the relative hydrophobicity of the surrounding environment. As an example, when NR is dissolved in hydrocarbon solvents such as heptanes or in neutral lipids such as triacylglycerol or cholesteryl ester droplets, NR fluoresces yellow-gold. On the other side, when NR is dissolved in more polar solvents such as ethanol or in phospholipids such as phosphatidylcholine vesicles, the dye fluoresces red [26,27].

We propose to use NR sensitivity to the pH of the surrounding medium to reveal the presence of small amounts of acid molecules. The accurate detection of acid molecules can be achieved monitoring laser emission from a laser-pumped cuvette which uses a solution containing NR as active medium. The emitted laser wavelength depends on the fluorescence properties of the dye, and it can be finely tuned when small amounts of acids are added to the solution. The shift in the emitted wavelength is strongly related to the species and quantities of acid molecules and can be monitored using a spectrometer. The proposed methodology offers several advantages such as a great accuracy and reliability in detecting and identifying acid molecules together with real-time output.

2. Experimental

2.1 Materials characterization

For the experiments ethyl alcohol (Carlo Erba, Italy) was used as solvent. Nile Red, a laser dye with 0.7 quantum yield, served as the acid sensitive component (Sigma-Aldrich). Nitric acid (70% grade), sulfuric acid (98% grade), acetic acid (99.7% grade), all from Sigma-Aldrich, were used as acidic substances to be detected. The absorption, fluorescence and laser emission spectra were monitored using a multi-channel fiber-optic spectrophotometer, having 1.5 nm resolution (AvaSpec-2048, Netherlands).

A solution of ethanol and NR, called reference solution, was prepared in the following concentrations in weight: 99.95wt% Ethyl Alcohol + 0.05wt% NR. The solution was stirred at 300 rpm, at room temperature for 2 minutes.

We investigated the effect of the presence of small amount of acids in solution on the absorption and fluorescence properties of the reference mixture. A small amount of sulfuric acid was doped to the reference solution. The change of the optical properties of the mixture was visible to the naked eye. Fig. 1 shows the change in the solution color when $m/M=10^3$ ppm where m is the acid amount and M is the amount of the reference solution, respectively. The color of the reference solution changed from red to blue after adding sulfuric acid.

Fig. 2 shows the shift in the absorption and emission spectra.

As reported in literature [28], there is a correlation between the amount of acid in solution and the spectral shift of the absorption and fluorescence peaks. This shift can be used to reveal the presence of the acid. Since the peaks are broad, around 70nm FWHM, the sensitivity of a sensor based on the detection of the absorption or emission spectra, is not sufficient to detect small amount of acid dopants, as an example 10 ppm concentration ratio.

2.2 Experimental set-up

In this perspective, using laser emission from a dye doped solution contained in a cuvette will dramatically improve the detection sensitivity. Laser emission from a cuvette containing a fluorescent material has been reported in the work of Schäfer et al. [29]. In this paper, the authors obtained laser emission from a 10mm square cuvette containing a dye mixture pumped by a ruby

laser, the laser emission was also tuned varying the dye concentration. As reported in [30], the fluorescent material acts as the active medium while the cuvette itself as the resonator. The resonator is formed by the two glass-air interfaces of the polished sides of the cuvette.

For this experiment, two cuvettes with cylindrical shape, 15mm height and 8mm diameter base, were prepared. One cuvette was filled with the reference solution, and served as control, while the other cuvette served as sample and was filled with the reference solution containing a small amount of acid.

The experimental set up is sketched in Fig. 3.

As pumping source the second harmonic of a Nd:YAG laser with an average power of 7.2 mW and 300 μ J of pulse energy was used (1). The pulse wavelength, width and repetition rate were 532nm, 4ns and 1-10 Hz, respectively. The pumping laser beam hit a beam splitter (2) and was split in two parts. One beam was directed to the cuvette containing the dye solution (4), while the second beam, using a mirror (3), was directed to the cuvette containing the same solution doped with different amounts of acid (5). A multichannel spectrometer (6) was used to capture the signals that were analyzed using a computer (7).

