Title
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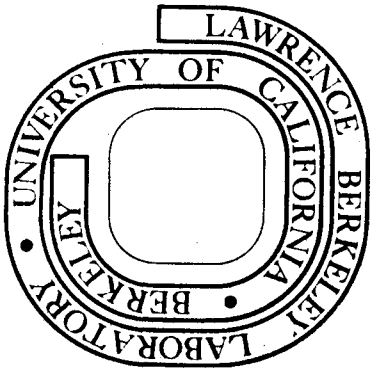

DISCLAIMER

MODULATED FLUORESCENCE AS A POSSIBLE IN SITU MONITOR FOR NO_2*

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Recently, Tucker et. al.[1] have reported the successful operation of an ambient NO_2 monitor based on laser excited broad-band molecular fluorescence. In order to avoid fluorescence from aerosols, however, it was necessary to filter the incoming air stream. This filtering procedure could change the measured NO_2 concentration either because of adsorption directly on the filter or on particulates trapped by the filter. We would like to suggest an alternate procedure which has the virtue that it requires no processing of the air sample and can monitor NO_2 and particulates simultaneously.

We have been investigating the excitation spectrum of the ν_2 fluorescence mode of NO_2 and have found several narrow spectral regions in which this re-emission mode is sharply enhanced.[2] Following the work of Tucker et. al.[1], we have looked at broad-band fluorescence from 1mm of NO_2 in 1 atmosphere of N_2 as we tuned a laser over the sharp excitation lines which were found in our earlier study. We find substantial modulation of the broad-band fluorescence. This modulation occurs when the laser is tuned over a very narrow spectral region and is characteristic of NO_2. Since particulate fluorescence is expected to change quite slowly

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with laser frequency, we feel that we have found the basis for an ideal way to separate NO_2 fluorescence from particulate fluorescence.

The laser used in this experiment was a nitrogen-laser-pumped dye laser using a 5×10^{-3} molar solution of 7D4MC in ethanol. Its bandwidth was narrowed by using a beam expanding telescope and a 1 cm^{-1} air spaced etalon in series with a grating which constituted one end mirror of the laser cavity. The etalon and the grating were enclosed in a vacuum tight chamber so that fine tuning could be accomplished by varying the pressure within the chamber. The laser had a bandwidth of .04cm^{-1} and an average power of .15mW. The laser beam was directed along the axis of a quartz cell 5 cm in diameter and 60 cm long which had Suprasil entrance and exit windows. The exit window was set at Brewster's angle to prevent the beam from being reflected back through the cell. The beam, after passing through the cell, was dumped in a beam absorber similar to that described in Tucker et. al.[1] The cell was filled with 1mm of NO_2 and 1 atm of N_2. Fluorescence from this sample was observed at right angles to the beam direction by an RCA 7265 photomultiplier located at the mid-point of the quartz cell. A liquid filter of $Na_2Cr_2O_7$ in distilled water (304g/ℓ) was placed in front of the photomultiplier to eliminate background at the laser frequency. Several baffles were inserted in the cell to prevent the detector from directly viewing the windows of the cell.

We have observed the broad-band fluorescence as we tuned the laser over the Q(15), Q(13) and Q(11) rotational lines of $X \rightarrow {}^2B_1$ transition in NO_2 located near 4545Å. Figure 1a shows the behavior of this fluorescence as a function of laser frequency and compares it to the ν_2 excitation spectrum of 1mm of NO_2 in vacuum shown in Fig. 1b. The figure clearly shows modulation of the broad-band fluorescence as the laser is tuned over

these sharp transitions. A background check with the cell filled with 1 atmosphere of N_2 gave a signal $< 1\%$ of the signal shown in Fig. 1a. The modulation which we have observed is large enough to allow one to use it easily to separate aerosol fluorescence from that of NO_2 in ambient air provided that the signal from aerosols is comparable to that from NO_2 and there is little additional background in the measuring apparatus. Gelbwachs and Birnbaum[3] have shown that, at least for some spectral regions, the aerosol fluorescence and that of NO_2 are comparable in intensity, and Tucker et. al.[1] have operated an apparatus which has very low background fluorescence. Our measurements therefore show that the use of a tunable source may allow measurement of both aerosols and NO_2 simultaneously at ambient levels with no processing of the polluted air.

We would like to acknowledge Owen Chamberlain for helpful discussions throughout the course of this work.

