The use of LIDAR as optical remote sensors in the assessment of air quality near oil refineries and petrochemical sites

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ABSTRACT

Petrochemical and oil refining facilities play an increasingly important role in the industrial context. The corresponding need for monitoring emissions from these facilities as well as in their neighborhood has raised in importance, leading to the present tendency of creating real time data acquisition and analysis systems. The use of LIDAR-based techniques, both for air quality and emissions monitoring purposes is currently being developed for the area of Cubatão, São Paulo, one of the largest petrochemical and industrial sites in Brazil. In a partnership with the University of São Paulo (USP) the Brazilian oil company PETROBRAS has implemented an Environmental Research Center – CEPEMA - located in the industrial site, in which the development of fieldwork will be carried out. The current joint R&D project focuses on the development of a real time acquisition system, together with automated multicomponent chemical analysis. Additionally, fugitive emissions from oil processing and storage sites will be measured, together with the main greenhouse gases (CO_2, CH_4), and aerosols. Our first effort is to assess the potential chemical species coming out of an oil refinery site and to verify which LIDAR technique, DIAL, Raman, fluorescence would be most efficient in detecting and quantifying the specific atmospheric emissions.

Keywords: LIDAR technique, Emissions monitoring, optical sensors, hydrocarbons, Volatile Organic Compounds (VOCs), Differential optical absorption, Raman scattering, resonance scattering, fluorescence, multicomponent analysis techniques.

1. INTRODUCTION

A practical monitoring sensor for industrial pollution emissions should allow for on site, continuous, and unattended operation over a long period of time, preferably achieved by an instrument with a simple and robust design[1]. Optical remote sensing techniques have obvious advantages for gas pollutant detection, e.g., they enable fast operation over large distances, and in hostile environments with large fluctuations of temperature and pressure. Differential optical-absorption spectroscopy provides realistic and reliable multispecies average concentration measurements [2–5]. Correlation spectroscopy is often employed in the petrochemical and gas industry for leak detection and remedy against explosion,[6–9] differential absorption LIDAR enables three-dimensional mapping and total flux measurements,[10–12] while tunable diode laser absorption spectroscopy provides miniaturization and high sensitivity detection.[13] Generally, optical techniques have experienced tremendous development in the past decades, largely stimulated by the information technology and advances in laser technology.

Certain industrial activities are of key influence on the air quality and nowadays have triggered the awareness over long term atmospheric changes as well. Their monitoring became not only a problem of mitigating human health impact due to air pollution but also a matter of climate change. Among the industries with influence on the air quality the petrochemical sector plays one of the most important roles since the economical growth has augmented the diversity of products and storage capacity.

Following this increase in activity the need for monitoring systems in these sites and their neighboring areas have also become tasks of great concern, especially because data acquisition and analysis in practically real time have turned into a sine qua non feature in such systems. Therefore the technique and equipments to be employed have to be capable of detecting in real time the emission of aerosols (particulate matter), air-polluting gases, such as NOx, ozone, sulphur compounds and fugitive gases in industrial and storage sites (namely Volatile Organic Compounds - VOCs). Recent

advances of tunable all solid state laser systems and in the LIDAR technique (Light Detection and Ranging) opened new perspectives in the 3D-analysis of atmospheric pollution dynamics. 3D mappings of concentrations of pollutants have been obtained, allowing a direct access to the physical and chemical dynamics of air pollution [14]. Besides their detection, these species have to be tracked along neighboring areas by the use of dispersion models. Given the extension and quantities involved, meteorological sensors and even satellites have to be employed. Based on the situation described, the use of LIDAR-based technique is proposed in the region of Cubatão, Brazil, one of the largest petrochemical and industrial sites in Brazil, where petrochemical activities exist since about 50 years.