3. Results and discussion

The reference solution was doped with different concentration of sulfuric acid and the spectral shift of laser lines was monitored. Fig. 4 shows the laser peaks obtained from different solutions, each of them doped with the following concentration ratio of sulfuric acid: 10ppm (curve a), 50ppm (curve b), 10^2 ppm (curve c), 5×10^2 ppm (curve d) and 10^3 ppm (curve e). The maximum obtained shift was 29nm when doping with the maximum concentration ratio of acid.

Similar experiments were carried out using nitric acid, acetic acid and purified water (pH=7) at the same concentrations as it was done for sulfuric acid. Fig. 5 shows the laser lines emitted by the reference solution confined in the cuvette. A shift of about 24 nm in the laser emitted wavelength from a sample solution containing nitric acid at a concentration ratio of 10^3 ppm is observed.

For acetic acid we observed a shift of 9nm, when the sample solution was doped with a concentration ratio of 10^3 ppm, while no shift was observed in laser emission for the reference solvent doped with deionized water.

The results show that the monitoring of the laser wavelength shift is a unique method to evaluate the presence of very small amounts of acid. Laser peaks are very narrow and quantities can be estimated with great accuracy. Furthermore, the idea is easy to be implemented in a device. In this perspective, calibration is one of the key issues for the reliability of a device. We performed a first attempt at calibration preparing a series of standard solutions with accurately known concentrations. The laser lines shifts obtained from the solutions could be easily measured and used to prepare a calibration curve, i.e. a graph of the emitted wavelength as a function of the concentration. In fig. 6 are shown the spectral-concentration dependences for the three acids and water.

Calibration curves allow to determine the concentration of a given acid at any point, within the studied range of concentration ratio variation. In fig. 6, given a wavelength λ_j , the information on the acid concentration can be calculated by the slope of the graph as follows:

$$\tan \phi_i(\lambda, C) = \frac{d\lambda_i}{dC_i}$$

The presence of acid molecules is detectable from concentration as small as 10ppm and the molecules can be easily identified. For high concentrations the shift in the laser wavelength due to acetic acid molecules can be distinguished from the shift due to the other kind of molecules. Unfortunately, in the range between 650nm and 662nm, it is difficult to immediately distinguish between sulfuric or nitric acid. Nevertheless, if several measurements are performed with different concentrations, the species can be uniquely determined from the slope of the curve. Finally, for practical applications, the method of calibration curves or the method of least squares could be used for the calibration and simultaneous detection of two or more species.

An estimation of the accuracy in evaluating the concentration can be also provided. As an example, for sulfuric acid we observe a shift within the spectral range $\Delta\lambda = (670-650)\text{nm} = 20\text{nm}$ in which the concentration ratio of the acid varies 10^2 times. If we assume that the half-width for each laser line is 1.5nm and that in this spectral gap there are 20 laser lines, we infer that the concentration of sulfuric acid can be defined with a 7.5% accuracy.

In this experiment the only limitation is represented by the accuracy of the spectrometer used. Using a spectrometer with a lateral resolution less than 1 nm, even smaller amounts of acidic substances can be detected.

Conclusion

In conclusion, we present a method based on laser spectroscopy to detect the presence of small amounts of acids. The system is based on the laser emission from a cuvette containing a Nile Red solution. The laser wavelength is sensitive to the chemical species and their concentration. This technique is precise and provides real time monitoring. Further, using other pH sensitive dyes, as Congo Red, more compact and cheap laser sources can be used to stimulate the laser emission from the pH sensitive mixture, as nitrogen lasers. We envisage versatile application in many fields of science and industry where the accuracy, rapidity and portability play an important role as in global and homeland security, medicine and food industry.

