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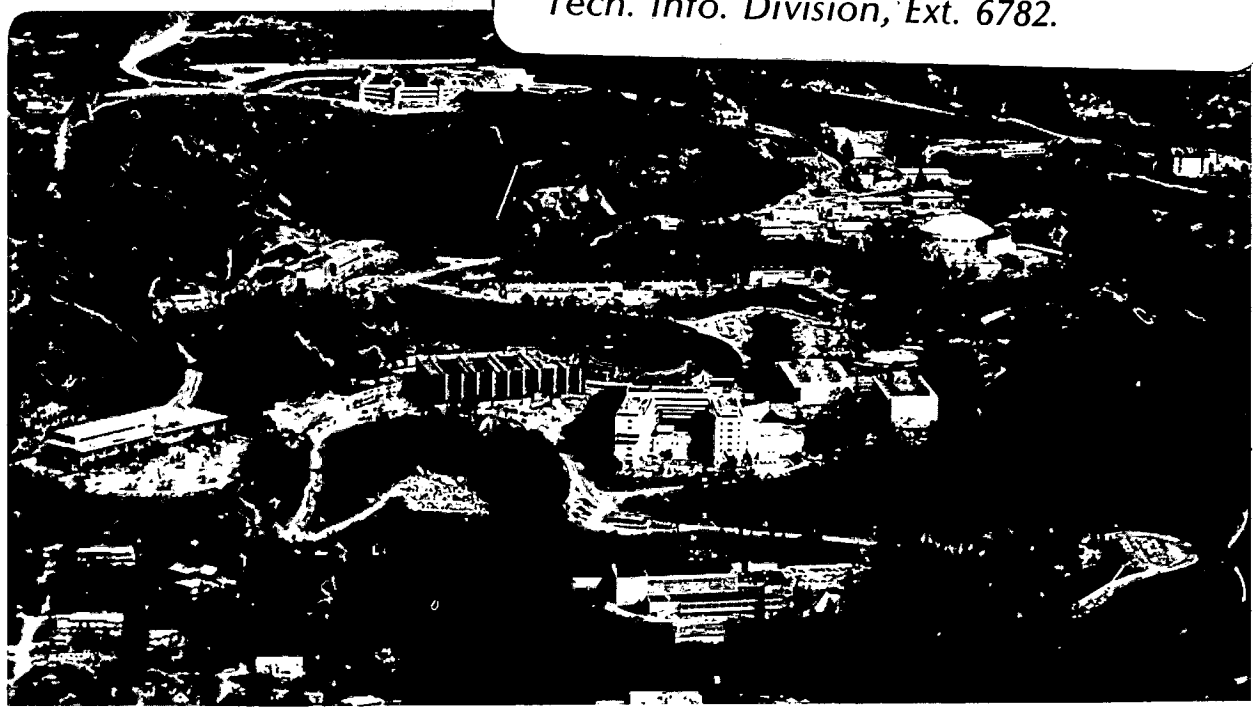
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TUNABLE ATOMIC LINE MOLECULAR SPECTROSCOPY OF BENZENE:

SIGNALS WITH Hg 253.7 NM AND Co 252.8 NM LINES

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Abstract

A method of locating appropriate atomic emission lines for the detection of complex molecules, e.g. benzene, with the TALMS technique is described. Atomic emission spectra are superimposed upon medium to high resolution absorption spectrograms of the molecules. It is then possible to calculate relative sensitivities associated with the various absorption features from the Zeeman splitting patterns and the absorption spectra. The TALMS signal is shown to be determined by the extinction coefficient difference, $\Delta\epsilon$, a concentration independent parameter. $\Delta\epsilon$ for benzene at the Co 252.8 nm and Hg 253.7 nm lines is estimated to be 100 and 8.4 respectively. The experimental TALMS signals using these lines are in the ratio 35:1.

BRIEF

A method of locating atomic emission lines for TALMS (tunable atomic line molecular spectroscopy) detection of complex molecules is described. TALMS signals for benzene are reported for the Co 252.8 nm and Hg 253.7 nm lines.

INTRODUCTION

A new spectroscopic technique for the detection of inorganic and organic compounds has recently been developed [1]. This technique, called TALMS (Tunable Atomic Line Molecular Spectroscopy), is essentially a high resolution, ultraviolet-visible absorption technique. TALMS signals are obtained by splitting a source atomic emission line with a magnetic field (Zeeman effect) and making a differential absorption measurement between Zeeman components that have been magnetically tuned to match a rotationally sharp analyte absorption line and the unmatched reference Zeeman components. The difference in polarization between the Zeeman components permits the matching and nonmatching wavelengths to be rapidly selected with an electro-optical device (a current controlled phase retardation plate). Since the wavelength separation between Zeeman components is small, a signal will only be obtained if the analyte absorption spectrum contains a sharp feature. The experimental equipment is described elsewhere [1].

To obtain optimum sensitivity and selectivity for a given compound with the TALMS technique, it is necessary to know wavelengths of atomic lines that can be shifted by the Zeeman effect (ca. 1.5 cm^{-1}) onto the rotationally sharp features in the absorption spectrum of the compound. This can be a tedious process since there are a large number of sharp features in the 260 nm band of benzene alone [2]. An effective way to accomplish this is to obtain medium to high resolution spectra of the compound and superimpose Zeeman split atomic emission lines directly on the photographic plates. Application of this procedure to determine Co 252.8 nm and Hg 253.7 nm coincidences with sharp absorption features in benzene will be illustrated. The importance of the extinction coefficient difference in determining the magnitude of the TALMS signal is discussed. Experimental TALMS results are given for the Co and Hg lines.

