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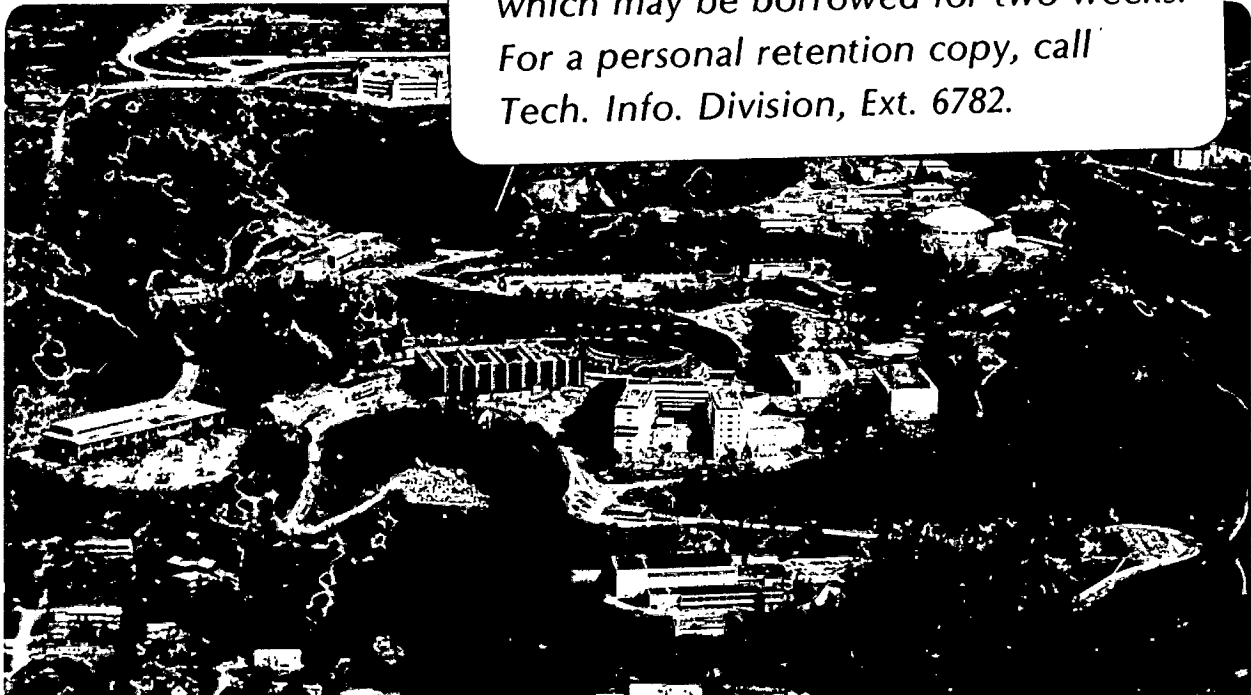
IN SITU, REAL TIME MEASUREMENT OF NO, NO<sub>2</sub>, AND SO<sub>2</sub> BY TUNABLE ATOMIC LINE MOLECULAR SPECTROSCOPY (TALMS)

Tetsuo Hadeishi and Ralph McLaughlin

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IN SITU, REAL TIME MEASUREMENT OF NO, NO<sub>2</sub>, AND SO<sub>2</sub> BY  
TUNABLE ATOMIC LINE MOLECULAR SPECTROSCOPY (TALMS)

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Tunable Atomic Line Molecular Spectroscopy (TALMS) is a newly developed technique for detection of molecules (as well as atoms) which is highly specific and sensitive even in the presence of high levels of background interference. The ideal analytical instrument would consist of a black box, through which a sample is transported, or is pointed to the sample to be measured, and without coming in contact with a surface that would cause alteration, would point out the level of all species in a specified concentration range. Of course, no such instrument exists today. The properties of such an ideal instrument are:

- No interference
- High sensitivity
- No matrix effect
- Inexpensive
- Precise
- Absolutely accurate
- Easy to use

TALMS is one of our attempts to construct an instrument that approaches this ideal.

