

## THE LASER INDUCED TIME-RESOLVED FLUORESCENCE STUDY OF THE HNO MOLECULE

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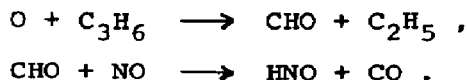
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## Introduction

The electronic spectra of the HNO molecule have been observed under a variety of experimental conditions.<sup>1-3</sup> The first transition  $A^1A'' \rightarrow X^1A'$  at  $\lambda > 600$  nm is seen in the absorption spectrum<sup>1</sup> resulting from the flash photolysis of  $CH_3ONO/H_2$  and in the chemiluminescent study of  $H + NO^2$  or HNO sensitized by excited  $O_2(^1\Delta)$  species.<sup>3</sup> The theoretical calculation of the oscillator strength indicates the natural lifetime  $\sim 7 \mu\text{sec}$ <sup>4</sup> but no experimental measurement has been reported. In this paper we report the fluorescence lifetimes of some vibrational levels of the HNO molecule in the excited  $^1A''$  state.

## Experimental

The laser induced fluorescence study of HNO was performed in a discharge flow system. Atomic oxygen was generated either by subjecting oxygen diluted in argon to a microwave discharge or by titrating active nitrogen with NO. The HNO molecule was then produced by the addition of NO to the reaction product of O atoms with  $C_3H_6$ ,



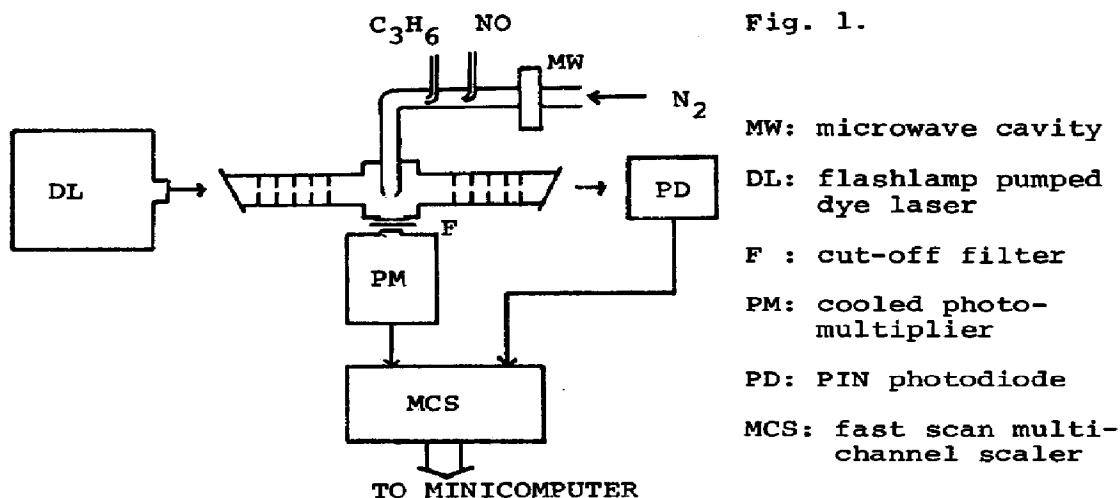
Fluorescence cell was located 80 cm downstream from the discharge region and 50 cm from mixing jets. Pulsed radiation from a flash pumped dye laser (FWHM 0.6  $\mu\text{sec}$ ,  $\sim 1 \text{ \AA}$ , 1mJ/pulse) entered the cell through the horizontal arm with a chain of baffles. Fluorescence was detected perpendicular to the beam by minicomputer onlined photon counting system with fast scan multichannel scaler. (Fig. 1)

## Results and Discussion

The excitation spectra of HNO molecule are shown in Fig. 2. The two vibrational structures at  $\sim 630$  nm and  $\sim 645$  nm can be assigned to the (020)-(000) and (011)-(000) vibrational bands, respectively. The signals of 672 nm and 669 nm correspond to the R-heads at  $K' = 6$  and 7 of the (010)-(000) band, respectively.

