

To the Graduate Council:

I am submitting herewith a dissertation written by Priscilla Johnson Gannicott entitled "Atomic Fluorescence Spectrometry via Photofragmentation of Volatile Beta-diketonate Chelates." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.



Earl L. Wehry, Major Professor

We have read this dissertation
and recommend its acceptance:





Accepted for the Council:



Vice Provost
and Dean of the Graduate School

ATOMIC FLUORESCENCE SPECTROMETRY VIA PHOTOFRAGMENTATION
OF VOLATILE BETA-DIKETONATE CHELATES

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ABSTRACT

Laser-based atomic spectroscopic methods for trace metals analysis offer many advantages of potential use to the analytical chemist; namely, extremely high sensitivity and selectivity. The key to achieving high sensitivity is efficient sample atomization. An atomization reservoir that is highly efficient with minimal background interferences is desirable in the achievement of ultra-trace metals analysis and is the focus of the research described herein. Multiphoton ultraviolet laser photolysis was the method chosen to generate gas-phase metal atoms from volatile metal chelates. The resulting emissive fragments were detected via atomic fluorescence spectrometry. The performance of photofragmentation of volatile metal chelates as an alternative to more conventional atomization reservoirs for atomic fluorescence spectrometry was investigated.

Fluorinated beta-diketonate complexes of Fe and Ga and carbonyl complexes of Mo and Fe were volatilized into a high vacuum chamber and subsequently photolyzed by a 193 nm ArF excimer laser to generate metal atoms, which were then detected by atomic fluorescence spectrometry. Measurements of analytically significant parameters (limit of detection, linear dynamic range, precision and dependence of the atomic fluorescence signal on photolysis laser pulse energy) were performed with each of these metal complexes. Good precision, wide dynamic range and low limits of detection were observed in each case.

In cases in which predominantly ground state atoms were presumed to form in the photofragmentation process, probe laser excitation of these ground state atoms was performed in an effort to improve even further the sensitivity of the technique. Measureable signal enhancement over the use of just the photolysis laser (193 nm) was observed in the cases of bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedione)diaquo copper (II), iron pentacarbonyl and tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedione) iron (III). Probe laser excitation was found to be only minimally useful for tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedione) gallium (III). No

measureable signal enhancement was observed with tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedione) chromium (III). The usefulness of the second (probe) laser in terms of sensitivity improvement was determined to be dependent on the compound under study, at least under the experimental conditions employed here. For those metal complexes which benefited from probe laser excitation, analogous figures of merit to those performed for the one-laser (193 nm) experiments (dependence of laser-induced fluorescence (LIF) signal on sample pressure, dependence of LIF signal on photolysis laser pulse energy and precision of the LIF signal) were measured.

The utility of laser photolytic atomic fluorescence spectrometry for superior limits of detection of metal-containing "real" samples in both solution and solid form was investigated. Determination of the concentration of metal ions in an aqueous solution via photofragmentation fluorescence spectrometry involved direct complexation of the analyte metal ion(s) in a sample with a beta-diketone ligand (1,1,1,5,5,5-hexafluoro-2,4-pentanedione or 1,1,1-trifluoro-2,4-pentanedione), volatilization of the resulting metal chelate into a high vacuum chamber, and laser photolysis of the gaseous chelates resulting in emissive fragments which were detected via their fluorescence. It was found that aqueous solutions (specifically Fe^{3+} , Cu^{2+} and Cr^{3+}) containing metal ion concentrations lower than ca. 10^{-5}M were incapable of detection, presumed to be as a result of the unfavorable characteristics of the chosen ligands when directly reacted with aqueous solutions.

Solid samples containing trace amounts of metals (specifically, NIST standard reference materials: aluminum casting alloy SRM 855a, silicon metal powder SRM 57a and bovine liver SRM 1577) were subjected to direct complexation with the ligand hfa (1,1,1,5,5,5-hexafluoro-2,4-pentanedione). The resulting volatile metal chelate(s) were volatilized and photofragmented via 193 nm laser radiation. The resulting metal atoms were detected via their fluorescence. Detectable atomic fluorescence signals generated from the 193 nm photolysis of an aluminum casting alloy and a silicon metal powder sample after being treated with hfa were observed. Detectable atomic fluorescence signals were not observed from the 193 nm laser photolysis of

the gaseous vapor produced as a result of complexation of hfa with metallic constituents of bovine liver.

