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Detection of Small Molecules by Magnetically Tuned Frequency Modulated Atomic Line Sources

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Abstract

Small molecules such as NO, OH, I_2, S_2, SO_2, NO_2 and HCHO display discrete sharp electronic rotational-vibrational lines. Utilizing the Zeeman effect, one component of an atomic emmission line can be made to exactly coincide with a sharp molecular line while the other component is shifted so that there is no over lap with this line. When large molecules undergo electronic transitions it is not possible to resolve the rotational structure in the vast majority of cases. Therefore, the difference in absorption between the $\sigma^{\pm}$ components is proportional to the density of the molecules showing sharp absorption but is not influenced by other molecules. These phenomena can be used to achieve highly sensitive and selective detection of small molecules.

It is well known that in some cases diatomic molecules display sharp rotational structure when undergoing electronic transitions. Since Wood first used a mercury line to excite one of the vibrational lines of I_2 in 1921,[1] atomic lines have been used to monochromatically excite transitions to a single level of a diatomic molecule.[2-5]

Recently, by magnetically scanning atomic lines, we observed rotational structure in molecular electronic transition in regions where predissociation was not occurring. Not only did this occur for diatomic molecules but also for some triatomic molecules and for one tetraatomic molecule. Thus, we have developed a new technique for the detection of small molecules, in which an atomic line is shifted using the Zeeman effect to obtain an exact match with a molecular rotational line. The matching component was used for measuring absorption caused by the sharp molecular line and the unmatched σ component for reference, resulting in a differential absorption measurement. This technique is very powerful for the in-situ detection of small molecules in smoke or various gas mixtures.

Because of the line sharpness, apparent absorption measured using a continuum source may be much less than that expected from a knowledge of the oscillator strength. For example, the true absorption coefficients of individual rotational line of NO γ band have been found to be several hundred times greater than the apparent absorption coeffients measure by using a low resolution monochromator.[6] With the present technique we can obtain the high sensitivity expected form a consideration of the absorption coefficient of the molecular line, since we use a sharp atomic line with a half width of about 0.1 cm^{-1} (3 GHz).

Usually, large molecules do not show rotational structure in their electronic transition spectra because the spacing of rotational lines is smaller than the Doppler width and because broadening due to predissociation is more likely to occur than in small molecules.[7] Electronic bands of a polyatomic molecule are often more complicated than the infrared bands of the same molecule, since large differences of rotational constants may arise in upper and lower states. Hence, for large molecules, there would be essentially no difference in absorption betaween the σ^+ and σ^- components of an atomic line, and, high selective detection of small molecules becomes possible.

Furthermore, the field strength for exact matching between an atomic line and a molecular line differs depending upon the small molecule. This means that the technique will be selective even if a mixture contains different small molecules. Of course a monochromator is used to isolate the matching atomic lines. The molecules detected with this technique are listed in Table 1. Intense atomic lines which could possibly coincide with molecular lines in the bands that do not show evidence of predissociation were chosen from the MIT Wavelength Table.[8]

Next, the possible atomic line source was place in an electromagnet and the diffenerence of absorption between the σ^+ and σ^- components was measured over the field strngth from 0 to 25 kG. Although we found many coincident lines, the lines listed in Table 1 were selecated for this technique because of the sensitivity (large differential absorption), emission intensity and simplicity of the Zeeman pattern. Some of the atomic lines in Table 1 have been used for molecular spectrosxopic measurements by others.[1-5]

Figure 1 is a block diagram of the experimental apparatus. An atomic line source was placed in the magnetic field, and the emission passes through a hole in the electromagnet in a direction parallel to the magnetic field. Atomic vapor in the light source was produced by sputtering the cathode material with an abnormal D.C. glow discharge (50-200 mA, 100-200 V) and an RF discharge (70MHz, 10W) acting simultaneaously. The electromagnet (Varian Associates Model V-4004) could apply a homogeneous magnetic field to the light source of up to 30 kgauss. The circularly polarizing $\sigma^{\pm}$ components were converted to linear polarized light and selected by a linear polarizer. We developed a variable phase retarder by applying stress to a Suprasil block[9] that was used to convert circular to linear polarized light. A rochon prism made of synthetic quartz blocks with optical contact was used for the linear polarizer. This retarder and polarizer can be used in the U.V region down to 175 nm. The Rochon prism was rotated in the shaft of a synbchronous motor at 3600 r.p.m. The length of absorption cells used were 1, 10, 25, 100 cm.