THE EXTINCTION COEFFICIENT DIFFERENCE, MEASURE OF THE TALMS SIGNAL

A TALMS signal can be detected with two experimental arrangements, with the atomic emission direction parallel to the direction of the magnetic field or perpendicular to the field. In the parallel configuration, differential absorption measurements are made between the higher wavenumber Zeeman components (σ^+ , $\Delta M = +1$) that are left circularly polarized and the lower wavenumber components (σ^- , $\Delta M = -1$) that are right circularly polarized. In the perpendicular configuration differential absorption measurements are made between Zeeman components polarized parallel to the field and components polarized perpendicular to the magnetic

field. The Zeeman components polarized parallel to the magnetic field are usually unshifted and almost always shifted less than the components polarized perpendicular to the field.

The concentration independent parameter that determines the magnitude of the TALMS signal, which is a differential absorption signal, is the difference in the extinction coefficients for the two differently polarized Zeeman components, $\Delta\epsilon$.

$$\Delta\epsilon = \epsilon^- - \epsilon^+$$

where ϵ^- = the extinction coefficient of the light shifted to lower wavenumber (σ^- components)

and ϵ^+ = the extinction coefficient of light shifted to higher wavenumber (σ^+ components). For the perpendicular configuration,

$$\Delta\epsilon = \epsilon^{\parallel} - \epsilon^{\perp}$$

where ϵ^{\parallel} is the extinction coefficient for light polarized parallel to the magnetic field (π components)

and ϵ^{\perp} is the extinction coefficient for light polarized perpendicular to the magnetic field (σ^- and σ^+ components).

The TALMS absorbance signal is equal to

$$S = \Delta\epsilon Cl$$

where C = concentration in M/L and l = cell length in cm.

It is easier to calculate the relative magnitude of the TALMS signal using the parallel configuration since there are less components and less overlap between components than with the perpendicular configuration. However, experimentally the perpendicular configuration is easier to use because it avoids problems associated with recording light passing through one of the poles of the magnet.

EXPERIMENTAL SECTION

The medium resolution absorption spectra were obtained on a Jarrell-Ash 3.4 meter spectrograph (Ebert mount) with a 600 l/mm grating used in the second order. Exposures were of the order of one minute using a 50 μ slit and a 10 mm cell. Atomic lines from a magnetically confined arc [1] were superimposed on the absorption spectra which were recorded on Eastman SA1 plates. The TALMS signals were obtained with the apparatus described in [1].

RESULTS

A comparison of the benzene spectrum from 247 to 259 nm with the Co emission spectrum is presented in figure 1. Using this technique, it was immediately noticed that two Co lines were in near coincidence with the sharp benzene maximum at $39,534.6 \text{ cm}^{-1}$ (vac.). The densitometer tracing shown in figure 2, demonstrates that the Co II line is more suitable than the Co I or a nearby Fe line for shifting onto the sharp benzene feature. Similarly, a coincidence of the Hg line at 253.7 nm with the benzene feature at $39,412 \text{ cm}^{-1}$ (vac.) was also found. Figure 3 shows the experimental absorption line shape of the benzene maximum that is centered near 253.7 nm along with the Zeeman pattern of the Hg line at a magnetic field of 20 kg (2.0 tesla). The extinction coefficient of this feature was determined to be 75. Using Lambert's exponential law of absorption and taking the transmission (intensity with benzene absorption divided by intensity without benzene absorption) from figure 3, we obtain

$$\epsilon^+ = 68.1, \epsilon^- = 63.2 \text{ and } \Delta\epsilon = -4.9$$

while the value for the perpendicular configuration is

$$\Delta\epsilon = \epsilon^{\parallel} - \epsilon^{\perp} = 9.4$$

Therefore, one should use the perpendicular configuration to detect benzene with the Hg 253.7 nm line. However, as the values of $\Delta\epsilon$ show, the TALMS signal with this feature is relatively low and a more intense band is desired for better sensitivity.

Figure 4 shows the relative position of the Co II 252.86 nm line and the intense benzene absorption at 252.87 nm ($\epsilon \text{ max } \sim 500$). This figure also shows the nearly coincident Co I 252.90 nm line. A consideration of intensities of the photographic plates and the Zeeman splitting patterns of these lines relative to the benzene absorption profile reveals that the main contribution to the TALMS signal comes from the Co II line. The extinction coefficient difference for the parallel configuration and this line is approximately equal to 400. For the perpendicular configuration it is about - 100. Therefore, the parallel configuration should give a better TALMS signal for this case.

We shall next compare the experimental TALMS signals that result from the perpendicular configuration for the Hg I and Co II lines. Figure 5 shows the absorption of the perpendicular and parallel polarized components of the Co II line at a magnetic field of 27 kg (2.7 tesla) by benzene vapor. There is almost no absorption of the parallel (π) components while $\sim 50\%$ of the intensity of the perpendicular

(σ) components is absorbed. This is due to the fact that the σ^- components overlap the benzene absorption band while the σ^+ components are outside the region of benzene absorption.

