

# A LIF monitor for potato-sprout inhibitors

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**Abstract.** It is shown that pulsed laser-induced fluorescence in combination with pulsed supersonic expansion is an appropriate technique for sensitive and selective analysis of gas mixtures containing different small polycyclic hydrocarbons that may play an important role in the sprouting of stored potato tubers. The vibronic excitation spectra of 1,4- and 1,6-dimethylnaphthalene are presented.

## 1. Introduction

A more detailed understanding of the sprouting of stored seed-potato tubers requires a sensitive technique to detect volatile organic compounds, present in the air surrounding the potatoes [1]. In addition, monitoring of volatiles may also reveal the presence of disease in stored potatoes [2,3]. Small polycyclic hydrocarbons as for example the 1,4- and 1,6-isomers of dimethylnaphthalene (DMN) [4] and the 1,4,6 isomer of trimethylnaphthalene [5] have been shown to play an important role in sprouting; these compounds cannot only be added to potatoes to prevent sprouting [6], some of them are actually produced by the potatoes themselves [7]. Because of possible carcinogenic properties of some of these compounds, a detailed analysis of storage conditions is desirable from the point of view of human health. In [8] different monitor techniques are compared. Current research on sprout inhibiting volatiles requires a detection technique with a selectivity high enough to distinguish between different isomers of aromatic molecules like DMN.

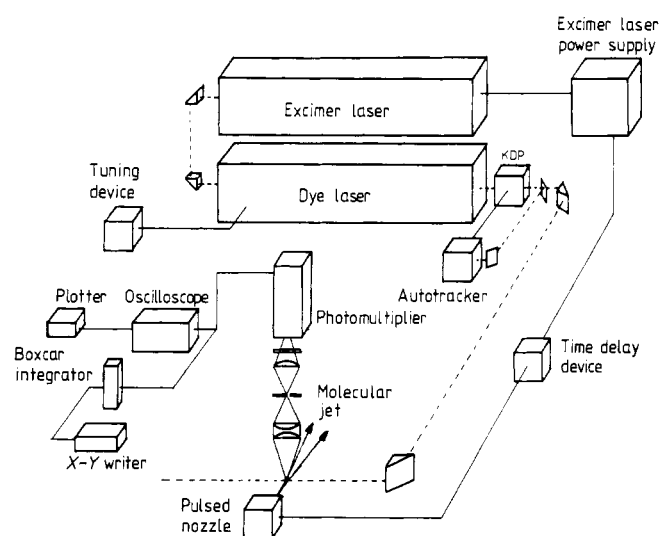
Laser-induced fluorescence (LIF) is widely recognised as a very sensitive and selective technique for trace analysis. Room-temperature LIF spectra, however, do not yield sufficient spectral resolution to distinguish between vibronic spectra of different isomers of a small polycyclic hydrocarbon. Cooling of the rotational degrees of freedom of the molecules can reduce the spectra congestion to such an extent [9] that these vibronic spectra can be unravelled. This cooling can be achieved by preparing the sample in a cryogenic matrix [10] or by expanding the sample in a supersonic

molecular jet [11].

We have employed pulsed LIF detection in combination with pulsed supersonic expansion to obtain a near real-time monitor set-up which will need no further sample preparation. Because of their relatively potent sprout-inhibiting properties [6] the 1,4 DMN and 1,6 DMN isomers were selected to demonstrate the vigour of the method presented.

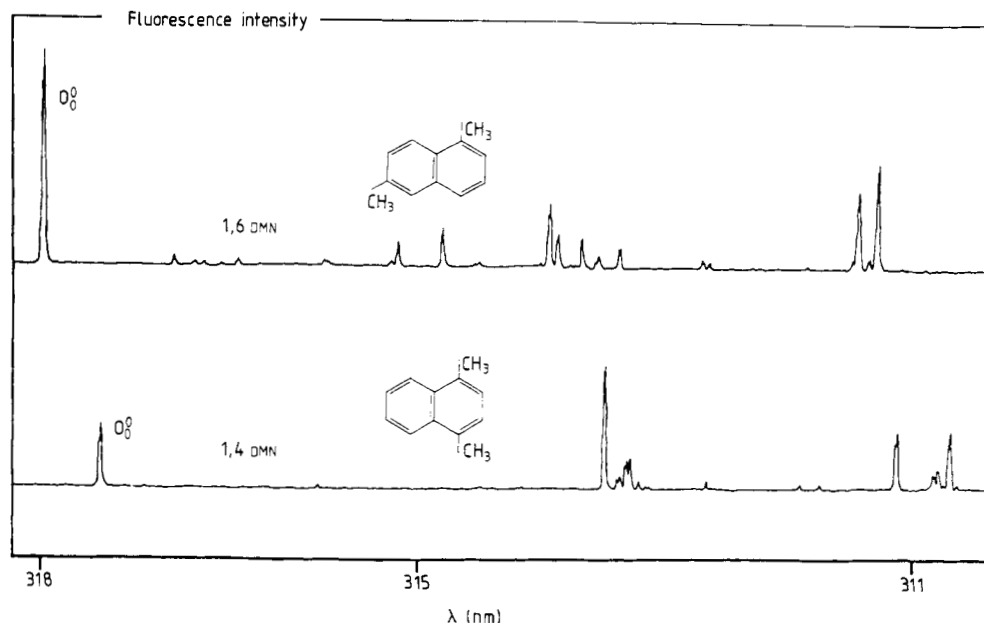
## 2. Experimental details

A schematic diagram of the experimental apparatus is shown in figure 1. Radiation from a Lambda Physik



