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TITLE LASER DETECTION OF TOXIC MOLECULES AND CARCINOGENS

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Laser detection of toxic molecules and carcinogens

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Abstract

Fluorescence from large organic molecules is broadband and relatively structureless. Thus, the detection of hazardous molecules in various environments using laser-induced fluorescence is difficult because of obscuration from other fluorescing sources (paints, other impurities, etc.). This paper discusses laser-optical techniques that can be used to avoid this problem. The techniques of Synchronous Detection of Laser-Induced Fluorescence (SDLIF), and Resonant Raman Scattering will be discussed.

I. Introduction

The remote and point detection of large organic molecules in the environment is becoming an increasingly important problem. The following is a partial listing of the types of situations encountered:

1. Carcinogenic aromatic effluents from coal conversion plants;
2. Chemical warfare agents in the battlefield;
3. Toxic chemicals leaching into the water supply.

Several uv-visible techniques have been proposed to solve these problems. Among these are the following:

(a) Laser-induced fluorescence (LIF),¹

(b) Raman scattering:

1. spontaneous Raman,²
2. inverse Raman,³
3. CARS.⁴

(c) uv-visible DIAL.⁵

II. Raman scattering techniques

Ideally one would like to have an unequivocal identification of the molecule of interest. This is the particular advantage of the Raman scattering techniques since this inelastic photon scattering process results in a spectrum of photon energies shifted from the excitation energy by an amount determined by the Raman active vibrational modes of the molecule. For example, Fig. 1 shows the spectrum of the organophosphate DMMP. With only 3 of the more than 14 Raman lines identified, it is clear that this spectrum is an excellent fingerprint of the molecule in question.

All of the Raman techniques have a problem with sensitivity. This stems from the very low cross section for Raman scattering (on the order of 10^{-30} cm²). The technique of resonance Raman scattering² can be used to increase this cross section by as much as a factor of 10^6 . In some cases, the resulting resonance Raman signals compete with the molecular fluorescence. An example of this is shown in Fig. 2 where the near resonant spontaneous Raman scattering from the CH₃ symmetric stretch of OSP is stronger than the fluorescence, both of which are excited by a 308 nm laser. The OSP is, however, a very weakly fluorescing molecule with a quantum efficiency of less than 0.01%.

Figure 3 shows a schematic of the fluorescence and Raman processes. The absorption of a photon at the frequency ν_0 leaves the molecule in an excited electronic state from which it either fluoresces or is nonradiatively quenched. The result is a broad emission spectrum (100 nm or more FWHM) which is relatively structureless.

On the other hand, the laser Raman scattering process results in the simultaneous absorption of a photon at ν_0 and emission (narrowband) of a photon shifted to lower energy from ν_0 by the Raman active vibrational modes. It is thus immune to quenching processes. The resonance Raman scattering process is operative when the virtual state is close to the real excited electronic state.

III. The synchronous detection of laser-induced fluorescence

For molecules which fluoresce strongly in the visible and near uv, such as the polynuclear aromatic hydrocarbons, laser-induced fluorescence will be a more sensitive technique than the resonant Raman scattering processes. The principal drawback with LIF is that the fluorescence emission spectra of the large organic molecules are broad and, in complex mixtures such as synfuel plant effluents, they tend to overlap one another, making identification impossible.

The technique of synchronous detection of laser-induced fluorescence (SDLIF) is a process whereby the emission band is artificially narrowed. Figure 4 shows an example of how this is done for perylene.⁶ For most large organic molecules, the absorption spectrum (the excitation spectrum is related to this) and the fluorescence spectrum overlap as shown. The SDLIF technique measures the fluorescence only in this region of overlap and hence there is an artificial narrowing of up to a factor of 10 in the bandwidth. This is accomplished by synchronously scanning the excitation wavelength (a tunable dye laser) and the fluorescence observation wavelength (a spectrometer) at a fixed wavelength separation (usually 23 nm). On either side of the overlap region no fluorescence is observed.

For complex mixtures, the narrowing of the fluorescence spectrum of each molecule allows for the resolution of the mixture into its components. An example of this is shown in Fig. 5. The ordinary LIF spectrum of a mixture of anthracene and four of its derivatives dissolved in hexane is shown. The SDLIF spectrum of one of the components (9, 10 diphenyl anthracene) allows its contribution to the total to be extracted.

IV. Conclusions

As discussed briefly in this report, resonance Raman scattering processes and laser induced fluorescence (SDLIF) are possible techniques for detecting large organic molecules in the environment. Because of sensitivity problems, it is doubtful that any of the Raman techniques will be useful for remote sensing of trace quantities in the atmosphere. For strongly fluorescing molecules (fluorescence quantum yields >1%) the SDLIF technique will prove useful for remote sensing of trace quantities (ppm) of these molecules in the vicinity of pollution sources such as synfuel plants.

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Figure 1. Raman Scattering in Dimethyl Methyl Phosphonate (DMMP).

Figure 2. Label-Induced Fluorescence in O-ethyl, S-ethyl, Methyl Phosphonothiolate (OSP).

FLUORESCENCE vs RAMAN SCATTERING

a) LASER INDUCED FLUORESCENCE

b) LASER RAMAN SCATTERING

Figure 3. Schematic representation of fluorescence and Raman scattering.

Figure 4. The synchronous fluorescence spectrum of perylene.

Figure 5. LIF and SPLIF spectra of a mixture of anthracene derivatives.