As shown in figure 3, when the TALMS signal is obtained using the Hg 253.7 nm line, the parallel components are more absorbed by the vapor than are the perpendicular components. This is completely opposite from the Co II case, i.e. the TALMS signals are 180 degrees out of phase. Figure 6 illustrates the periodic change in the light intensity as the phase-squeezer-polarizer unit switches from detection of parallel to perpendicularly polarized light. The peak to peak amplitude represents the differential absorption signal that corresponds to the TALMS signal. This amplitude is proportional to the quantity of benzene in the light path. It is quite clear that a phase difference of 180 degrees exists between the signal from the Co II line and the Hg I line.

The strength of the TALMS signal in the perpendicular configuration is directly proportional to the extinction coefficient difference. For the Hg 253.7 nm line the signal, S, is given by

$$S = 8.4 C_1$$

while for the Co II line it is

$$S = 100 C_1.$$

Therefore the Co II signal should be 12 times the Hg I signal.

Figure 7 shows the experimental TALMS results. These data indicate the TALMS signal for the Co II line is 35 times that of the Hg I line. The disagreement of the estimated and experimental signals is due to difficulties in determining absolute absorbances from photographic plates and the contribution of the Co I Zeeman components to the experimental signal. The Co I line was not taken into account in obtaining the estimated value.

CONCLUSIONS

The use of high to medium resolution absorption spectroscopy with superimposed atomic lines is an efficient method for locating near coincidences between atomic lines and sharp molecular absorption features. The difference in extinction coefficients is shown to be an important parameter in determining the magnitude of the TALMS signal. It

was shown that the TALMS signal at the Co II 252.8 nm line is 35 times greater than that for the Hg I 253.7 nm line.

LITERATURE CITED

- [1] T. Hadeishi, H. Koizumi, R.D. McLaughlin, and J.E. Mil-
laud, Spectrochem. Acta 37B, 501 (1982)
- [2] G.H. Atkinson and C.S. Parmenter, Mol. Spectros. 73, 52
(1978).

Mention of trade names or commercial products does not constitute endorsement or recommendation for use. Although the research described in this article has been funded wholly or in part by the U. S. Environmental Protection Agency through agreement AD-89-F-2-A008 to the Lawrence Berkeley Laboratory (U.S. Department of Energy contract number DE-AC03-76SF00098); it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency. No official endorsement should be inferred.

FIGURE CAPTIONS

Figure 1. Tracings of spectrographic plates. Upper: benzene absorption spectrum. Lower: Co emission spectrum.

Figure 2. Medium resolution benzene absorption spectrum and emission spectra of Co and Fe in the region of 252-253 nm.

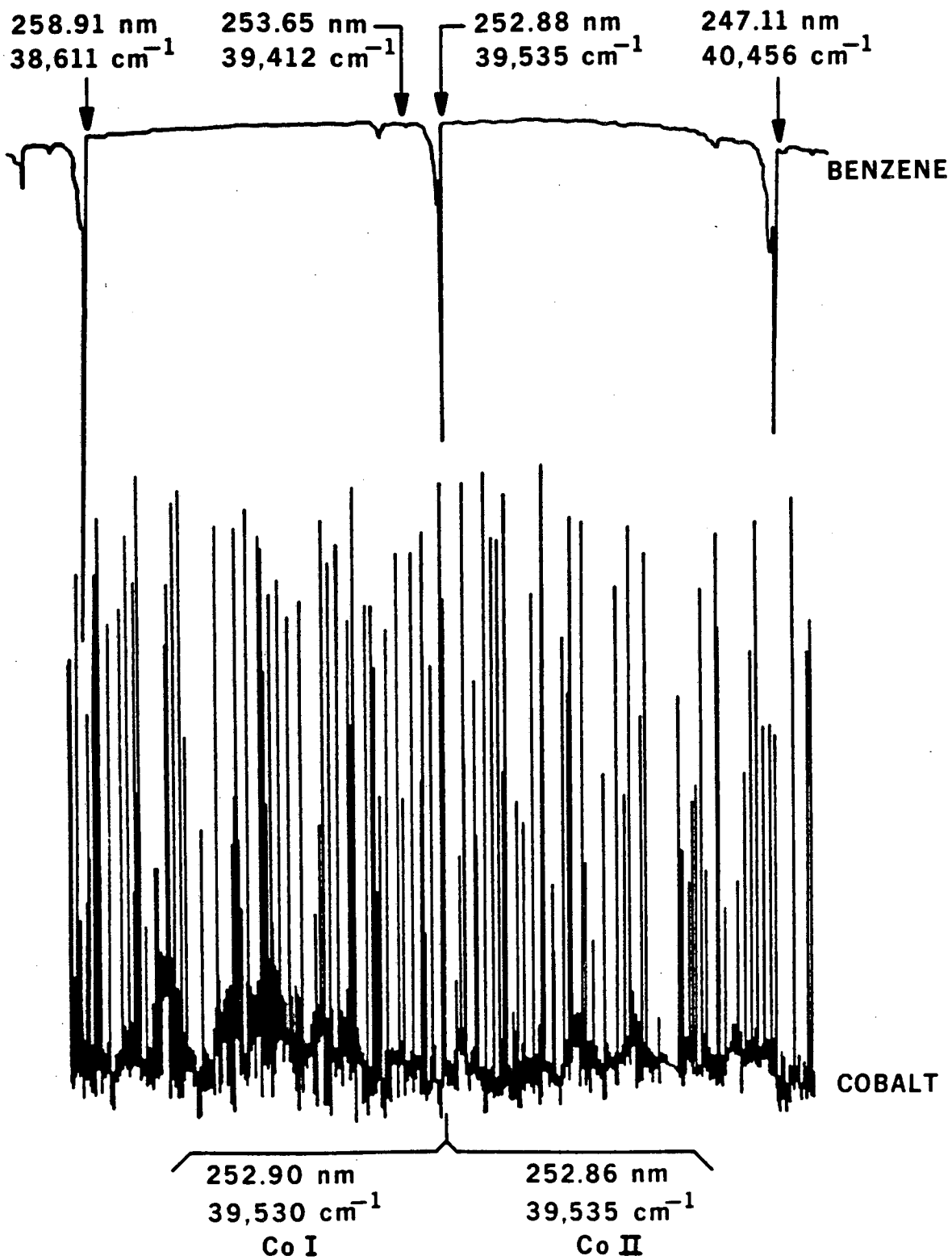
Figure 3. Benzene absorption and Hg Zeeman pattern at 253.7 nm. A: absorption spectrum from reference 2. B: Zeeman scan (using isolated σ^+ and σ^- components) and Hg Zeeman pattern of region dotted in A. C: Zeeman components transmitted by benzene at 2 tesla (20 kg).

