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James E. Lawler
University of Wisconsin, Madison, WI (USA)

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"UV/VUV High Sensitivity Absorption Spectroscopy for Diagnosing Lighting and Processing Plasmas and for Basic Data"

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UV/VUV High Sensitivity Absorption Spectroscopy for Diagnosing Lighting and Processing Plasmas and for Basic Data


Department of Physics, University of Wisconsin, 1150 University Ave., Madison, WI 53706 USA

Abstract. High sensitivity absorption spectroscopy involves the use of modern diode and CCD (charge coupled device) detector arrays to observe fractional absorptions of ultraviolet (UV) and vacuum ultraviolet (VUV) radiation as small as 0.00001. Stable arc lamps provide a continuum in some experiments, but experiments at very high spectral resolution or at VUV wavelengths require the greater spectral radiance of a synchrotron. Absolute densities of excited atoms, atomic ions, and molecular radicals are measured in both processing and lighting plasmas. Basic spectroscopic data needed for the analysis of astrophysical observations from the Hubble Space Telescope are measured using absorption of Fe\textsuperscript{+} in a hollow cathode discharge.

INTRODUCTION

Absorption spectroscopy has long been used to diagnose glow discharge plasmas. Although it lacks the spatial and temporal resolution of laser induced fluorescence, absorption spectroscopy provides absolute densities, a major advantage over other detection schemes. It is also useful for recording the spectra of atomic or molecular species that do not radiate because the excited level predissociates or is collisionally quenched. The measurement of absolute densities is often critical in an analysis of the ionization, power, or chemical balance of a glow discharge plasma.

Early absorption experiments often involved using one glow discharge (line emission source) to diagnose another glow discharge (absorbing sample). This approach is effective so long as the experimentalist has knowledge of the spectral line profiles in both discharges. Laser absorption spectroscopy offers superior spatial and temporal resolution but is not routinely used at far UV or VUV wavelengths, since the high order nonlinear effects required to shift the laser radiation to these short wavelengths usually degrades the amplitude stability of the radiation and limits the sensitivity of the experiment. It is also possible to use an arc lamp or a
synchrotron (continuum source) to diagnose a glow discharge (absorbing sample). Experiments of this type now achieve a remarkable sensitivity to very small fractional absorptions because of the use of diode or CCD detector arrays. The use of a detector array provides two key advantages over a single channel, sequentially scanned absorption experiment. First, a sequentially scanned spectrometer maps any noise or drift in the continuum source onto the spectrum and thus limits the sensitivity of the absorption experiment. A multielement array detects all spectral channels simultaneously and largely avoids this source of noise as long as the continuum does not change its spectral shape. Photon shot noise is then the primary limit on sensitivity. Second, a detector array rapidly accumulates good photon statistics in all spectral channels.

The following sections of this paper describe the use of detector arrays for high sensitivity absorption spectroscopy in the study of a Hg-Ar glow discharge lighting plasma, in the study of a H$_2$-CH$_4$ glow discharge used for chemical vapor deposition (CVD) of diamond films, and in the determination of atomic oscillator strengths for the analysis of astronomical data.

**Hg-Ar GLOW DISCHARGES**

Wamsley *et al.* experimented with the use of an intensified CCD array to perform high sensitivity absorption spectroscopy on Hg-Ar glow discharges very similar to the discharge in commercial fluorescent lamps (1). The discharge consisted of a 400 mA axial dc current passed through a 35 mm inside diameter fused silica tube containing 2.5 Torr of Ar and 5.2 mTorr of Hg. Although the positive column of fluorescent lamp discharges is fairly well understood, the negative glow and the Faraday dark space regions near the hot cathode are not so well understood. Cathodic phenomena limit the life of most fluorescent lamps.

Wamsley *et al.* used a Xe arc lamp as a continuum source, a 0.5 m focal length echelle spectrometer, and an image-intensified CCD array (1). Figure 1 is a schematic diagram of their experiment. The use of an echelle grating in high order produces a high resolving power, but requires a premonochromator to separate orders. This experiment achieved sensitivity to fractional absorptions of 0.001 with only 6 sec of integration, as shown in Fig. 2.