Figure 2 shows the relation between the σ^+ component, σ^- component and the rotational line. In this case, the emission line is from Zn at the 213.8 nm $({}^1S_0 - {}^1P_1)$ and the absorption line is from NO $[A^2\pi\text{-}x^2\Sigma,\ (1,0,Q(k=29)]$. The absorption line profile is measured by scanning the $\sigma^{\pm}$ component through the molecular line. The emission line was assumed to be Doppler broadened at a temperature of 384^0K and the contribution of isotope shift to the line width was also included. These corrections have not been made to the absorption line profile displayed in Figure 2. Instead, this figure shows how the selectiveity of this technique depends upon the magnetic field.

As far as we know, only a few large molecules exhibit rotational structure in the electronic spectrum.[7,10] Therefore, in the vast majority of cases, interference caused by absorption and scattering of large molecules will be non existant with the present technique. Figure 3 is an example of the interference corrections obtained with this technique. The lower trace shows the differential absorption between the σ^+ and σ^- components of the Cd(II) line at 214.4 nm. The upper trace shows the light intensisty of the photomultiplier. When NO gas was introduced into the absorption cell, a big difference between the absorptions of σ^+ and σ^- was produced which was related in a linear fashion to the amount of NO. However, when acetic acid vapor was introduced into the cell there was no difference in absorption between σ^+ and σ^-, even though the incident light was strongly absorbed by CH_3COOH vapor. The pressure of CH_3COOH vapor at 3 Torr was low enough to avoid pressure broadening. We also looked at nitro-benzene which has strong absorption bands near the Cd line at 214.4 nm. No signal for C_6H_5NO was observed with this technique. It was also confirmed lthat light scattering in the cell which attenuated the incident light 70% did not produce a signal.

For the Zn line at 213.8 nm, exact matching between the atomic line and the rotational line of NO can be achieved at a field strength of 19 kG. Because of the high J value of 29 1/2, this line is suitable for NO detection at high temperature. For the measurement at room temperature, Cd(II) lines at 214.4 nm and 226.5 nm gives rise to high sensitivity becuase the J values of the coincident molecular line 11 1/2 and 10 1/2, respectively. The Boltzman distribution of rotation-vibrational levels of the ground state peaks at J = 7 at 300°K. However, the detection limit for NO with this technioue was about 50 ppb. The field strength for matching was 16.5 kG for th e ^{114}Cd(II) line at 226.5 nm and 8.5 kG for the ^{114}Cd(II) line at 214.4nm.

Sulpher dioxide did not show discrete rotational lines near the Cd line at 228.8 nm or the Zn line 213.8 nm. However, we could observe differential absorption between the $\sigma^{\pm}$ componets due to rotational structure of SO_2. The spacing of the peaks due to the rotational structure was about 10 GHz and the difference between the peak and the bottom of the absorption was about 30% of the average absorption. The lower detection limit of SO_2 was about 5 ppm with this technique. The field strengths that produced the largest differential absorption were 6, 14, and 20.5 kG.

We also observed clear rotational lines of HCHO to the higher frequency side of a Ag line at 338.3 nm[11]. It is very rare that tetraatomic molecules show sharp structure in this wavelength region. The field strengths for matching were 8, 14.3 and 17.2 kG. The predissociation region of NO_2 in the ultraviolet band system near 245 nm is between 4.98 ~ 5.04 eV[7]. Predissocation of NO_2 can be observed below 248 nm. The lines of the band of 249.1 nm are quite sharp, those of the band at 245.9 nm are slightly broadened while the band at 244.7 nm is completely diffuse.[12,13] Using Zeeman scanning, we found the bands starting at 249.1 nm exhibit discrete rotational lines near an intense Cu line at 249.2 nm. Figure 4 shows the relation between the strength of the magnetic field and the diffenential absorption for $\sigma^{\pm}$ components. This Cu line shows anomalous Zeeman effect, and has two σ components of the same circular polarization with relative intensities of 3:1 and with frequency displacements in the ration of 8/5 : 28/15. Both ^{63}Cu (69.1%) and ^{65}Cu (30.9%) have nuclear spin of 3/2. Thus, the scanned σ

component is broadened and the true profile of the NO_2 rotational line to the higher frequency side of the Cu line is sharper than that appearing in Figure 4. Because the coponents are broadened, the pressure dependence of the signal for NO_2 is less than that for NO. With N_2 at 1 atmosphere pressure, the sensitivity remained at 63% of that at 5 Torr. The detection limit of NO_2 with this techniques was about 10 ppm.