Figure 4. Benzene absorption and Co II Zeeman pattern at 252.9 nm. A: absorption spectrum from reference 2. B: experimental benzene maximum with Co I and Co II lines (present study). C: theoretical Zeeman components of the CoII 252.9 nm line at 2.7 tesla (27 kg). (NOTE, SCALES ARE NOT THE SAME.)

Figure 5. Absorption of the Co II Zeeman components at 252.9 nm by benzene. A: before absorption. B: after absorption.

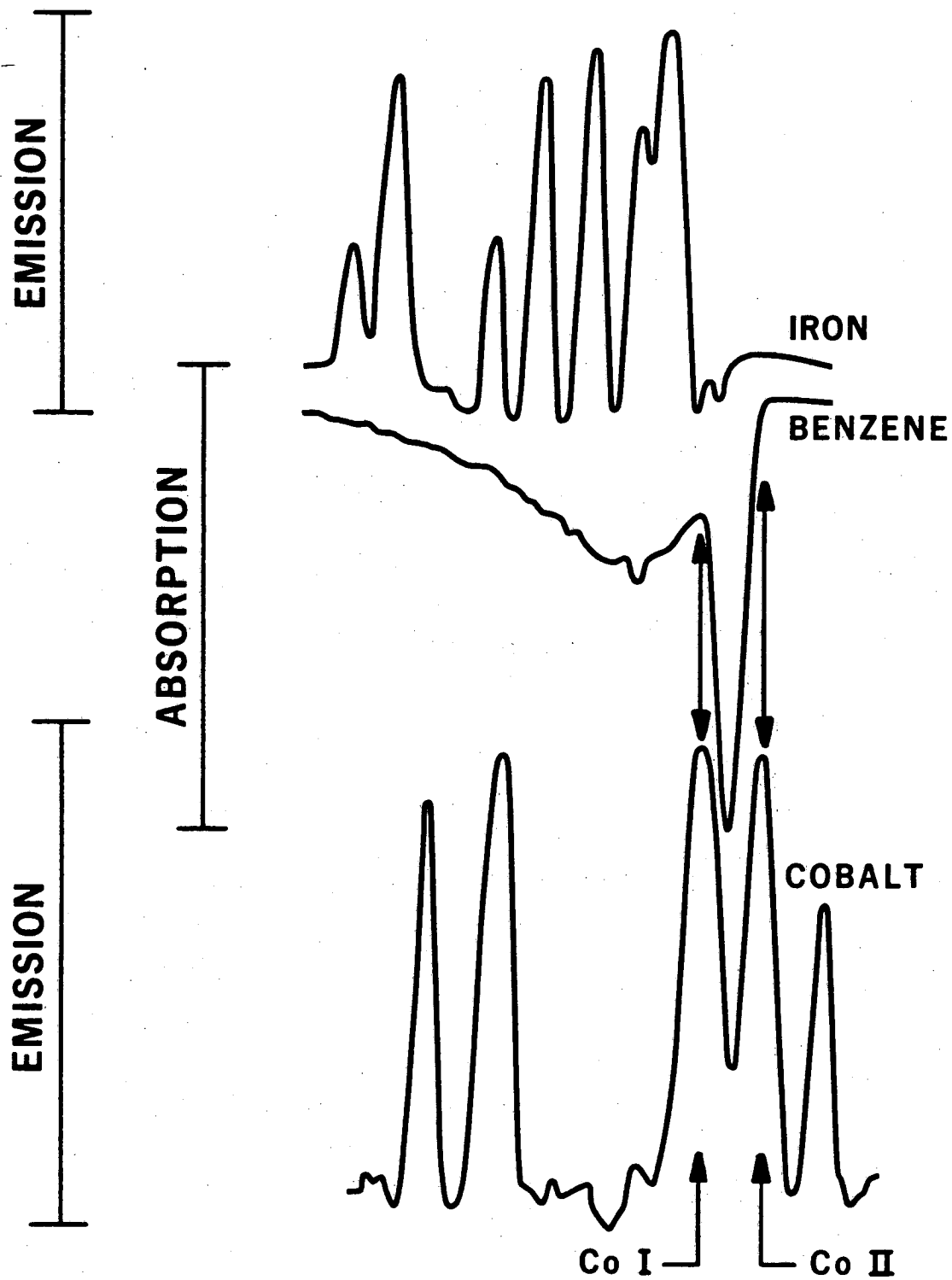
Figure 6. TALMS phase differences for benzene. A: 252.9 nm Co II signal at 2.7 tesla (27 kg). B: 253.7 nm Hg signal at 2.0 tesla (20 kg).