TALM spectroscopy consists of splitting a source atomic emission spectral line by means of a magnetic field (Zeeman effect) and making a differential absorption measurement between one Zeeman component that has been magnetically tuned to match an analytic absorption line and unmatched Zeeman reference component. The difference in polarization between Zeeman components permits the matching and non-matching wavelengths to be alternately selected and the differential absorption measured very rapidly with an electro-optical device called a current controlled retardation (CCR) plate. This process is illustrated in Fig. 1. The line with label

$\Delta M = +$  (lower tracing) is tuned with the magnetic field to exactly match the electronic-vibrational-rotational line of a specified molecule (upper tracing) in the sample. The TALM spectrometer detects the difference between  $\Delta M = +1$  and  $\Delta M = -1$  reference Zeeman components and the differential absorption is proportional to the concentration of molecules in the sample.

The components of the TALMS system are pictured in Fig. 2. The light from a light source placed in the electro-magnet is passed through the hole drilled in the magnetic core, then through an absorption cell, a variable phase retardation plate, a linear polarizer, and finally focused on a small monochromator. Right and left circularly polarized light, hence the higher and lower Zeeman wavelength components, are selected by CCR and a linear polarizer combination.

For in situ measurement, the absorption cell is replaced by real system such as combustion or combustion chamber. These components, that utilize features of Zeeman effect, form the heart of the TALM spectrometer. This simple device is capable of a surprising resolving power (in excess of 500,000) with a large acceptance angle. To determine the shape of the absorption features a plot is made of ratio of intensities ( $I/I_0$ ) with the sample in and out of the optical path as a function of magnetic field.

Cd II at 214.2 nm at 10 KG and Zn at 213.8 nm at 20 KG magnetic field can be used to detect NO molecules by TALM spectrometer. Figures 3 and 4 show, respectively, NO line absorption profiles scanned by a Cd II 214.4 nm and a Zn 213.9 nm atomic emission line.

Figure 5 shows one example of NO signals obtained with a 20 cm cell.

By means of similar technique, NO<sub>2</sub> and SO<sub>2</sub> can be measured. Figure 6 shows a line profile of NO<sub>2</sub> by means of TALMS magnetic scanning of a Cu 249.2 nm line. Figure 7 shows differential absorption line profile of SO<sub>2</sub> using a Zn 213.8 nm line magnetic scanning.

#### Acknowledgment

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#### References

1. B.D. Zak, B. Chang, and T. Hadeishi, *Appl. Opt.* 14, 1217 (1975).
2. H. Koizumi, T. Hadeishi, R.D. McLaughlin, *Appl. Physics Ltrs.* 34, 382 (1979).
3. H. Koizumi, T. Hadeishi, R.D. McLaughlin, *Anal. Chem.* 52, 500-504 (1980).
4. H. Koizumi, T. Hadeishi, R.D. McLaughlin, *Spectro. Chem. Acta* 36B, 483-485 (1981).

TABLE 1. Small Molecules Measured With TALMS

Molecule	Atomic Line	Wavelength (nm)	Transition	
NO	Cd(II)	214.4	$2S_{1/2} - 2P_{3/2}$	
		226.5		
OH	Zn	213.8	$1S_0 - 1P_1$	
	Bi	306.8	$4S_{3/2} - 4P_{1/2}$	
I <sub>2</sub>	Zn	307.2	$3P_2 - 3P_1$	
	Hg	546.1	$3P_2 - 3S_1$	
S <sub>2</sub>	Mg(II)	279.6	$2S_{1/2} - 2P_{3/2}$	
		280.3	$2S_{1/2} - 2P_{1/2}$	
SO <sub>2</sub>	Zn	213.8	$1S_0 - 1P_1$	
	Cd	228.8	$1S_0 - 1P_1$	
NO <sub>2</sub>	Cu	249.2	$2S_{1/2} - 4P_{3/2}$	
		B	249.7	$2P_{1/2} - 2S_{1/2}$
			249.8	$2P_{3/2} - 2S_{1/2}$
CH <sub>2</sub> O	Ag	338.3	$2S_{1/2} - 2P_{1/2}$	