REFERENCES

1. A. W. Tucker, M. Birnbaum and C. L. Fincher, Appl. Opt. 14, 1418 (1975).

2. P. Robrish and H. Rosen, Chem. Phys. Letts. 37, 156 (1976).

3. Jerry Gelbwachs and Milton Birnbaum, Appl. Opt. 12, 2442 (1973).

FIGURE CAPTION

Figure 1a Intensity of broad-band fluorescence of 1mm of NO_2 in 1 atm. of N_2 as a function of laser frequency.

Figure 1b Intensity of ν_2 fluorescence for 1mm of NO_2 as a function of laser frequency.

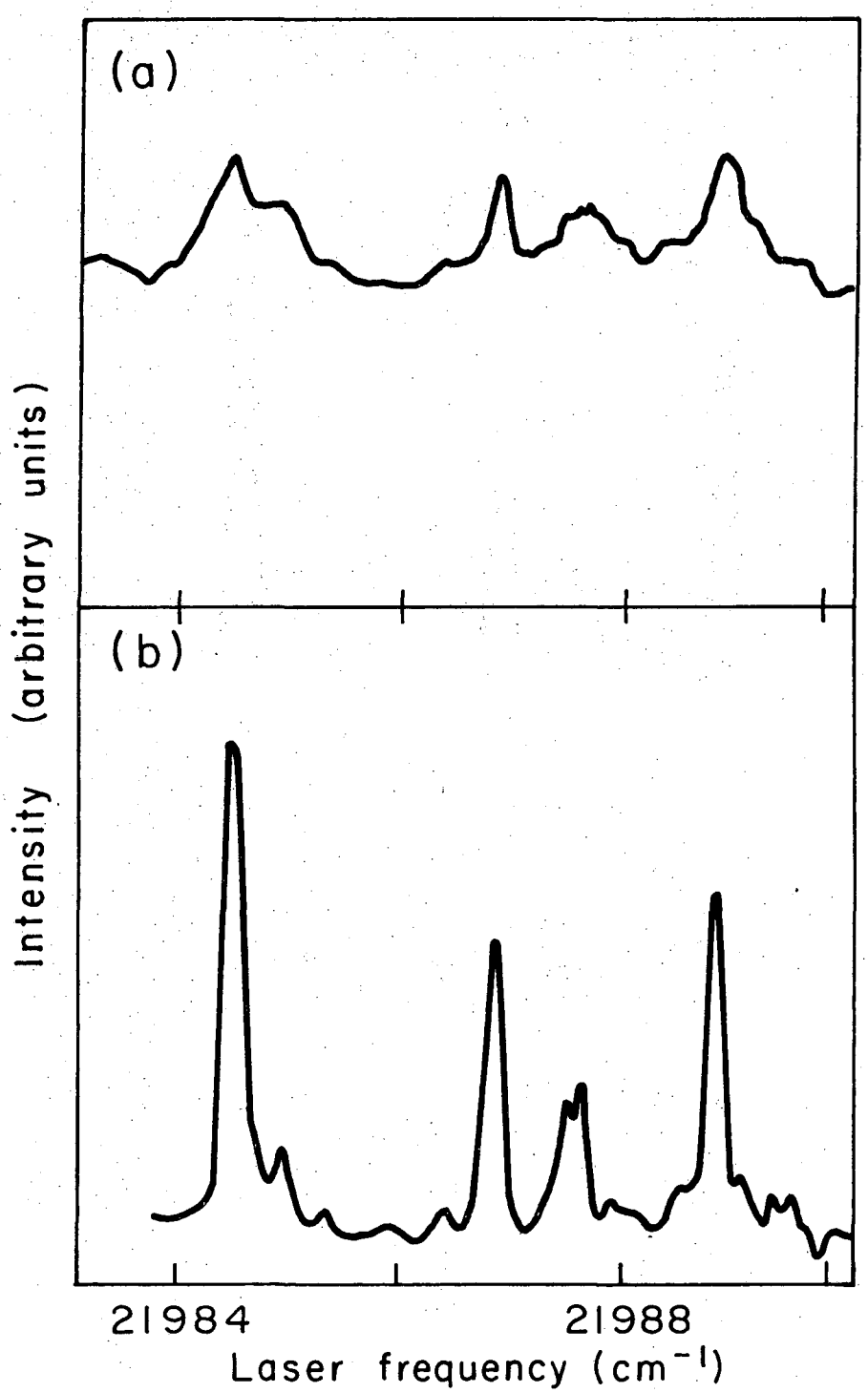
(a)
(b)
Intensity (arbitrary units)
21984
21988
Laser frequency (cm⁻¹)
XBL7511-9531

Fig. 1 a + b

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