Figure 7. Benzene TALMS signal at Hg and Co II lines. A: 78 ppmv benzene, Co II 252.9 nm, 2.7 tesla (27 kg), gain = 1. B: 78 ppmv benzene, Hg 253.7 nm, 2.0 tesla (20 kg), gain = 10.



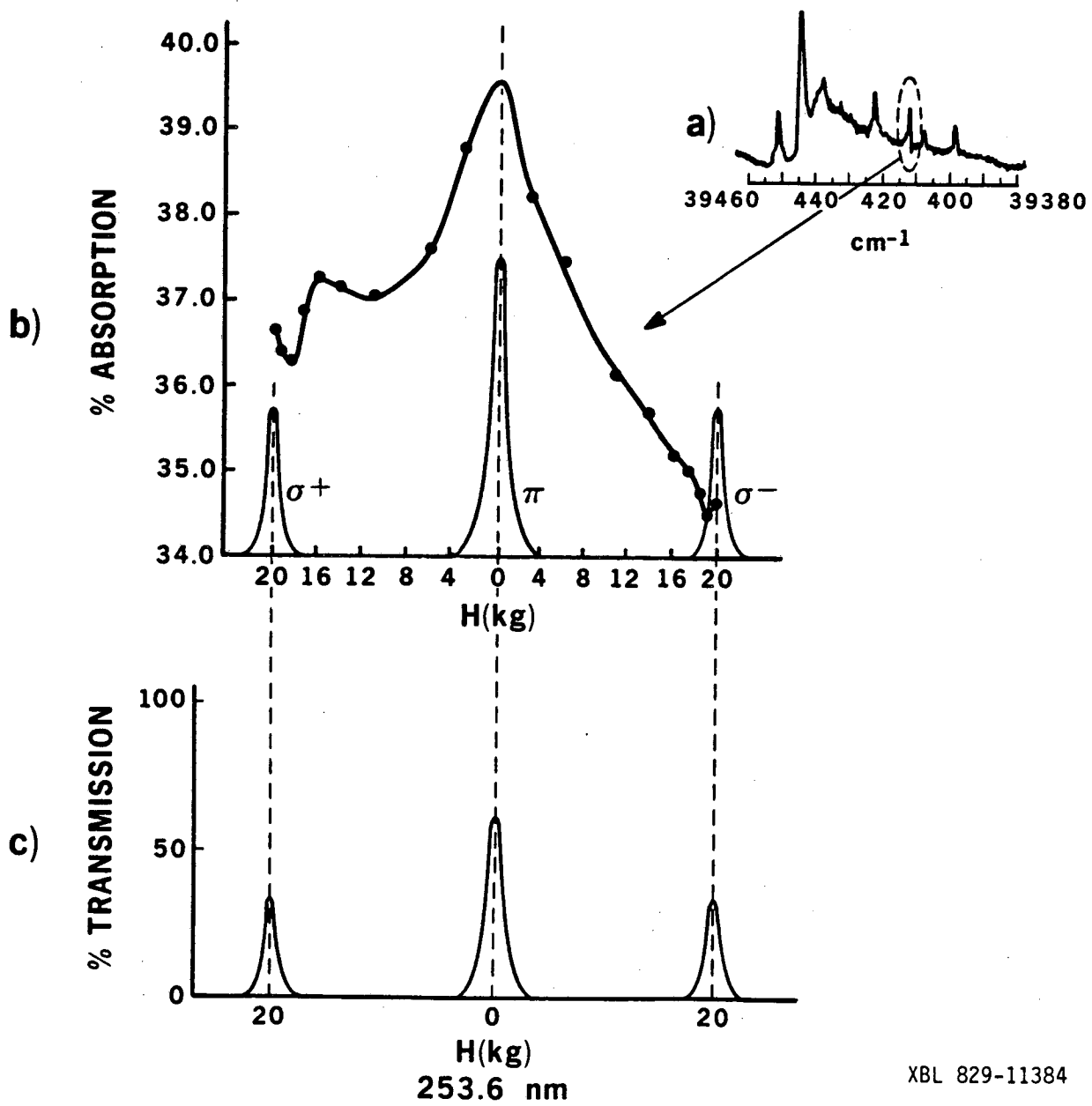
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Figure 1