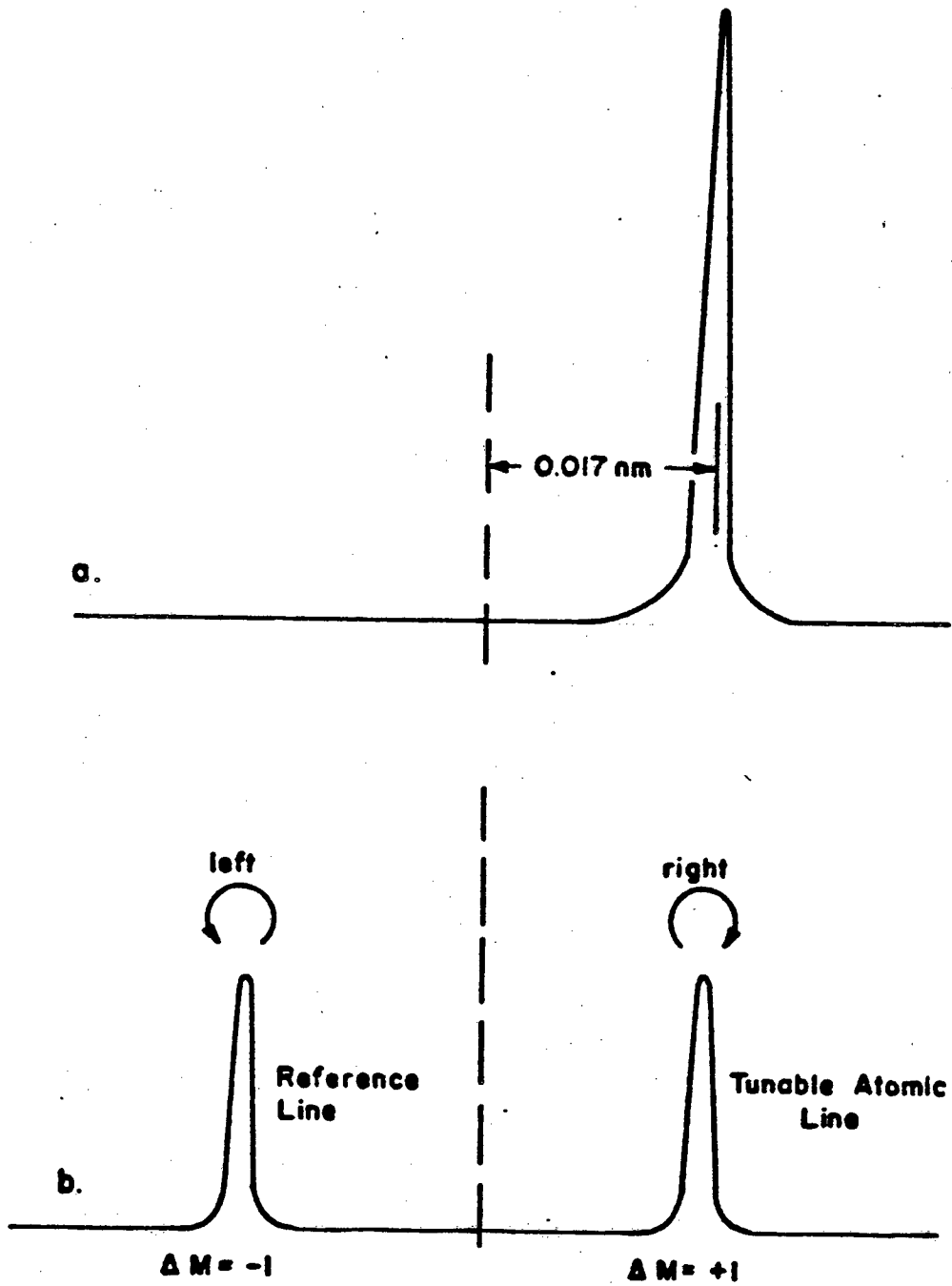


Fig. 1 Tunable Atomic Line Molecular Spectroscopy  
a) Molecular absorption line  
b) Zeeman split atomic emission line  
Note: the  $M = +1$  line is right-circularly polarized and the  $M = -1$  line is left-circularly polarized.