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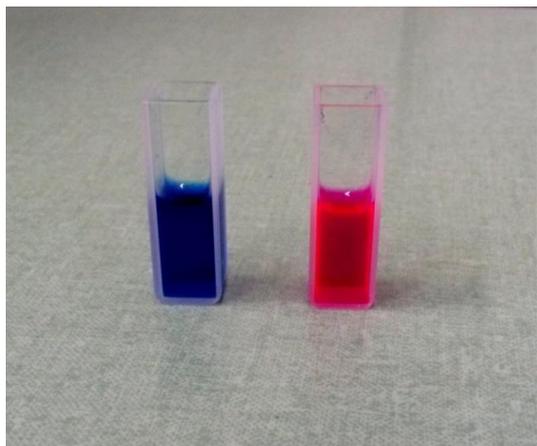


Fig. 1. Reference solution without (red) and with 10^3 ppm of sulfuric acid (blue)

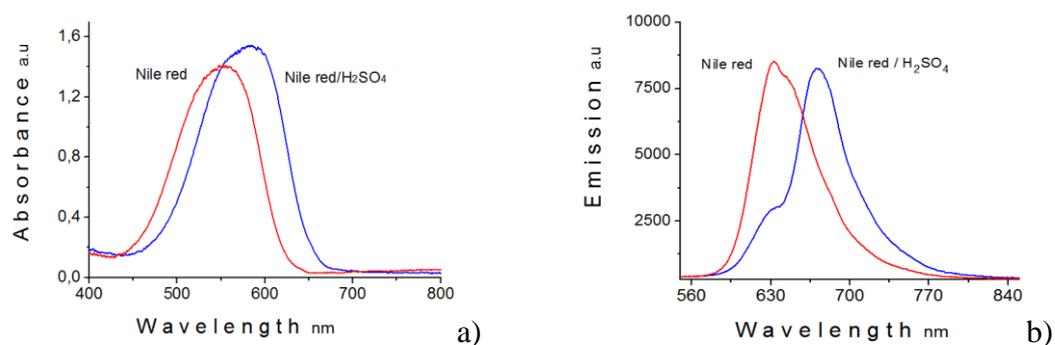


Fig. 2. Spectral shift in the absorption a) and fluorescence b) spectra after doping the reference solution (red curve) with sulfuric acid (blue curve), 10^3 ppm concentration ratio .

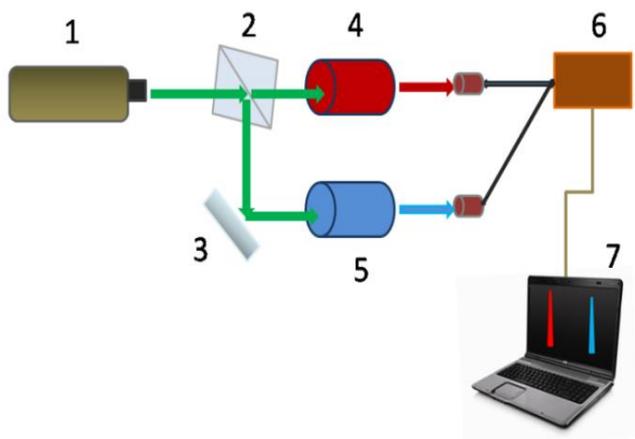


Fig. 3. Experimental set up: Nd:YAG laser (1), beam splitter (2), mirror (3), reference solution (4), sample solution (5), multichannel spectrophotometer (6) and computer (7).