This experiment was motivated in part by an earlier single channel, sequentially scanned experiment (2). Phase-sensitive detection was used in the single channel experiment to discriminate against the line emission from the glow discharge and detect the continuum from a Xe arc discharge that had absorption features after transmission through the glow discharge. Wamsley *et al.* measured absorption of a resonance line at 194 nm to determine the absolute density of the ground level of Hg$^+$ and measured absorption of various lines at visible and near-UV wavelengths to determine the absolute density of excited 6$^3$P Hg atoms (2). The measurements were
FIGURE 1. Schematic diagram of the experiment used by Wamsley et al. to probe Hg-Ar discharges (1).

made in the negative glow, Faraday dark space, and positive column regions of an operating fluorescent lamp discharge. Wamsley et al. realized that the sensitivity of the single channel, sequentially scanned experiment was limited by shot noise (Poisson statistical noise) at 194 nm and was limited by arc lamp drift or low frequency noise at visible wavelengths, where the arc lamp is brighter. Both of these noise sources were suppressed in a second experiment that utilized a CCD detector array. The detector array made the improved experiment largely insensitive to arc lamp drift or noise and simultaneously accumulated good photon statistics in all

FIGURE 2. Absorption spectrum of the 404.7 nm transition of Hg obtained using the apparatus of Wamsley et al. (1) Note that sensitivity to a fractional absorption as small as 0.001 was achieved.
spectral channels.

Detector arrays usually cannot be "read out" rapidly enough to perform multichannel phase-sensitive detection. It is necessary to use a different technique to discriminate against the line emission from the glow discharge and detect the continuum from the arc discharge with absorption features after transmission through the glow discharge. Wamsley et al. demonstrated a digital subtraction technique to solve this problem. They also explored the relative spectral radiance of glow discharges, arc discharges, and synchrotrons. They found that under many conditions the spectral radiance of a glow discharge, even at the center of emission lines, is comparable to, or less than, the spectral radiance of an arc discharge. This is important because the signal from the glow discharge line emission must be comparable to, or less than, the signal from the arc discharge for the digital subtraction to be practical. The spectral radiance of synchrotron is much greater than either. The basic procedure used by Wamsley et al. involved recording a spectrum of the arc plus glow discharge emission and then a spectrum of the glow discharge by itself. The latter spectrum is subtracted from the former. The difference spectrum is then divided by a (dark count corrected) spectrum of the arc lamp continuum to eliminate effects from pixel-to-pixel variations in the detector array and from any structure in the arc lamp continuum (1).

These experiments used an image intensifier to provide precise electronic gating of the CCD array. Integration times must precisely match if one is to subtract two spectra and detect very small fractional absorptions. Mechanical shutters are not well suited to matching the integration times to part-per-million accuracy, although they are used to block the arc lamp during alternate spectra. Diode arrays provide such gating automatically during read out, but CCD arrays are somewhat less convenient because stored charge is moved across the CCD array during readout. The read out process can smear the spectrum unless precautions are taken. More recently Bergeson et al. have found that gating can be accomplished by using a frame transfer to a shielded part of the CCD array as described below (3). This approach is preferable because an image intensifier is both expensive and fragile.

The choice of a diode or CCD array must be based upon the expected light level of the experiment. CCD arrays are much more sensitive than diode arrays. A CCD array is typically required for an experiment with a spectrometer that has a very high spectral resolving power and a small etendue. A good scientific grade CCD array will have a read noise of 5 to 10 photoelectrons, while a good scientific grade diode array will have a read noise of 1500 to 2000 photoelectrons. A well designed experiment should collect signal photoelectrons rapidly enough to overwhelm dark noise and should collect sufficient signal photoelectrons during readout such that shot noise exceeds the read noise.

The goal of the work by Wamsley et al. was to understand the ionization balance of the cathode region of hot cathode Hg-Ar discharges (2). The results from the absorption spectroscopy experiment using the detector array were encouraging
because fractional absorptions of 0.001 were detectable. This represented an order of magnitude improvement over the sensitivity of the single channel, sequentially scanned experiment.

**CH$_4$ - H$_2$ GLOW DISCHARGES**

Childs *et al.* and Menningen *et al.* used high sensitivity absorption spectroscopy to study molecular radicals in CH$_4$ - H$_2$ glow discharges used for diamond film CVD (4-6). Glow discharges in molecular gases are widely used for plasma processing, such as (semiconductor) etching, film deposition, and various surface treatments. Measurements of molecular radical densities in these discharges requires high sensitivity because numerous rotational and vibrational levels of the molecule are appreciably populated, effectively reducing the density of absorbers for a particular transition. Growth of diamond and diamond-like carbon films in CH$_4$ - H$_2$ glow discharges, although not yet in widespread industrial use, is particularly interesting for study because of its great potential.