 In a partnership with the University of São Paulo (USP) the Brazilian oil company PETROBRAS has created CEPEMA, an Environmental Research Center located in the industrial site, where the development of the monitoring technique is supposed to take place. It is intended to develop a system capable of real time acquisition and by the use of automated multicomponent chemical analysis techniques, this system should be able to identify fugitive gases from oil processing and storage sites, and also the main greenhouse gases, CO_2 and CH_4; and aerosols. The use of ancillary equipment should be carried out for validation and calibration purposes. The system should operate with a Fourth-Harmonic-Generated Nd:YAG UV laser source (266 nm) and detect the Raman scattered lines of the species mentioned above. Lower harmonics (355 nm, 532 nm and 1064 nm) should be used for the aerosol backscattered signal, and also capable of particle size determination. This paper describes the specific needs for an air monitoring spectrocopy system for in situ operation in a refinery site.

2. LIGHT DETECTION AND RANGING (LIDAR) TECHNIQUE

LIDAR is widely used in laser remote sensing for detection of pollutants in the atmosphere. It is the optical equivalent of radar, except for the use of an optical laser rather than a microwave source. In this technique, short wavelength laser radiation is transmitted through the atmosphere where gas molecules and particles along the beam path cause absorption and scattering of the laser beam. The absorption and/or scattering is then detected. A small fraction of the radiation is backscattered from molecules and aerosols in the direction of the LIDAR system. The detected signal is used to identify and measure chemical concentrations based on either differential absorption or scattering.

Since light travels at a known velocity, the time interval between sending the light out and receiving the signal from back-scattering can be used to obtain ranging information. The direct observation of the backscattered laser beam provides spatially resolved concentration data of a target compound in the atmosphere. Differential absorption measurements in combination with LIDAR make it possible to determine the presence and concentration or air pollutants using selective wavelengths (v_{on}, v_{off}), specific to the compound of interest. There are different scattering processes. These include Raman scattering, resonance scattering and fluorescence.

2.1 Raman

2.1.1 The Raman Effect and Normal Raman Scattering

When light is scattered from a molecule most photons are elastically scattered. The scattered photons have the same energy (frequency) and, therefore, wavelength, as the incident photons. However, a small fraction of light (approximately 1 in 10^7 photons) is scattered at optical frequencies different from, and usually lower than, the frequency of the incident photons. The process leading to this inelastic scatter is the termed the Raman effect. Raman scattering can occur with a change in vibrational, rotational or electronic energy of a molecule. Chemists are concerned primarily with the vibrational Raman effect. We will use the term Raman effect to mean vibrational Raman effect only.

The difference in energy between the incident photon and the Raman scattered photon is equal to the energy of a vibration of the scattering molecule. A plot of intensity of scattered light versus energy difference is a Raman spectrum.

2.1.2 Raman Scattering Process

Raman scattering is one of the processes that occur when optical radiation is scattered from the molecules of the atmosphere. It is most useful because the vibrational Raman scattering provides distinct wavelength shifts for species[15].

The Raman effect arises when a photon is incident on a molecule and interacts with the electric dipole of the molecule. It is a form of electronic (more accurately, vibronic) spectroscopy, although the spectrum contains vibrational frequencies. In classical terms, the interaction can be viewed as a perturbation of the molecule's electric field. In quantum mechanics the scattering is described as an excitation to a virtual state lower in energy than a real electronic transition with nearly