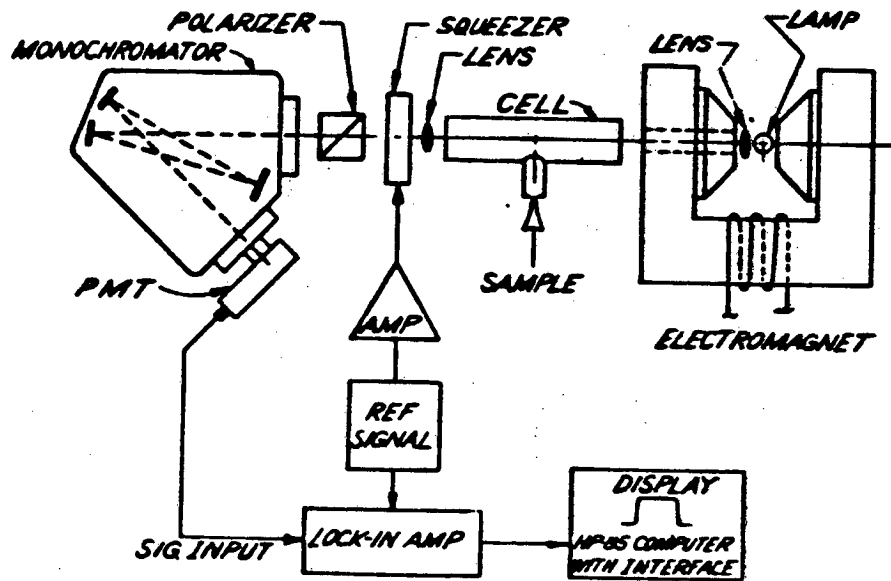


Fig. 2 Block diagram of TALMS instrumentation

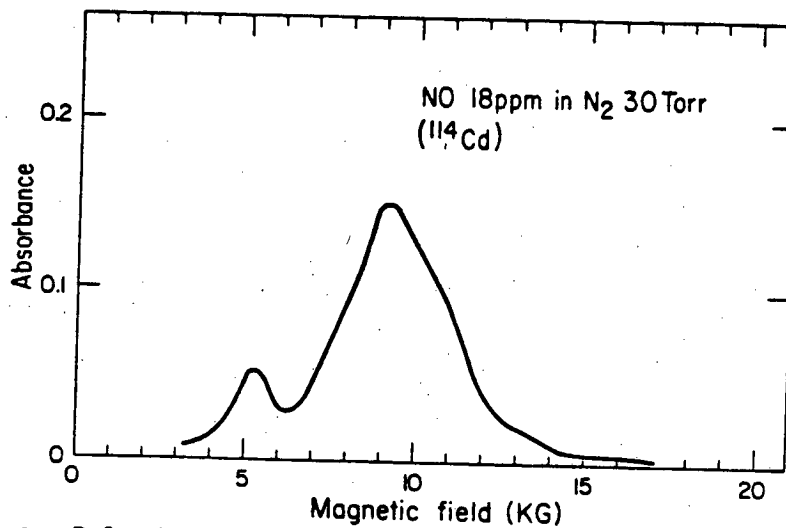


Fig. 3 Relation between the magnetic field strength and the differential absorption caused by NO for the Cd(II) line at 214.4 nm.



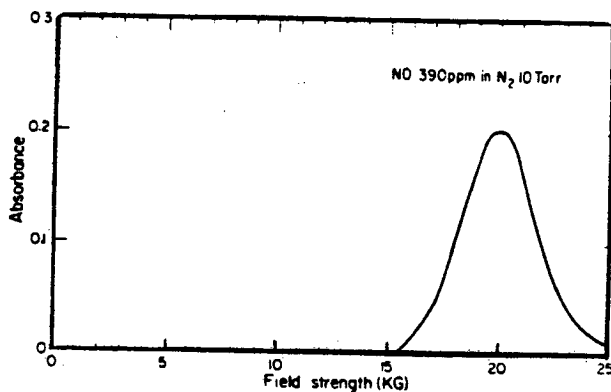


Fig. 4 Relationship between the field strength and the differential absorption caused by NO for the Zn line at 213.9.

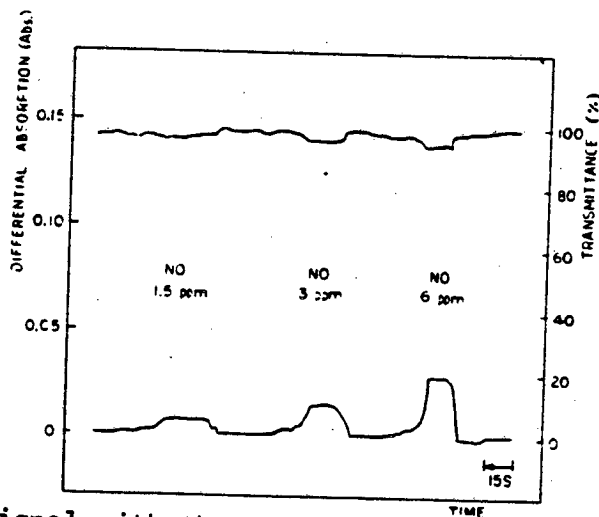


Fig. 5 NO signal with the present technique. Lower trace: differential signal; upper trace: transmittance of light through the cell.

