Selection of Atomic Emission Lines for Tunable Atomic Line Molecular Spectrometry of Benzene

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A method of locating appropriate atomic emission lines for the detection of complex molecules, e.g., benzene, with the tunable atomic line molecular spectrometry (TALMS) technique is described. Atomic emission spectra are superimposed upon medium- to high-resolution absorption spectrograms of the molecules. It is then possible to estimate relative sensitivities associated with the various TALMS signals at different wavelengths from the Zeeman splitting patterns and the molecular 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 from photographic measurement to be 100 and 8.4, respectively. The experimental TALMS signals using these lines are in the ratio 35:1.

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 spectrometry), is essentially a high-resolution, ultraviolet–visible, differential, 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 electrooptical 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*). The resolution obtainable, which is dependent on the line width of the atomic probe line, is commonly 500 000 or better. This has been demonstrated from measurements on the formaldehyde 339 nm absorption feature (*2*).

To extend the applicability of this new technique and to obtain optimum sensitivity and selectivity for a given compound, it is necessary to catalog 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 spectra of the compounds. Unfortunately, available high-resolution spectra for organic compounds in the literature are limited to relatively narrow spectral regions. These studies were usually made for analysis of rotational or vibrational structure and do not necessarily cover the regions that are important to determinations for analytical chemistry. Furthermore, listings of wavelengths for high-resolution, ultraviolet–visible, absorption spectra do not exist for most organic compounds. Manual searching for TALMS signals can be a tedious process.

There are a large number of sharp features in the 260-nm band of benzene alone (*3*). An effective way to find matches of atomic lines with molecular absorption features is to obtain medium- to high-resolution spectra of the compounds and superimpose various Zeeman split atomic emission lines directly on the photographic plates. Application of this procedure has led to the finding of a Co 252.8 nm coincidence with a sharp absorption feature in benzene. The previously reported Hg 253.7 nm coincidence with another sharp benzene absorption feature (*1*) was verified. The importance of the extinction coefficient difference in determining the magnitude of the TALMS signal is discussed. A method of estimating the magnitudes at the Co and Hg lines from photographic intensities is described. Experimental TALMS results are given for the Co and Hg lines.

EXPERIMENTAL SECTION

The medium resolution absorption spectra were obtained on a Jarrell-Ash 3.4-m spectrograph (Ebert mount) with a 600 lines/mm grating used in the second order. Exposures were of the order of 1 min using a 50-μm 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. To obtain the TALMS signal the magnetic field strength was varied from 0 to 2.7 T (27 kG). Benzene was introduced into the absorption cell by injection with a gastight syringe of measured amounts of vapor in equilibrium with the solid (at 0 °C). The TALMS signals were obtained with the apparatus described in ref 1, equipped with a 15 cm path length cell.

RESULTS AND DISCUSSION

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 filed (π) and components polarized perpendicular to the magnetic field (σ). 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 (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^- is the extinction coefficient of the light shifted to lower wavenumber (σ^- components) and ϵ^+ is the extinction coefficient of light shifted to higher wavenumber (σ^+ components). For the perpendicular configuration

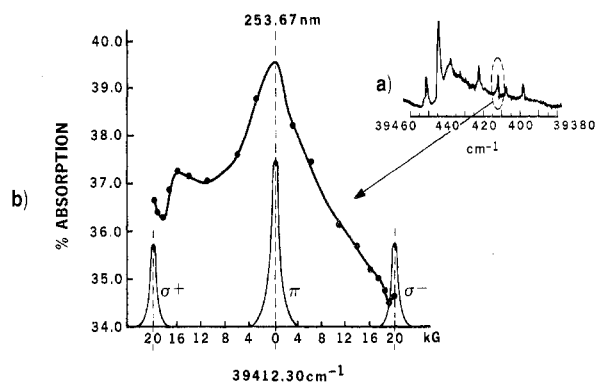$$\Delta\epsilon = \epsilon^\| - \epsilon^\perp$$

Figure 1. Benzene absorption and Hg Zeeman pattern at 253.7 nm: (a) absorption spectrum ref 3; (b) Zeeman scan (using isolated σ^+ and σ^- components) of region dotted in (a) and Hg Zeeman pattern at 20 kG (2.0 T).

where $\epsilon^{\parallel}$ is the extinction coefficient for light polarized parallel to the magnetic field (π components) and $\epsilon^{\perp}$ is the extinction coefficient for light polarized perpendicular to the magnetic field (σ^- and σ^+ components). The TALMS absorbance signal is equal to

$$S = \Delta\epsilon C l$$

where C is the concentration in mol/L and l is the cell length in cm. If these extinction coefficients were known as a function of wavelength, it would be a simple matter to calculate minimum detection limits for the TALMS technique. No such data exist for the very high resolution, i.e., narrow probe line width, utilized in the TALMS technique. Therefore, an efficient, semiquantitative estimation procedure must be used.

It is easier to estimate the relative magnitude of TALMS signals from photographic spectral intensities by using the parallel configuration since there are less Zeeman 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.

A coincidence of the Hg line at 253.7 nm with the benzene feature at that wavelength, which was previously reported (1), was verified. Figure 1 shows the experimental high-resolution absorption line shape (1) 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 T). With this Hg line a change in magnetic field of 10 kG (1.0 T) corresponds to a spectral scan of ca. 0.7 cm^{-1}. This scan was manually obtained with the TALMS instrument. 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 1, 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, for greater sensitivity 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.

