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RESONANCE ABSORPTION LINESHAPE OF NO USING A ZEEMAN TUNED Cd LAMP:
APPLICATION TO COMBUSTION

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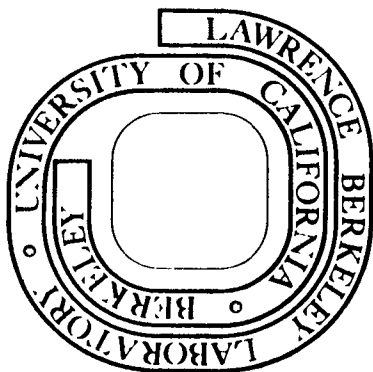
T. Hadeishi, Y. Agrawal, R. D. McLaughlin, and
F. Robben

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RESONANCE ABSORPTION LINESHAPE OF NO USING A
ZEEMAN TUNED Cd LAMP: APPLICATION TO COMBUSTION

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January 6, 1976

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The need for the development of non-interfering, in-situ measurement techniques for the oxides of nitrogen is underlined by the continued discrepancies in measurements reported in the literature. These discrepancies exist in measurements made using different probes⁽¹⁾ and also between probe measurements and optical measurements⁽²⁾. Here we describe a technique, first developed in our laboratory for atomic absorption spectroscopy, which is non-interfering, sensitive and capable of distinguishing between NO and any other absorbing species that might be present. Essentially, resonance excitation of a single rotational level of NO is achieved by Zeeman tuning of an atomic line. We have measured the absorption line-shape and effective collision broadening cross-section for excitation of a single line corresponding to the $\Lambda^2\Sigma$, $K=13$ transition of the 0-1 vibrational band of NO, using Zeeman scanning of the 2144.38 Å CdII line. Some un-calibrated measurements under combustion conditions have also been made.

The experimental apparatus used is essentially the same as described elsewhere^(3,4) in the context of atomic species measurements. It consists of an electrodeless discharge lamp placed between the poles of a variable field magnet, a quarter-wave plate, a polarizer and a monochromator-photodetector. Each atomic line is split into its σ^+ and σ^- Zeeman components corresponding to $\Delta M = \pm 1$. Only these two components are obtained when light is extracted along the magnetic field direction. Selective transmission of either the σ^+ or σ^- component is achieved by mounting the quarter-waveplate in a magnetically driven squeezer⁽⁴⁾. The squeezer is driven by a sinusoidal signal, and the quarter-wave plate transmits either the σ^+ or σ^- component. One of the two components, moving away from the coincident resonance wavelength, is used as a reference for light intensity and synchronous detection is employed to measure the absorption

of the other component. By use of synchronous detection and thus measuring only the differential absorption between σ^+ and σ^- components, interference due to other species and effects is eliminated. To obtain the absorption lineshape of NO, the absorption is measured as a function of the applied magnetic field.

The $5^2P_{3/2} - 5^2S_{1/2}$ transition of Cd II splits into four Zeeman components with transitions

$$|{}^2P_{3/2}, M_J=3/2\rangle \rightarrow |{}^2S_{1/2}, M_J=1/2\rangle$$

$$|{}^2P_{3/2}, M_J=1/2\rangle \rightarrow |{}^2S_{1/2}, M_J=-1/2\rangle$$

for $\Delta M_J = 1$ (right circularly polarized σ^+ lines, and

$$|{}^2P_{3/2}, M_J=-1/2\rangle \rightarrow |{}^2S_{1/2}, M_J=+1/2\rangle$$

$$|{}^2P_{3/2}, M_J=-3/2\rangle \rightarrow |{}^2S_{1/2}, M_J=-1/2\rangle$$

for $M_J = -1$ (left circularly polarized σ^- lines).

The energy splitting of these lines is given by

$$h(\nu_i - \nu_0) = \beta H \{g_{J_i} ({}^2P_{3/2}) m_{J_i} - g_{J_i} ({}^2S_{1/2}) m_{J_i}^1\}$$

where the g_J 's are Lande's functions, the m_J 's are the magnetic quantum numbers, β is the Bohr magneton and H is the applied magnetic field. The zero field frequency is ν_0 . It is to be noted that two σ^+ lines are obtained with intensity ratio 3:1. The measured absorption profile is a

convolution of the Doppler-broadened lines emitted by the lamp with the NO line. The absorption of the two σ^+ lines from the lamp overlap the NO line, leading to a measured absorption line shape (versus magnetic field) which is somewhat complex and asymmetric. Measurements were made with 0.5 Torr NO in the absorption cell, and with 1 atm N_2 added to 0.5 Torr NO, to produce a collision broadened absorption line. The absorption line shape was modelled by a convolution of Doppler and Lorentz line shapes (the well-known Voigt Line shape). Numerical convolution of this line shape with an assumed Doppler lamp profile was performed, and the parameters of these line shape functions were determined by comparing the numerical convolution with the experimental results. Adjustment of the parameters was made until satisfactory agreement with the experimental measurement was obtained⁽⁵⁾. Since the 0.5 Torr NO line shape will be only Doppler broadened at 300°K, a lamp temperature of 600°K was determined from this measurement. In order to fit the measured line shape for the 1 atm N_2 collision broadened measurement a Lorentzian collision frequency⁽⁶⁾ corresponding to a collision cross-section of $1.0 \times 10^{-15} \text{ cm}^2$ was required. This value is in reasonably good agreement with the results of Melton and Klemperer⁽⁷⁾.

Work is currently under progress to determine the NO line-shape under actual combustion conditions. We are convinced that the technique holds great promise for both absorption measurements along the line of sight, and point measurements through detection of NO fluorescence.

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