Childs *et al.* studied a discharge occurring between a 3 mm diameter tantalum tube, that served as the hollow cathode, and a 50 mm x 12 mm x 0.5 mm strip of silicon wafer, that served as the anode and growth substrate (4). The feed gas, a few percent mole fraction CH$_4$ in H$_2$, flowed through the hollow cathode at 40 sccm. A pressure of 0.0001 Torr was maintained and dc currents of 650 mA to 1.0 A were used. The optical apparatus consisted of a Xe arc lamp as a continuum source, a 0.5 m focal length spectrometer, and a diode array. Figure 3 is a schematic diagram of the experiment. The more modest spectral resolving power (without an echelle grating) and the resulting larger light flux enabled Childs *et al.* to use a diode array. Diode arrays, although less sensitive than CCD arrays, offer the advantage that the readout mechanism provides precision gating, as discussed earlier. A narrow band interference filter was used to reduce stray light in the spectrometer. The light shutter used to block the arc lamp continuum during alternate spectra is not shown in Fig. 3. Childs *et al.* (5) achieved sensitivities to fractional absorptions of 0.00001 and measured the absolute densities of several important molecular radicals, including CH$_3$ and CH, as shown in Fig. 4.

It is widely believed that CH$_3$ is a key gas phase precursor of diamond films under many conditions. This radical, like many polyatomics, cannot be detected using emission spectroscopy or laser-induced fluorescence because it dissociates when electronically excited. The CH$_3$ absorption feature at 216 nm is quite broad, about 1.2 nm (see Fig. 4), due to rapid dissociation. This allowed Childs *et al.* to open the entrance slit of the spectrometer to a spectral bandpass of 0.76 nm and achieve very high signal-to-noise ratios in the far UV using only an arc lamp continuum and a diode array. This experiment is sufficiently inexpensive and simple that it may ultimately be useful as a real time, *in situ* diagnostic in a production
FIGURE 3. Schematic diagram of the apparatus used by Childs et al. (4) to obtain absorption spectra in a hollow cathode dc discharge chemical vapor deposition system.

Measurements of the CH density are very valuable because the ratio of the CH to CH₃ densities, [CH]/[CH₃], is simply related to the hydrogen dissociation ratio, [H]/[H₂]. The fast, two body abstraction reactions, H + CH₃ → H₂ + CH₂ and H + CH₂ → H₂ + CH, are equilibrated in typical diamond CVD systems at pressures

FIGURE 4. Sample absorption spectra taken with the apparatus of Childs et al. (5) (a) The CH A²Δ → X²Π transition near 314 nm. Several R and P branch lines are visible to either side of the line-like Q branch. Note that sensitivity to a fractional absorption of 0.00001 was achieved. (b) The CH₃ B²Σ⁺ → X²Σ⁺ feature near 216 nm. The feature between 211 and 213 nm is a weak CH₃ absorption feature. The features below 205 nm are due to C₂H₂.
in the tens of Torr. Their reactions rates are sufficiently large to dominate diffusive transport and thus reach equilibrium at the local gas temperature. Both the rates of these reactions and the equilibrium constants, as well as most of the gas phase chemistry of diamond CVD systems, are well known because of earlier research on combustion systems. These basic ideas were used to determine the hydrogen dissociation ratio in a hot filament deposition system by Childs et al. (5) and in a glow discharge deposition system by Menningen et al. (6). Atomic hydrogen is a key radical in almost all diamond CVD systems. It plays many roles including: (a) driving the gas phase abstraction reactions which initiate the hydrocarbon chemistry as described above, (b) passivating the diamond surface to inhibit reconstruction into graphite, (c) opening growth sites on the passivated surface through surface abstraction reactions, and (d) preferentially etching graphite deposits as they form (7). A reliable, low cost, and fairly simple spectroscopic experiment for monitoring the hydrogen dissociation ratio is quite valuable.

Menningen et al. report using the CH and CH\(_3\) densities to determine the hydrogen dissociation ratio in a CH\(_4\) - H\(_2\) glow discharge used to grow diamond films. Menningen et al. also thoroughly explored the issue of detector array nonlinearity, which can affect the accuracy of digital subtraction (6).

Absorption spectra of CH as shown in Fig. 4 required sensitivities to fractional absorptions of about 0.00005. These sensitivities were achieved in integration times of less than 30 minutes. Research by Childs et al. and by Menningen et al. has led to a more quantitative understanding of the gas phase chemistry of diamond CVD.