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CHAPTER 1

INTRODUCTION

1. Atomic Fluorescence Spectrometry

a. Principles of Atomic Fluorescence Spectrometry (AFS)

Atomic fluorescence occurs when an atomic vapor absorbs radiation of a characteristic wavelength from an excitation source and the resulting excited atoms undergo radiational deactivation over a very short time period (on the order of nanoseconds) (1). The measured fluorescence signal is observed at wavelengths characteristic of the atomic species present. The emission can occur at the same wavelength as that of the excitation source, at a longer wavelength or, in rare instances, at a shorter wavelength (1).

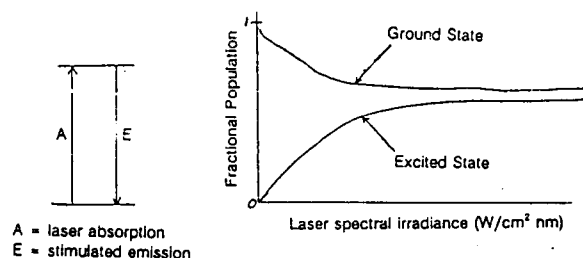
Assuming that an atom has only two energy levels (ground state and first excited state), the simplest expression for the fluorescence radiance (units: W/m^2 per unit solid angle in steradians) is given by

$$B_F = (l/4\pi)Y_{21}E_{\nu_{12}} \int \kappa_{\nu} d\nu \quad (1.1)$$

where l = path length (units: m) in the direction of the detector, Y_{21} = quantum efficiency for fluorescence, $E_{\nu_{12}}$ = spectral irradiance (units: $Wm^{-2}Hz^{-1}$) of excitation source radiation at the absorption line of ν_{12} , and $\int \kappa_{\nu} d\nu$ (units: $m^{-1}Hz$) is the absorption coefficient integrated over the absorption line (2). The most important conclusion that can be reached upon inspection of this equation is that the fluorescence radiance (B_F) is linearly dependent on the excitation source intensity and fluorescence quantum efficiency. However, if a very powerful source (e.g. a laser) is used to excite the atoms, then saturation of the upper state can be achieved, in which case,

B_F is independent of the excitation source irradiance and fluorescence quantum efficiency.

Atomic energy level saturation can be achieved when the populations of an atom's upper and lower state become equal (3) :



As the incident laser radiation upon a group of atoms is increased, a greater number of atoms is excited and are subsequently capable of depopulation via collisional deactivation (radiationless process), resonance fluorescence or stimulated emission. At low incident light levels, stimulated emission is infrequent due to the low concentration of excited atoms. However, at high laser irradiance, upward and downward transitions occur at equal rates, and the process of stimulated emission occurs more frequently than resonance fluorescence or collisional deactivation. This is a highly desirable situation from an experimental standpoint. Laser saturation of the fluorescence excitation transition is desired for several reasons: (a) the atomic fluorescence signal is maximized (under conditions of saturation, an atom is capable of emitting as many as 10^8 photons/sec) (b) a reduction of signal dependence upon laser intensity fluctuations is observed and (c) the fluorescence becomes less susceptible to quenching by other species (3).

In the course of an atomic fluorescence experiment performed under conditions of laser saturation of the quantum transition, as discussed directly above, multiple reradiation of photons can occur. That is, one atom is capable of cyclically interacting with the laser radiation, the result of which is the spontaneous reradiation of the absorbed radiation (multiple photon emissions) (4). The exact scheme by which this can be realized is dependent on both the energy level structure of the atom in question as well as the spectrum of the exciting laser

radiation (4). This reradiation process results in a substantial increase in the number of photons emitted by an atom that can be detected, which is one of the foremost attractions of laser-excited atomic fluorescence spectrometry.