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Table 1. List of small molecules measured with this technique.

Molecule	Atomic Line	Wavelength (nm)	Transition
NO	Cd(II)	214.4	$^2S_{1/2} - {}^2P_{3/2}$
		226.5	$^2S_{1/2} - {}^2P_{1/2}$
	Zn	213.8	$^1S_o - {}^1P_1$
OH	Bi	306.8	$^4S_{3/2} - {}^4P_{1/2}$
	Zn	307.2	$^3P_2 - {}^3P_1$
I_2	Hg	546.1	$^3P_2 - {}^3S_1$
S_2	Mg(II)	279.6	$^2S_{1/2} - {}^2P_{3/2}$
		280.3	$^2S_{1/2} - {}^2P_{1/2}$
SO_2	Zn	213.8	$^1S_o - {}^1P_1$
	Cd	228.8	$^1S_o - {}^1P_1$
NO_2	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_2O	Ag	338.3	$^2S_{1/2} - {}^2P_{1/2}$

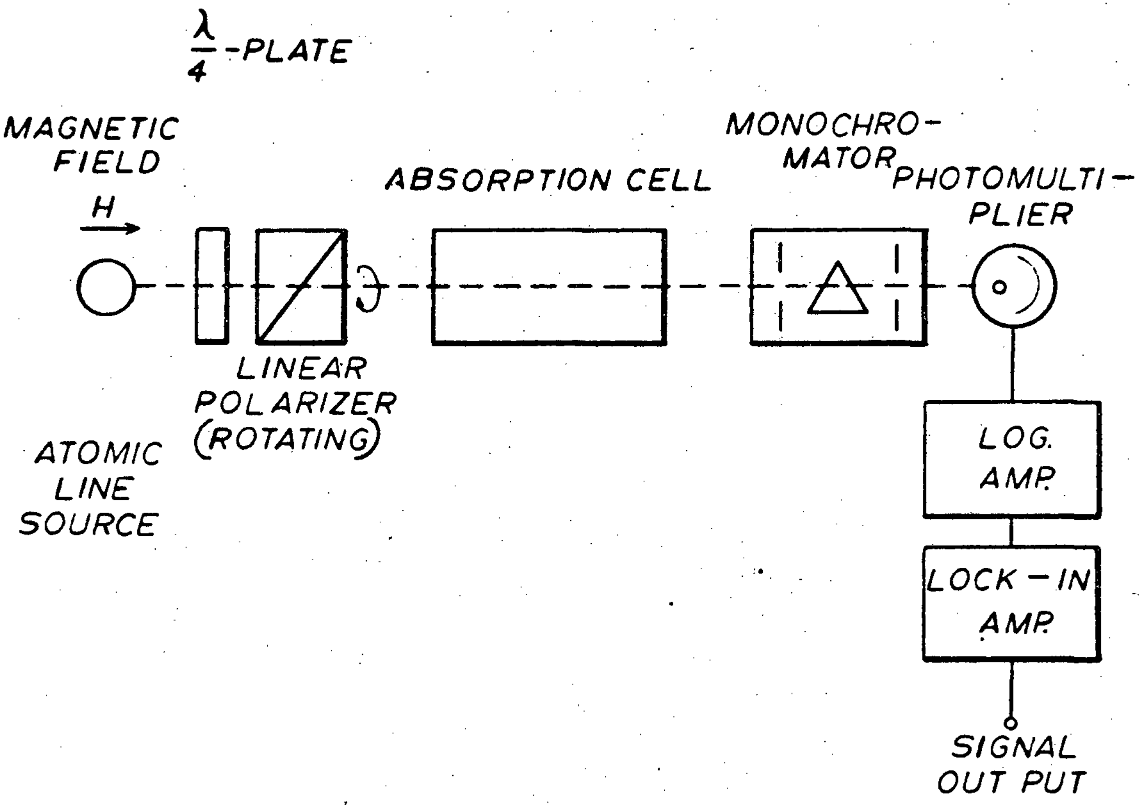
Figure Captions

Fig. 1. Block diagram of experimental apparatus.