coincident de-excitation and a change in vibrational energy. The scattering event occurs in 10^{-14} seconds or less. The virtual state description of scattering is shown in Figure 1a.
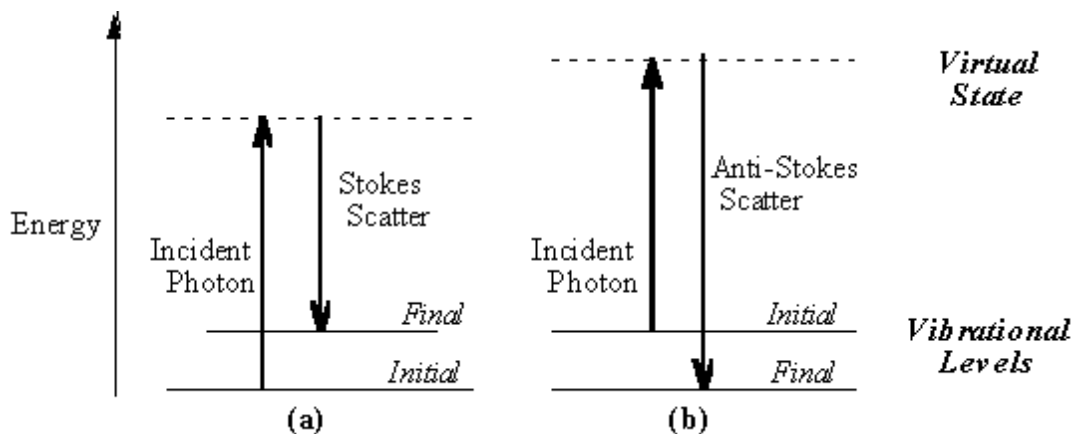

Figure 1. Energy level diagram for Raman scattering; (a) Stokes Raman scattering (b) anti-Stokes Raman scattering.

The energy difference between the incident and scattered photons is represented by the arrows of different lengths in Figure 1a. Numerically, the energy difference between the initial and final vibrational levels, $\bar{v}$, or Raman shift in wave numbers (cm^{-1}), is calculated through equation 1:

$$\bar{v} = \frac{1}{\lambda_{incident}} - \frac{1}{\lambda_{scattered}}$$

(1)

in which $\lambda_{incident}$ and $\lambda_{scattered}$ are the wavelengths (in cm) of the incident and Raman scattered photons, respectively. The vibrational energy is ultimately dissipated as heat. Because of the low intensity of Raman scattering, the heat dissipation does not cause a measurable temperature rise in a material.

At room temperature the thermal population of vibrational excited states is low, although not zero. Therefore, the initial state is the ground state, and the scattered photon will have lower energy (larger wavelength) than the exciting photon. This Stokes shifted scatter is what is usually observed in Raman spectroscopy. Figure 1a depicts Raman Stokes scattering.

A small fraction of the molecules are in vibrationally excited states. Raman scattering from vibrationally excited molecules leaves the molecule in the ground state. The scattered photon appears at higher energy, as shown in Figure 1b. This anti-Stokes-shifted Raman spectrum is always weaker than the Stokes-shifted spectrum, but at room temperature it is strong enough to be useful for vibrational frequencies less than about 1500 cm^{-1}. The Stokes and anti-Stokes spectra contain the same frequency information. The ratio of anti-Stokes to Stokes intensity at any vibrational frequency is a measure of temperature. Anti-Stokes Raman scattering is used for contactless thermometry. The anti-Stokes spectrum is also used when the Stokes spectrum is not directly observable, for example because of poor detector response or spectrograph efficiency.

2.1.3 Resonance-Enhanced Raman Scattering

Raman spectroscopy is conventionally performed with green, red or near-infrared lasers. The wavelengths are below the first electronic transitions of most molecules, as assumed by scattering theory. The situation changes if the wavelength of the exciting laser within the electronic spectrum of a molecule. In that case the intensity of some Raman-active vibrations increases by a factor of 10^2-10^4. This resonance enhancement or resonance Raman effect can be quite useful. Metalloporphyrins, carotenoids and several other classes of biologically important molecules have strongly allowed electronic transitions in the visible. The spectrum of the chromophoric moiety is resonance enhanced and that of the surrounding protein matrix is not. This allows the physical biochemist to probe the chromophoric site (often the active site) without spectral interference from the surrounding protein. Resonance Raman spectroscopy is also a major probe of

the chemistry of fullerenes, polydiacetylenes and other "exotic" molecules which strongly absorb in the visible. Although many more molecules absorb in the ultraviolet, the high cost of lasers and optics for this spectral region have limited UV resonance Raman spectroscopy to a small number of specialists.