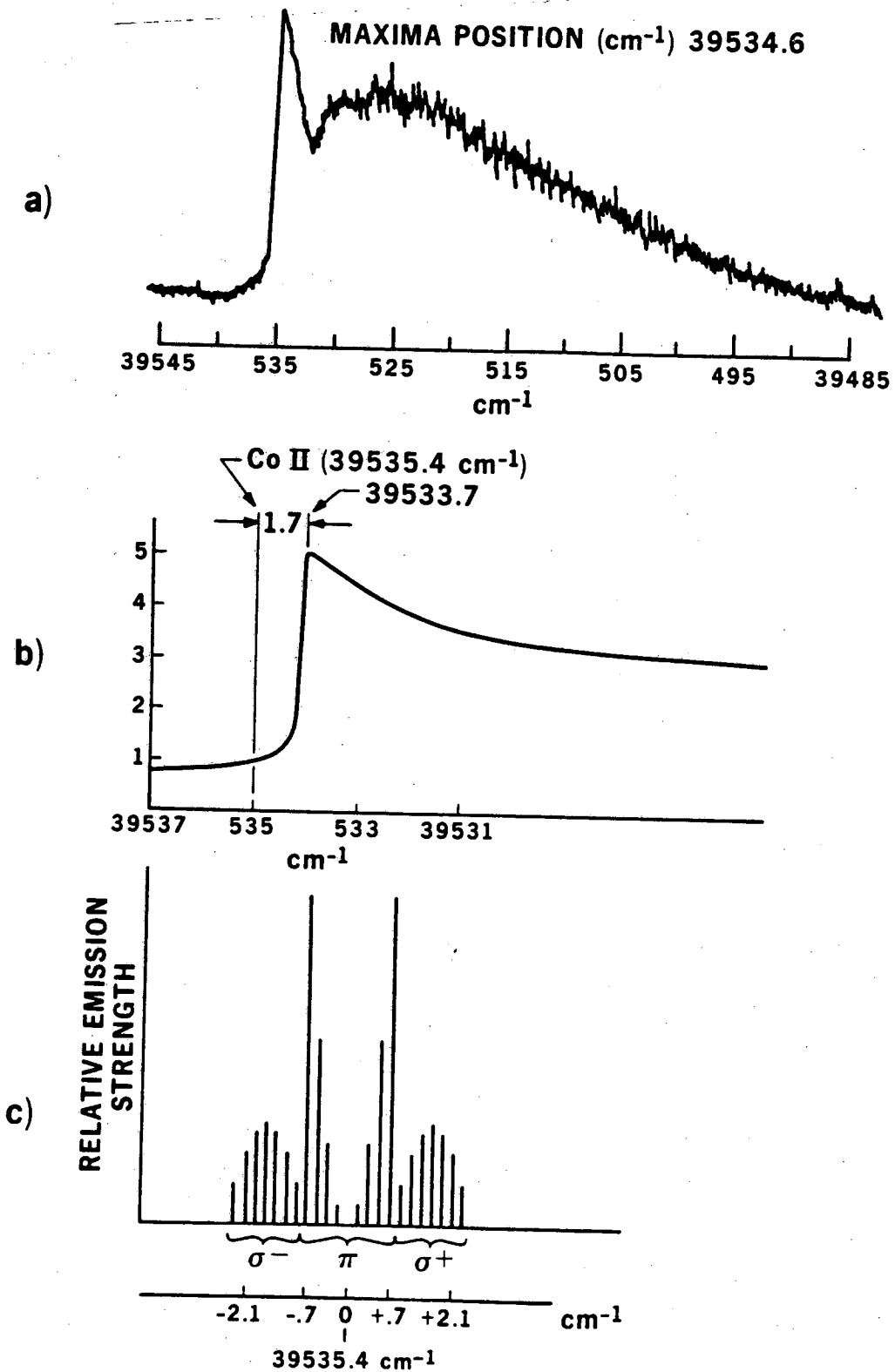
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Figure 2