Fig. 2. Relation betaween the vibrational-rotational line of NO $A^2\Sigma^+-X\pi_{1/2}$, (1,0), Q_1(29 1/2) and the σ^+ and σ^- components of the Zn line at 2138.56A ($^1S_0$ - $^1P_1$).

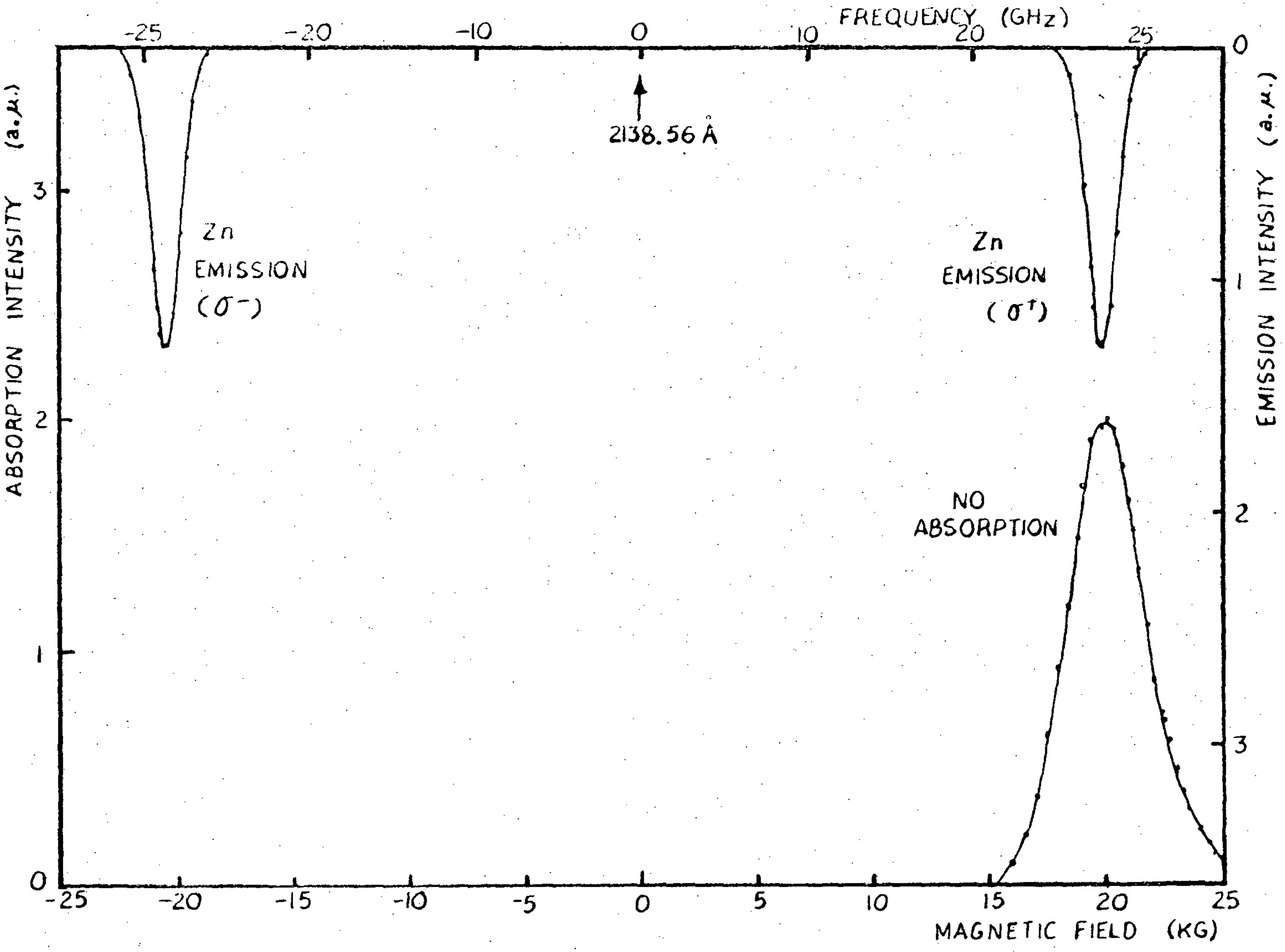
Fig. 3. NO signals with the present technique and the correction of background absorption caused by CH_3COOH. Upper trace: light intensity on the photomultiplier. Lower trace: differential absorption for σ^+ and σ^- components.