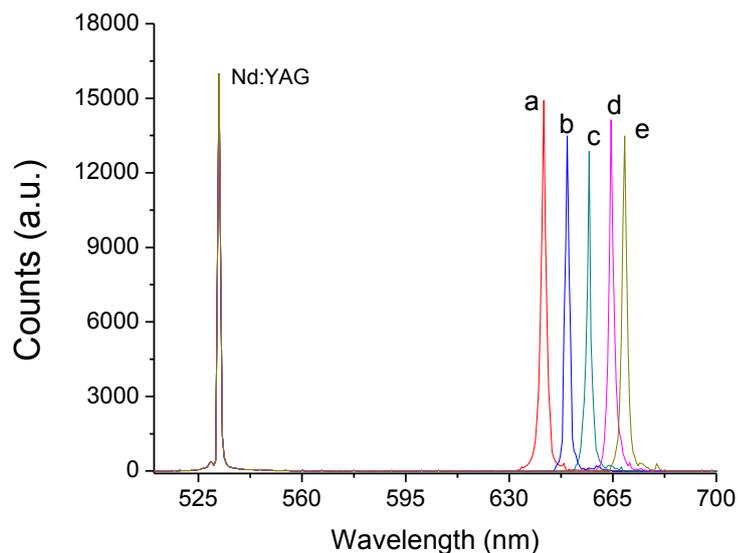


Fig. 4. Emitted laser lines from different sample cuvettes containing the reference solution doped with sulfuric acid in the following concentration ratio: 10ppm (curve a), 50ppm (curve b), 10^2 ppm (curve c), 5×10^2 ppm (curve d) and 10^3 ppm (curve e).

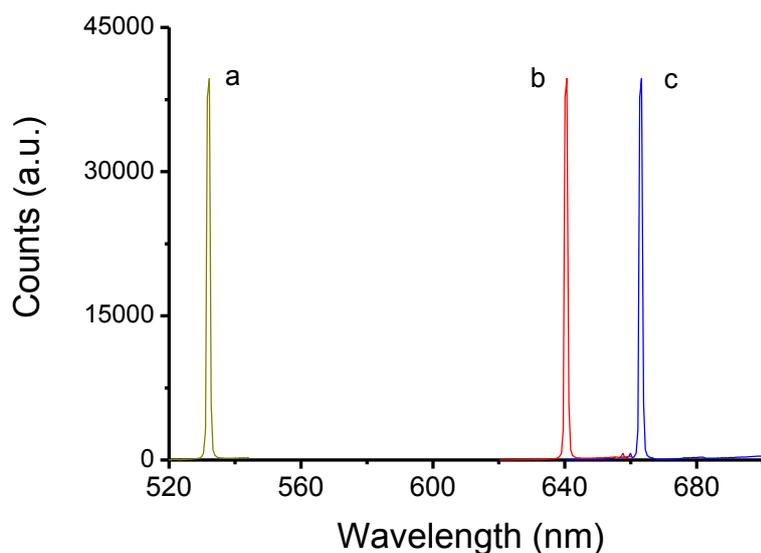


Fig. 5. Shift in the laser emission wavelength. (a) Nd:YAG 2nd harmonic laser line, (b) emission from the cuvette containing the reference solution, (c) emission from a cuvette filled with the reference solvent doped with a 10^3 ppm concentration ratio of nitric acid.

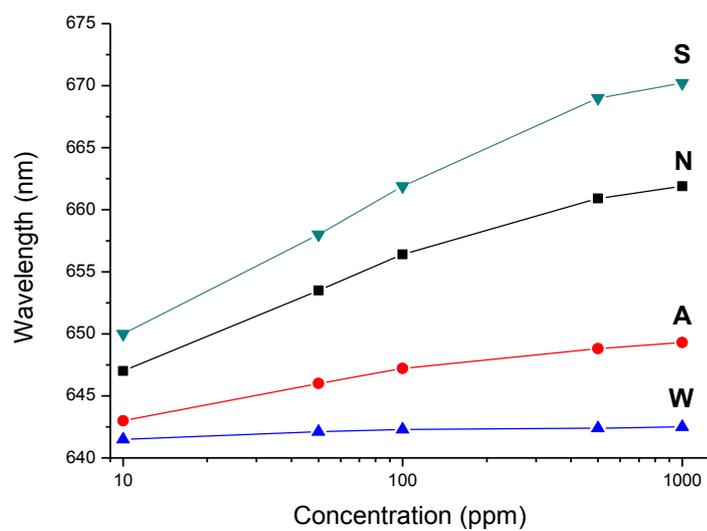


Fig. 6. Laser emitted wavelength as a function of the concentration for the investigated acids: S-sulfuric acid, N-nitric acid, A-acetic acid, W-water.