The vibrations whose Raman bands are resonance enhanced fall into two or three general classes. The most common case is Franck-Condon enhancement, in which a component of the normal coordinate of the vibration is in a direction in which the molecule expands during an electronic excitation. The more the molecule expands along this axis when it absorbs light, the larger the enhancement factor. The easily visualized ring breathing (in-plane expansion) modes of porphyrins fall into this class. Vibrations which couple two electronic excited states are also resonance enhanced. This mechanism is called vibronic enhancement. In both cases enhancement factors roughly follow the intensities of the absorption spectrum. The theory of resonance enhancement is beyond the scope of this tutorial. The interested reader is referred to specific reviews [16].

Resonance enhancement does not begin at a sharply defined wavelength. In fact, enhancement of 5X-10X is commonly observed if the exciting laser is even within a few hundred wave numbers below the electronic transition of a molecule. This pre-resonance enhancement can be experimentally useful.

2.2 Fluorescence

Fluorescence is a luminescence that is mostly found as an optical phenomenon in cold bodies, in which the molecular absorption of a photon triggers the emission of another photon with a longer wavelength. The energy difference between the absorbed and emitted photons ends up as molecular vibrations or heat. Usually the absorbed photon is in the ultraviolet range, and the emitted light is in the visible range, but this depends on the absorbance curve and Stokes shift of the particular fluorophore.

2.3 Differential absorption LIDAR (DIAL

Differential absorption LIDAR (DIAL) operating in the infrared have been used to monitor chemical emissions from chemical plants and refineries. Shell Global Systems used a DIAL system to examine fugitive emissions from floating roof storage tanks. Their findings indicated that the flux varied by the position of the roof in the tank, with the highest flux occurring when the tank was full and the roof was high relative to the walls of the tank. When the tank was half full, a recirculation air pattern formed within the tank that tended to keep the hydrocarbon escape rate down. The conclusions were that the model being used to predict fugitive emission flux from tank farms might underestimate the actual amount escaping [17]. In another project, the DIAL system was used to provide an overall look at numerous tank facilities located at a port. The DIAL was able to image emissions from the facilities and provide for overall flux estimates. The study identified a small number of tanks that were responsible for a majority of the emissions.

In 2006, the Alberta Research Council published the results of a study to demonstrate the applicability of remote sensing technologies to ascertain hydrocarbon emissions at a refinery. The effort involved the use of an infrared imaging camera and a LIDAR DIAL system. The imaging camera successfully located fugitive emissions at the facility and the refinery has since purchased one. The DIAL system was used to estimate the rate of loss of methane, aliphatic hydrocarbons with two or more carbons (C2+), and benzene. The study found that approximately 1,240 kg of C2+ hydrocarbons, 300 kg of methane, and 5 kg of benzene were escaping from the refinery every hour. Emissions from storage tanks accounted for over 50 percent of the total and the coker area and cooling towers were the main sources of emissions in the production area. The report also showed that standard emission-estimating equations greatly understated actual emissions. Chambers et al. (2006)[18] report on the utility of using DIAL for measuring fugitive emissions from natural gas plants and compare the actual measurements with emission factor estimates. For the five gas plants surveyed, methane emissions ranged from 100 to 146 kg/hr, and hydrocarbons with two or more carbon atoms (C2+) ranged from 38 to 342 kg/hr. Condensate storage tanks and compressors were significant sources for the emissions, with pilot flares accounting for 10 to 15 percent of total methane emissions. Actual emissions were four to eight times higher than values calculated using emission factor estimates.

Frisch (2003) [19] summarizes the results of DIAL surveys conducted at Swedish refineries during the 1980s and 1990s and describes a protocol for conducting a DIAL survey. The first DIAL measurements were conducted at one Swedish refinery in 1988 and 1989. They showed that the refinery was losing approximately 14,000 tons of hydrocarbons per year. The measurements also showed that the equations for estimating standard fugitive emissions were undercounting the emission losses by about 20 times. During the 1990s, DIAL surveys were used by the refineries to identify areas that had excessive releases due to design problems, and measures were taken to correct them.