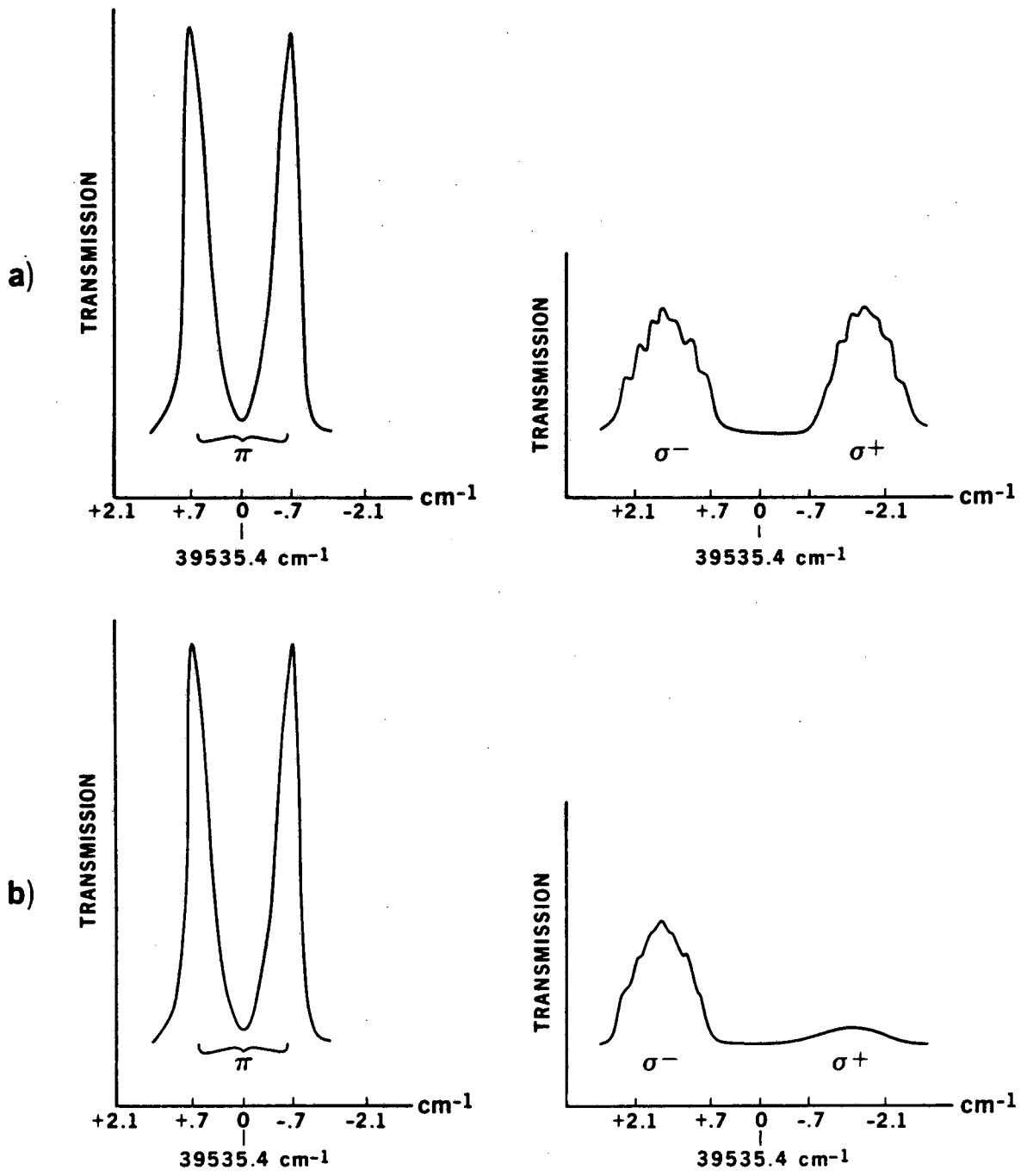
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Figure 3



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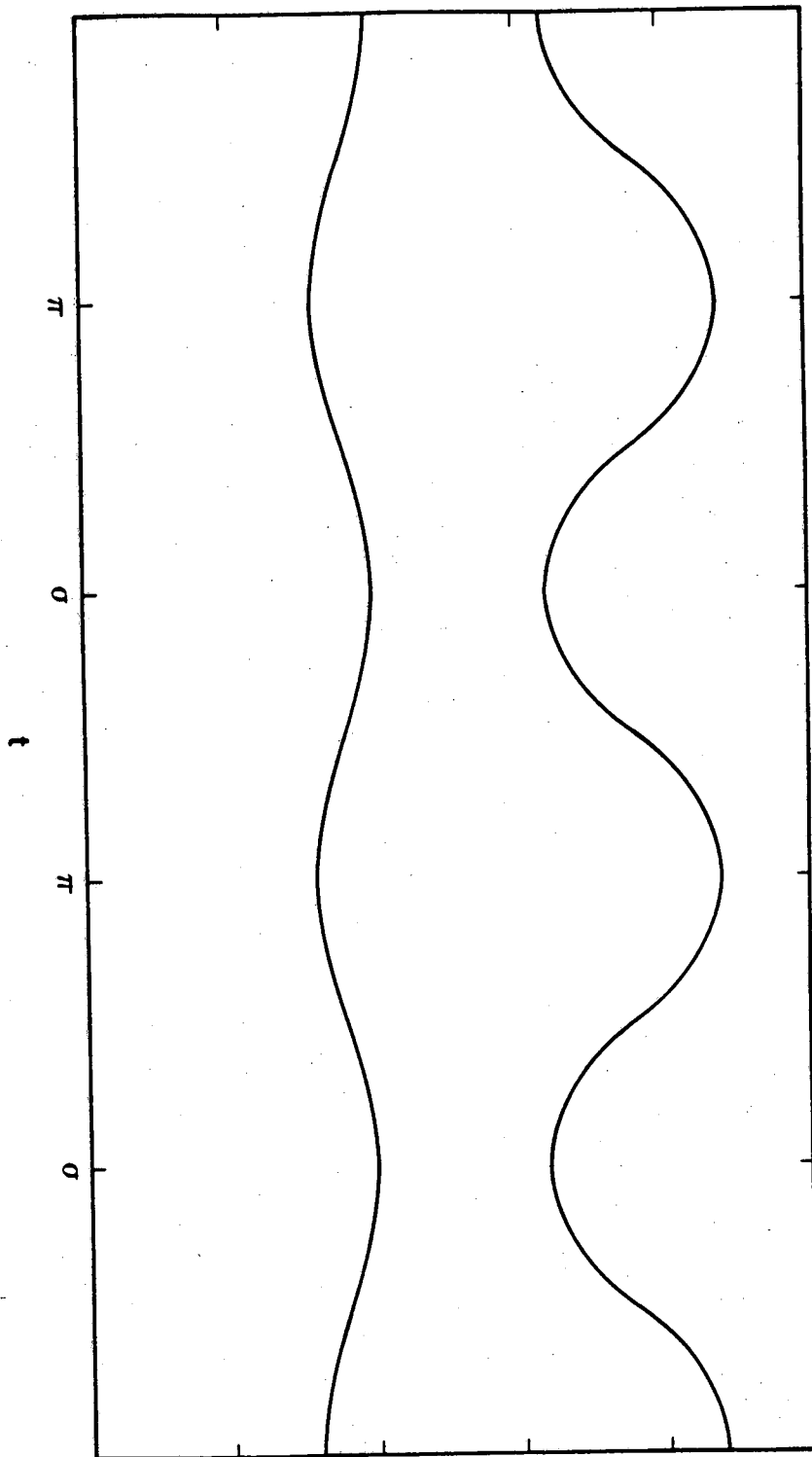
Figure 4