**Figure 1.** Schematic diagram of the experimental set-up. The optical path is represented by a broken line.

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**Figure 2.** Vibronic 'fingerprint' excitation spectra of 1,4 and 1,6 DMN around their band origins. The total fluorescence intensity is plotted as a function of the wavelength of the incident radiation.

FL 2002 dye laser, pumped by a Lambda Physik EMG 201 excimer laser, was frequency doubled in a KDP crystal. The angle of the KDP crystal with respect to the laser beam was actively corrected for maximum conversion efficiency during a mechanical frequency scan of the dye laser. In this way, we obtained tunable radiation around 315 nm, with a band width of  $0.4 \text{ cm}^{-1}$  and an energy of 1 mJ in a 10 ns pulse. The molecular jet was produced by expanding room-temperature DMN vapour seeded in 1 bar of helium through a pulsed nozzle into a vacuum chamber, pumped by a  $270 \text{ m}^3 \text{ h}^{-1}$  Roots pump. The average background pressure in this chamber was  $10^{-4}$  mbar. The pulsed valve, a modified version of a Bosch fuel-injection valve with a nozzle diameter of 1 mm, provided  $300 \mu\text{s}$  full width at half-maximum gas pulses. The laser beam crossed the molecular jet perpendicularly, 15 mm downstream from the nozzle opening. The interaction area was imaged on the cathode of an EMI 9863 photomultiplier tube. Spatial filtering was applied to reduce any stray light background. The current from the photomultiplier was simultaneously fed into a LeCroy 9400 digital oscilloscope and into a SRS 250 boxcar averager, to allow time-resolved and continuous averaging measurements, respectively. The repetition rate of the experiment was 10 Hz. With this experimental set-up, frequency scans over  $1500 \text{ cm}^{-1}$  could be obtained within 15 min.

### 3. Results and discussion

In order to obtain an estimate for the frequencies of the pure electronic ( $O_0^0$ ) transitions of the DMN isomers, we have extrapolated the red shift of the band origin

caused by the addition of a methyl group to the naphthalene frame. The frequencies of the band origins of naphthalene [9],  $\alpha$ - and  $\beta$ -monomethylnaphthalene [12] are  $32019$ ,  $31773$  and  $31705 \text{ cm}^{-1}$  respectively. We therefore estimated the band origins of the DMN isomers to lie around  $31480 \text{ cm}^{-1}$ , corresponding to 318 nm.

Figure 2 shows the spectra of 1,4 DMN and 1,6 DMN which result from the excitation from the electronic ground state to a few low energetic vibrational states in the electronically excited state. The measured frequencies of the pure electronic transitions of 1,4 DMN and 1,6 DMN,  $31491.2(5) \text{ cm}^{-1}$  and  $31446.0(5) \text{ cm}^{-1}$  respectively, clearly justify the extrapolation mentioned above. No attempt has been made to assign the vibronic transitions. As can be seen in figure 2, the two spectra clearly differ, not only in the absolute frequencies of the lines, but also with respect to their overall structures. This is of great importance for spectroscopic analysis of mixtures of DMN-like molecules expected in the air surrounding stored potatoes. In fact, the two spectra exhibit such different features that they can be regarded as 'fingerprints' for the two isomers. Furthermore, the selectivity is increased by the fact that the fluorescence lifetime of the excited electronic state is directly monitored with the oscilloscope, which produces additional information to discriminate between different molecules present in a mixture. Absolute values of the radiative lifetimes of the DMN isomers under investigation have not been determined so far, because the transit time through the detection volume is short compared with the radiative lifetimes.

The concentrations of DMN and related hydrocarbons in a realistic potato environment are expected

to be less than 1 PPM. An extrapolation of data for the vapour pressures of 1,8, 2,3 and 2,6 DMN taken from [13] yields a value of  $2 \times 10^{-3}$  mbar for the saturated vapour pressure of 1,6 DMN at room temperature. Our signal-to-noise ratio on the strong lines in the spectra exceeded 1000. Because we used a stagnation pressure of 1 bar, this means that a partial pressure of  $2 \times 10^{-6}/1 \times 10^3$ , i.e. 2 PPB is detectable.

#### 4. Conclusion

This result clearly shows that the method discussed in this paper yields both high sensitivity and selectivity, which will make it a valuable tool for the detection of DMN isomers and related hydrocarbons in a realistic potato environment. Work is underway to apply this technique to samples taken from such an atmosphere.

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