**Fe HOLLOW CATHODE GLOW DISCHARGES**

Bergeson et al. are pushing the technique of high sensitivity absorption spectroscopy in the UV and VUV to the limits of existing technology (3). The scientific goal of their laboratory astrophysics experiment is to measure accurate oscillator strengths for Fe\(^+\) lines and lines of other atoms and ions in the UV and VUV. Relative absorption oscillator strengths from a common lower level are combined with emission branching fraction measurements to obtain very accurate sets of relative oscillator strengths. This somewhat redundant approach to determine relative oscillator strengths reduces the uncertainty in VUV emission branching fractions due to the difficulties of VUV radiometric calibration. The relative oscillator strengths are normalized using radiative lifetimes measured using laser induced fluorescence. This data is urgently need for the analysis of astrophysical spectra in the UV and VUV recorded by the Goddard High Resolution Spectrograph on the Hubble Space Telescope.
Bergeson et al. are using an intense Fe hollow cathode discharge (3). The cathode is 1.0 cm in diameter and 13.0 cm long and is lined with Fe. The discharge occurs in 1.2 Torr of Ar with currents up to 2.0 A. The very rich Fe and Fe\(^+\) spectra require extremely high spectral resolving powers at UV and VUV wavelengths. A 3 m focal length vacuum echelle spectrometer with a spectral resolving power of several hundred thousand is being used. The high spectral resolving powers and resulting diminished light throughput require an advanced VUV sensitive CCD array.

**FIGURE 5.** Schematic diagram of the apparatus used by Bergeson et al. (3) to measure oscillator strengths of various Fe\(^+\) transitions.

**FIGURE 6.** Sample Fe\(^+\) absorption (top graph) and emission (bottom graph) spectra obtained from the reference channel (1 m focal length spectrometer with an entrance slit width of 25 \(\mu\)m) in the apparatus of Bergeson et al. (3)
Synchrotron radiation from an electron storage ring provides the UV and VUV continuum. The 800 Mev, 200 mA storage ring with a 2.083 m magnetic radius provides a spectral radiance more than 1000 times greater than that of an arc lamp at UV and VUV wavelengths. Figure 5 is schematic of this experiment. A reference channel uses a 1 m focal length vacuum spectrometer with an 2400 groove/mm holographic grating and a diode array. This channel is used to monitor a reference line arising from the lower level of interest and chosen so that it can be resolved with the 1 m spectrometer. Error from possible drifts in the Fe hollow cathode discharge are avoided by simultaneously monitoring the reference line and the unknown line absorption.

Figure 6 shows sample emission and absorption spectra which demonstrate the resolving power and signal-to-noise ratio of the reference channel. Figure 7 shows sample emission and absorption spectra taken with the 3 m focal length echelle spectrometer and the CCD detector array. The Fe lines that are partly resolved near the center of Fig. 6 are completely resolved in Fig. 7. The 3 m focal length vacuum spectrometer with the 300 groove/mm echelle grating is used in 25th order and produces a reciprocal linear dispersion of 0.022 nm/mm. For comparison the 1.0 m focal length spectrometer with the 2400 groove/mm grating used in first order produces a reciprocal linear dispersion of 0.42 nm/mm.

The quality of the data and the broad applicability of this experiment indicate that it will be very important for laboratory astrophysics by producing accurate oscillator strength data. It will also be useful as a diagnostic in a variety of lighting and processing plasmas. Although this experiment cannot be described as simple or
inexpensive, it does offer the possibility of measuring absolute atom or ion column densities as small as $10^8 \text{ cm}^{-2}$. Such a column density corresponds to a density of $10^7 \text{ cm}^{-3}$ in a 10 cm long plasma. By comparison it is not easy to detect a density of $10^7 \text{ cm}^{-3}$ atoms or ions using laser induced fluorescence in a typical glow discharge due to background light from discharge.

**SUMMARY**

The development of multielement detector arrays such as photodiode arrays and CCD arrays has made it possible to greatly enhance the performance of absorption spectroscopy experiments. The measurement of the absolute densities of small numbers of atoms, ions, or molecular radicals in glow discharges has provided very valuable data for the understanding of lighting plasmas, chemical vapor deposition environments, and astrophysical spectra. The simplicity and relatively low cost of the basic apparatus, together with the high sensitivity achievable in such experiments, indicates that future application of the techniques described above to a diverse range of systems will yield many important and exciting results.

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**REFERENCES**