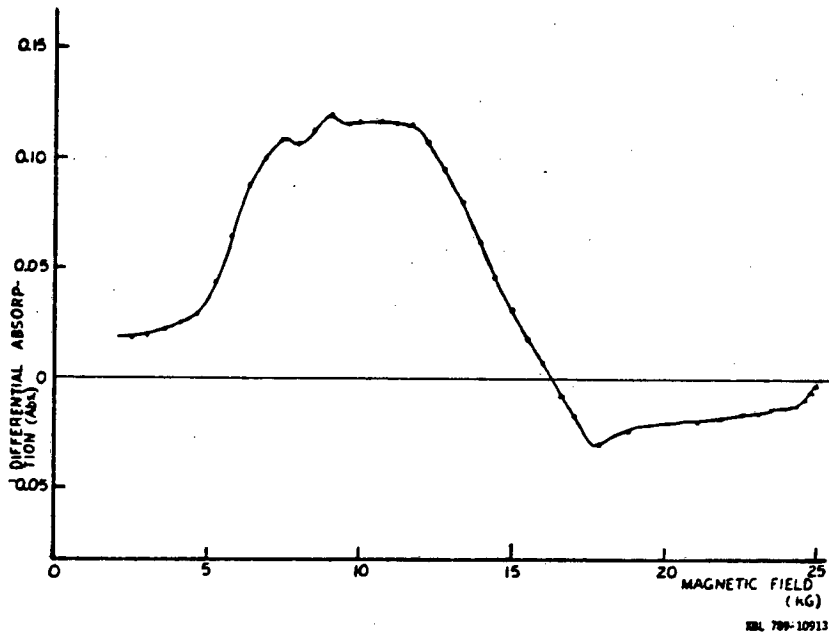


Fig. 6 High resolution absorption of NO<sub>2</sub> obtained by TALMS measurement.

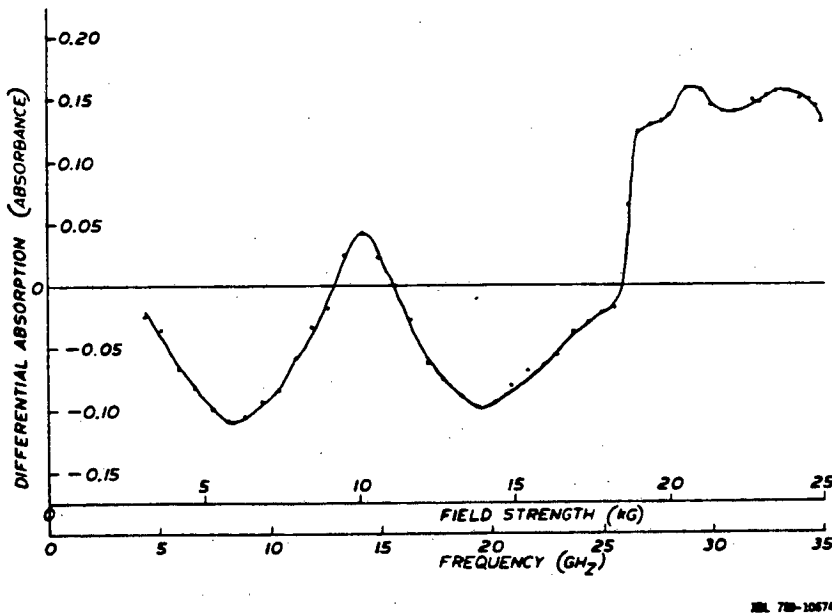


Fig. 7 Relation between magnetic field strength (shift of  $\sigma^+$  and  $\sigma^-$  components) and differential absorption of  $\sigma^+ - \sigma^-$  (SO<sub>2</sub> 0.46 torr, 10 cm cell).

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