3. LIDAR SYSTEM REQUIREMENTS

3.1 Oil Refinery Gas Inventory

The air environment near petrochemical and oil refinery sites can contain hydrocarbon compounds which have rotational vibrational transitions in the mid-IR wavelength region. Of the most popular carbon-containing compounds present in such an environment we highlight the class of alkanes or paraffins, such as Methane CH_4, Ethane C_2H_6, and other light alkanes, the class of alkenes, such as Ethene or ethylene C_2H_4 and Propene or propylene C_3H_6, followed by the Alkynes with Acetylene C_2H_2, Aromatics Benzene C_6H_6 and Toluene C_7H_8 and finally the Aldehydes, Formalaldeyde *HCHO* and Acetaldehyde *CH_3CHO*. Its is estimated that globally around 17.5 Tg per year of Nonmethane Volatile Organic Compounds is emitted to the atmosphere by the fuel production/distribution industry, from that about 30% is due to the Oil refining branch.[20]

3.2 Remote Sensing of VOCs in the atmosphere

In general remote sensing of hydrocarbon gases are mainly detected by fluorescence as a first guess. However, some issues with collision quenching and the broadband nature of the emission concomitant with high aeroticulate background might impair a fluorescence-based system performance, the next step would accurately take measurements of the Raman scattering on this HC compounds and despite some extraordinary small cross section associated with this type of interaction it still possesses several desirable characteristics which make it suitable, such as:[15]

• The spectral shift of the Raman scattered radiation is specific to each molecule.
• The intensity of a given Raman signal is directly proportional to the density of the appropriate scattering molecule and independent of the others.
• The narrow spectral width and shift of the Raman signal is good to both eliminate solar background and elastically scattered laser signal.
• Good spatial and temporal resolution is possible, since a backscattering process is involved.
• Only a single, fixed-frequency laser is required greatly enhancing the multiplexing capabilities.

In Figure 2 it can see one LIDAR Design to perform at a refinery site.

OIL REFINERY LIDAR SYSTEM

LASER @ 266 nm (30 mJ)
355 nm (150 mJ)
532 nm (300 mJ)
1064 nm (1 J)
Rep Rate 10 Hz
Pulse Duration < 10 ns

Scanning Telescope

Elastic channels 266,355...
Raman channels 266,355...
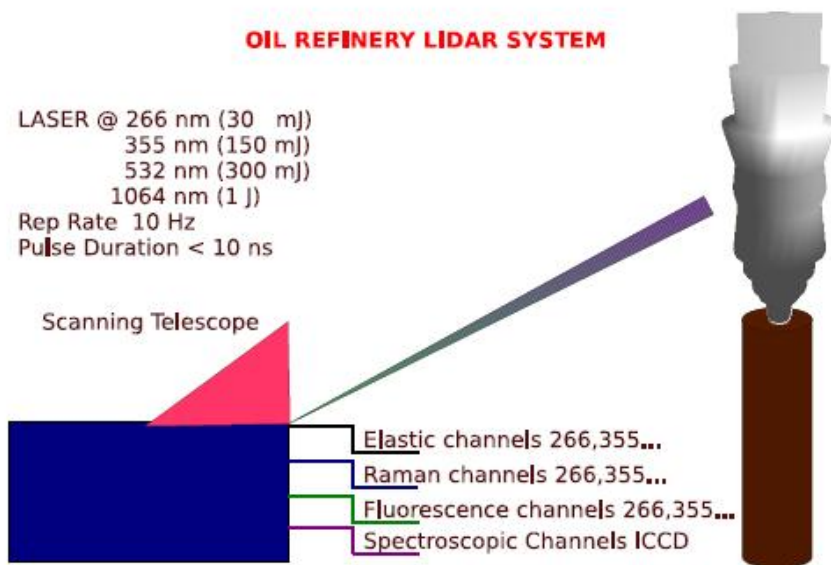Fluorescence channels 266,355...
Spectroscopic Channels ICCD

Figure 2. Lidar Design to perform at a refinery site.