The reciprocal values of the observed lifetimes at the two bands are plotted against the total pressure from 0.01 to 1 Torr. (Fig.3) The fluorescence lifetimes extrapolated to zero pressure were found to be 5.0  $\mu\text{sec}$  for the (020) band and 1.8  $\mu\text{sec}$  for the (011) band. From the theoretical calculation of the oscillator strength of  $A^1A''-X^1A'$  transition, the natural lifetime is estimated to be  $\sim 7$   $\mu\text{sec}$ .<sup>4</sup> This long lifetime is attributed to the forbidden character of the  $n\pi^*$  transition. The quenching study of HNO chemiluminescence also suggests the long lifetime of the  $^1A''$  state.<sup>5</sup>

The lifetime of the (011) band is shorter than that of the (020) band. This may be attributed to the mixing of  $X^1A'$  and  $A^1A''$  states through  $\nu_3$  bending mode. The effect of K sublevels on the lifetime of HNO fluorescence is now being studied.



Schematic Diagram of Apparatus

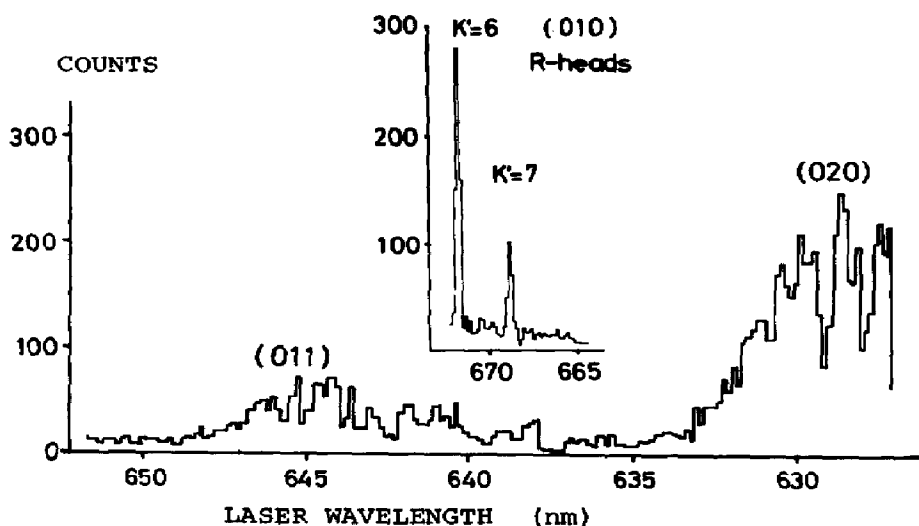


Fig. 2

Excitation Spectra of HNO,  $A^1A''-X^1A'$  transition. Total Pressure = 0.3 Torr.

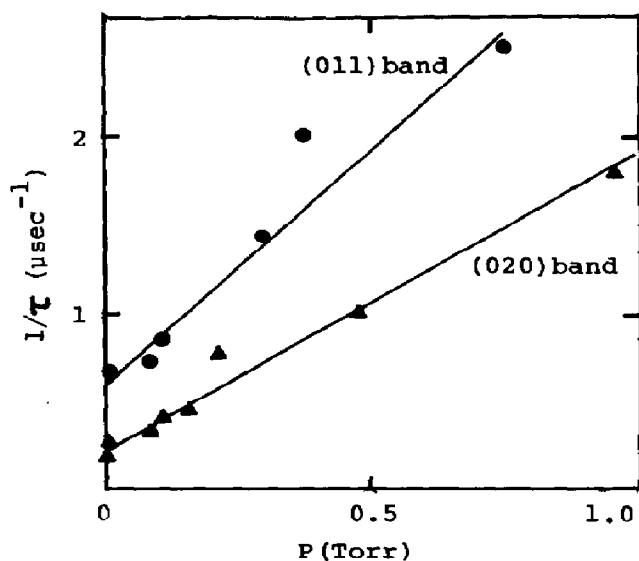


Fig. 3

Reciprocal values of the observed lifetimes against total pressure; (020)-(000) and (011)-(000) bands of HNO  $A^1A''-X^1A'$  transition.

## References

1. J. L. Bancroft, J. M. Hollas, and D. A. Ramsay, *Can. J. Phys.*, **40**, 322 (1962)
2. M. J. Y. Clement and D. A. Ramsay, *Can. J. Phys.*, **39**, 205 (1961)
3. T. Ishiwata, H. Akimoto, and I. Tanaka, *J. Phys. Chem.* in press
4. G. R. Williams, *Chem. Phys. Lett.*, **30**, 495 (1975)
5. M. A. A. Clyne and B. A. Thrush, *Discuss. Faraday Soc.*, **33**, 139 (1962)