Fig. 4. Relation between the intensity of differential absorption and field strength for NO_2.



XBL 789-10676

Figure I



XBL 769-10914

Figure II

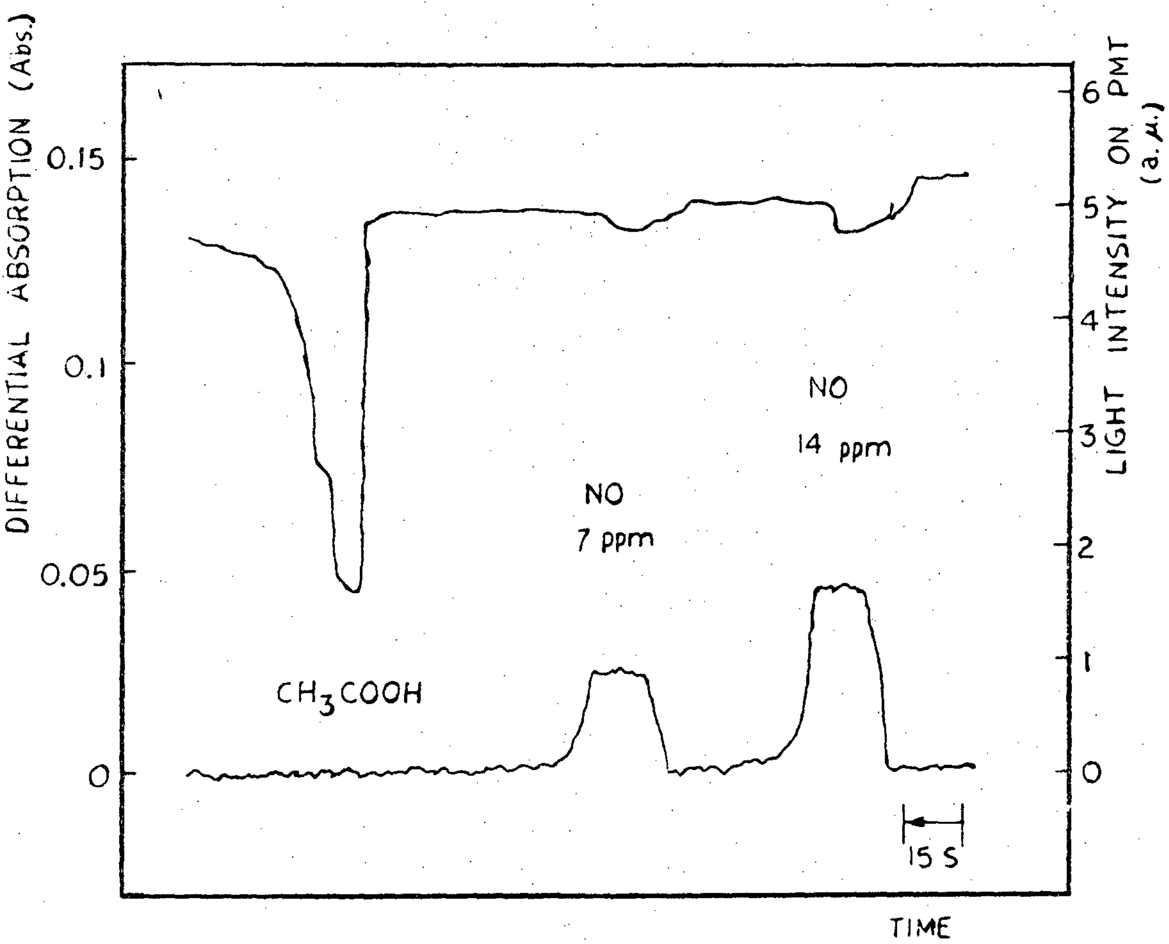