However one additional problem might arise when a trace constituent of a trace gas could be masked by the O and S branch Raman signal of a major compound such as N_2 and O_2. If that becomes a major hindrance one could get grip of a

DIAL (differential and absorption Lidar) system with an additional feature of being multiwavelength as pointed out by Weibring *et al.*[21,22]. The multi-wavelength lidar concept together with the DIAL capabilities showed some results for 4 different HC compounds and dealt with the spectral overlap of the different laser returns, however they [15] had to deal with a lot of multivariate techniques and robust algorithms to extract the different spectral signatures of the gas mixings employed.

3.3 The detection of trace gas species by DIAL

3.3.1 DIAL measurements in the UV (200 to 450 nm)

Aromatic Hydrocarbons

Benzene (C_6H_6) and toluene (C_7H_8) can be measured by a UV DIAL in the 240 to 260 and the 250 to 270nm wavelength regions, respectively, where they show narrow absorption features. The wavelength pairs which minimize the interference of ozone, SO2, NO2, and other hydrocarbons are the 266.9nm ON-line and the 266.1nm OFF-line wavelengths for toluene, and the 252.9nm ON-line and the 252.0nm OFF-line wavelengths for benzene. The existing experimental configurations include Nd:YAG pumped dye lasers with frequency doubling [23].

3.2.2 DIAL measurements in the near-IR (1 to 5 µm)

Volatile Organic Compounds (VOCs)

It is now recognized that methane contributes strongly to the greenhouse effect, and therefore there is a need to identify the sources and the transport processes for this gas. Methane has suitable absorption bands for DIAL in the near-IR (1.5 to 4 mm) spectral region. With a $Co:MgF_2$ laser, the absorption of methane at the on-line wavelength of 1.6713mm was demonstrated, but no attempt was made towards retrieval of CH4 concentrations [24]. Airborne DIAL measurements of methane have been reported [25] where the DIAL wavelength pair used is 3.313nm (ON-line) and 3.309nm (OFF-line). Only integrated vertical profiles using the surface return were evaluated, but the system was able to detect methane plume downwind of a cattle feed lot. There have also been obtained range resolved profiles from a ground-based station [26,27].

3.4 Lidar system design

In order to achieve maximum performance not only in directivity but also in multiplexing we elaborated a system in which many channels should be retrieved at the same time, namely:

• Four elastic channels at 266 nm, 355 nm, 532 nm and 1064 nm from a Nd:YAG laser source;
• At least 4 Raman channels produced in a specific gas;
• At least 2 fluorescence channels for gas identification;
• A Spectroscopic Channel based on a Intensified Coupled Charged Camera for species identification; In principle a DIAL channel is not discarded but this should be added only after the first operational system is available. This system should be deployed at CEPEMA, Centro de Pesquisa do Meio Ambiente, Cubatão, in a neighboring region to a PETROBRAS refinery station. This system should be built not only to monitor the air quality but also to diagnose the refining process performance by inspecting the particle size distribution coming out of the chimneys. The telescope employed should be able to scan from 0° to 90° azimuthally and thus be capable of full spatial coverage.
The dates will be analyzed by Statistical technical to interpreted results.

4. CONCLUSION

Lidar technology has matured over the last decade to an extent that many applications are becoming routine. Meteorological parameters like the wind and temperature, as well as trace gas concentrations, can be measured in short time periods with high spatial resolution in three dimensions, often at large distances. Plumes containing air pollutants like hydrocarbons , VOCs and others can be measured by lidar at strategic sites.

The current joint R&D project focuses on the development of real time acquisition system, together with automated multicomponent chemical analysis. Additionally fugitive emissions from oil processing and storage sites will be measured , together with the main greenhouse gases (CO_2, CH_4) and aerosols. Our first effort is to assess the potential chemical species coming out of an oil refinery site and to verify which LIDAR technique, DIAL, Raman, Fluorescence would be most efficient in detecting and quantifying the particular gas.

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