A densitometer tracing of the benzene absorption spectrum from 252 to 253 nm obtained photographically with superimposed Co and Fe emission lines is presented in Figure 2. The benzene absorption in this figure is 70 times more intense than
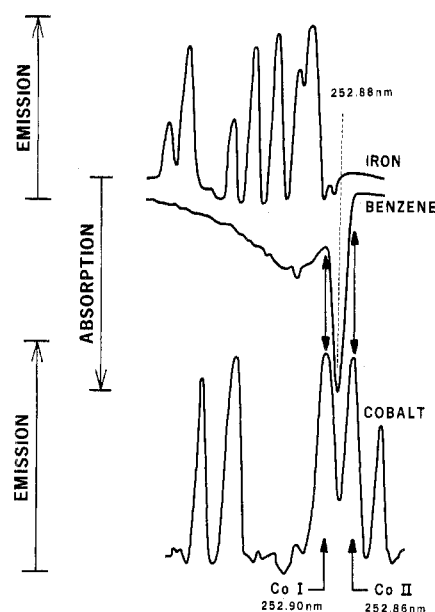

Figure 2. Medium-resolution benzene absorption spectrum and emission spectra of Co and Fe in the region of 252–253 nm.
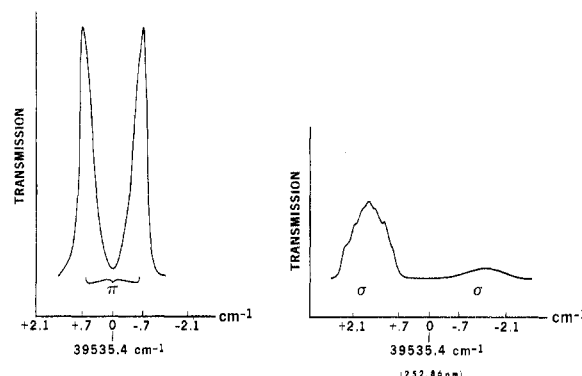

Figure 3. Absorption of the Co II Zeeman components at 252.9 nm by benzene: (left) π components; (right) σ components.

that at 253.7 nm (3). Two Co lines lie on either side of the sharp maximum at 252.88 nm (39534.6 cm^{-1}). The Fe lines are at higher wavelength and cannot be shifted onto the benzene maximum with reasonable magnetic fields. 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 will be from the Co II line. The extinction coefficient difference obtained by using the parallel configuration and this Co line is estimated from the Zeeman splitting and the photographic intensities to be 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 3 represents the absorption of the perpendicular (σ) and parallel (π) polarized components of the Co II line at a magnetic field of 27 kG (2.7 T) 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 1, when the TALMS signal is obtained with the Hg 253.7 nm line, the parallel (π) components are more absorbed by the vapor than are the perpendicular (σ) components. This is completely opposite from the Co II case;
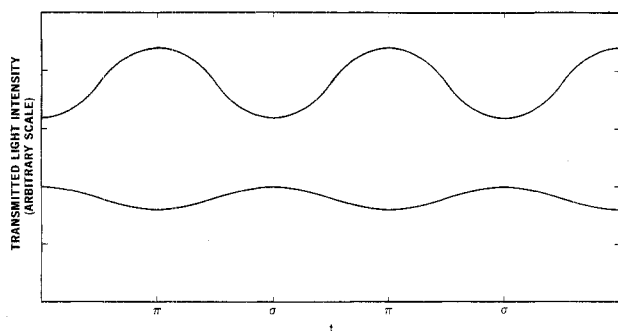
Figure 4. TALMS phase differences for benzene: (upper) 252.9 nm Co II signal at 2.7 T (27 kG); (lower) 253.7 nm Hg signal at 2.0 T (20 kG).
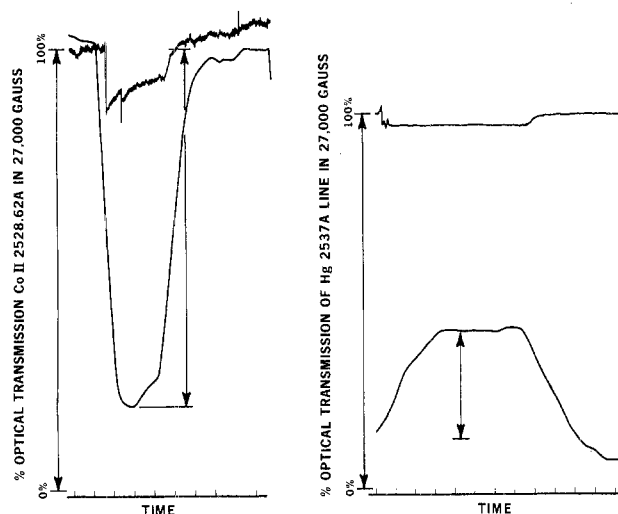

Figure 5. Benzene TALMS signal at Hg and Co II lines: (left) 400 μg of benzene, Co II 252.9 nm, 2.7 T (27 kG), gain = 1; (right) 400 μg of benzene, Hg 253.7 nm, 2.0 T (20 kG), gain = 10. The upper curves are transmission, as samples were injected into and then removed from the cell. The lower curves are the TALMS signals.

i.e., the two TALMS signals are 180° out of phase. Figure 4 illustrates the periodic change in the light intensity as the current controlled retardation plate 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° 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

$$S = 8.4Cl$$

while for the Co II line it is estimated from photographic plates that

$$S = \sim 100Cl$$

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

Figure 5 shows the experimental TALMS results. In each case 400 μg of benzene was injected as a pulse into a 15 cm path length cell. Note, there was a difference in gain of a factor of 10 between these two signals. 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 neglect of 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. The detection limit for benzene at the Hg line is ca. 300 ppmv in a 15-cm cell. Therefore, the detection limit at the Co II line should be 9 ppmv with the same length cell.

Registry No. Co, 7440-48-4; Hg, 7439-97-6; benzene, 71-43-2.

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