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Figure 5

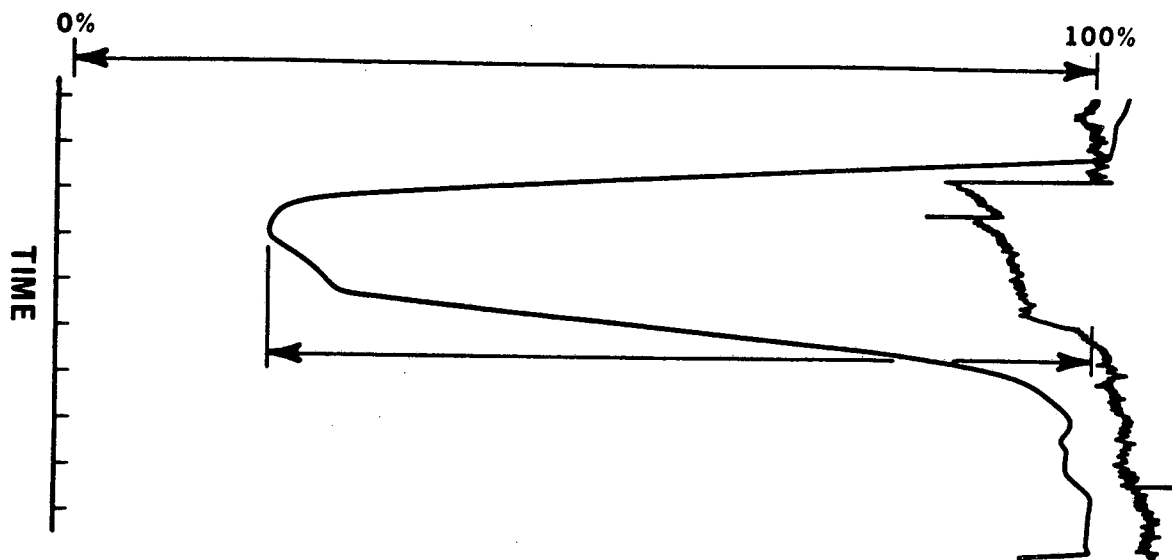
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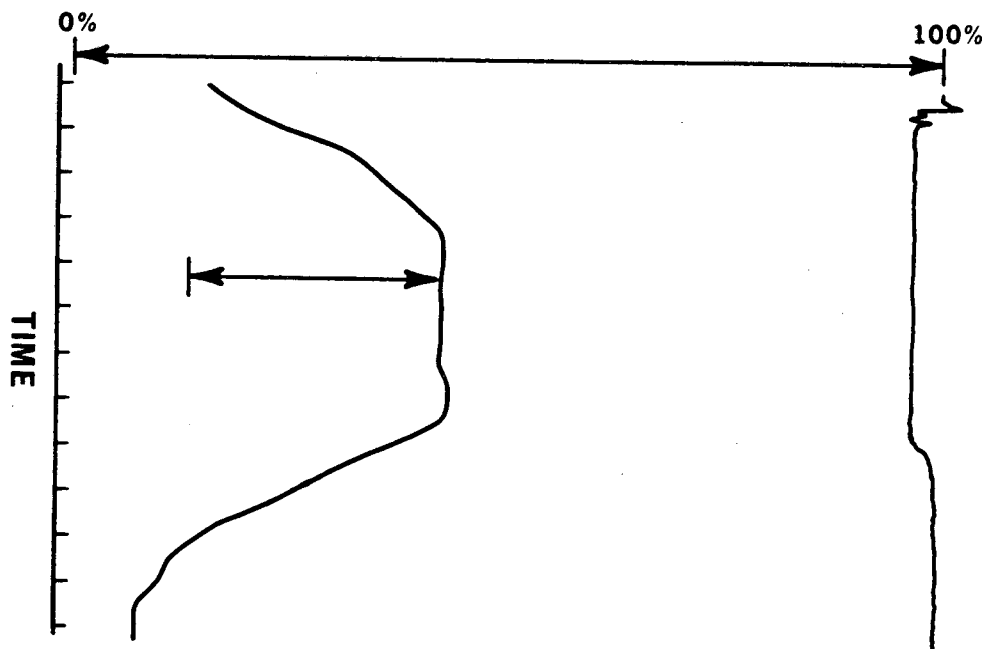
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Figure 6

% OPTICAL TRANSMISSION Co II 2528.62A IN 27,000 GAUSS



% OPTICAL TRANSMISSION OF Hg 2537A LINE IN 27,000 GAUSS



XBL 829-11381

Figure 7

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