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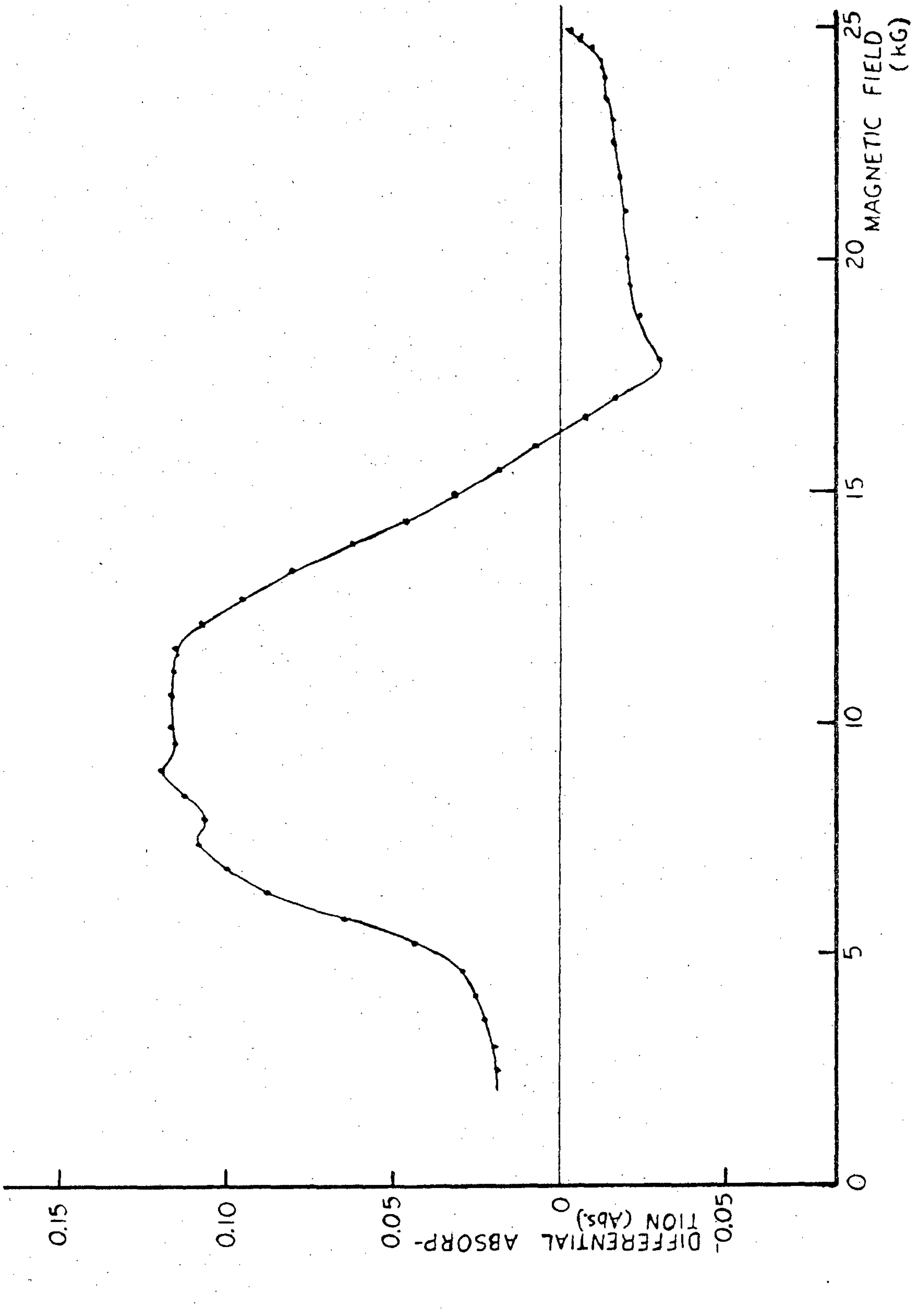
Figure III



XBL 789-10913

Figure IV

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