From Equation 1.1, it is evident that, in the limit of low absorbance, B_f is linear in the concentration of atoms in the reservoir which give rise to the signal. An analytical calibration curve [$\log(B_f)$ vs. $\log(\text{analyte concentration})$] is generally constructed which can be used to relate relative fluorescence signal intensity to analyte atom concentration. A linear response over a wide range of concentrations is typically attained. The linearity between the intensity of the fluorescence with the concentration of analyte atoms at low concentration levels makes AFS a particularly useful method of trace metal analysis.

In summary, the fluorescence signal intensity depends primarily on the intensity of the source radiation at the exciting wavelength, the analyte concentration in the atomizer which is irradiated by the source, and the fraction of source radiation that is absorbed (5). To a lesser extent, the fluorescence signal intensity can also depend on the amount of re-emitted self-absorbed fluorescence radiation in the atomizer, but only under conditions of high analyte concentration (5).

b. General Objectives of AFS as a Method of Trace Analysis

Over the past several decades, the development of atomic fluorescence spectrometry (AFS) as an analytical tool has been directed toward the practical realization of potential benefits over atomic absorption and atomic emission spectrometry for trace analysis. These potential advantages include improved limits of detection, an extended linear dynamic range and the potential for simultaneous multielement analysis (5). For these benefits to be experimentally realized, a high intensity excitation source and an atomization reservoir that is highly efficient with minimal background interferences are necessary. Inasmuch as lowering the limits of detection is the fundamental goal, the sample must be efficiently dissociated into free atoms and

the signals resulting from the ensuing atoms must be distinguished from any interfering signals. There are three basic approaches to this task: differentiating between the atomic fluorescence and interfering signals based on the temporal characteristics of atomic fluorescence, developing new methods for atomization of samples, and trapping the atoms so that the longer observation period will make excitation and detection more efficient (3). The focus of the research described herein is the initial development of an efficient atomization technique providing minimal background for atomic fluorescence spectrometry.

c. Traditional Methods for Performing AFS

There are two primary types of atomic fluorescence spectrometric configurations: non-dispersive and dispersive, of which the latter is currently dominant (6). In the case of dispersive instrumentation, a sample is atomized and then excited by an excitation source; the resulting atomic fluorescence is imaged onto collection optic(s) and dispersed through a monochromator. The fluorescence signal is detected (typically via a photomultiplier tube), processed electronically, and recorded. Attractive features of a dispersive configuration include the possibility of lower detection limits as a result of a very narrow radiational band-pass that the detector sees, and a reduction in detected background chemiluminescence from the atom cell. The disadvantages inherent in a dispersive system are the expense of the monochromator and a decreased optical throughput.

In a non-dispersive system, a line source of radiation passes into an atom population that is created by an atomizer. The resulting atomic fluorescence is then detected with a photomultiplier tube (typically solar-blind). Phase-sensitive detection is often employed and concave mirrors tend to improve the signal collection efficiency (5). Generally, a non-dispersive system can only be relied upon if very pure single element line excitation sources are used because the source itself serves as the sole wavelength discrimination device. Therein lies the primary disadvantage of a non-dispersive configuration, because the wide band-pass of radiation

that the detector sees may result in severe non-specific background interferences, which leads to a corresponding degradation of the signal to noise ratio. However, the advantages that accrue from the use of a non-dispersive configuration are higher optical throughput and the fact that the instrumental components (other than the source) are relatively inexpensive (5).

Excitation sources generally used in AFS include vapor discharge lamps, hollow cathode lamps, exploding wires, electrodeless discharge lamps and lasers (2,5). Since achieving very low limits of detection is currently the most active area of emphasis in atomic fluorescence, a pulsed laser excitation source exhibiting a high duty factor (defined as laser repetition rate $\times$ pulse width) is preferred, if cost is not a factor. Moreover, in order to achieve the lowest detection limits possible, the fluorescence excitation transition must be optically saturated, which is generally only feasible if a laser excitation source is used (7).

Atomization reservoirs reported in the literature include flames (e.g., H_2 -based, nitrous oxide, and inert gas-sheathed air/acetylene or nitrous oxide/acetylene), inductively coupled plasmas, electrothermal atomizers, cathodic sputtering and hollow cathode glow discharges (7). Though most of the initial work dealing with analytical atomic fluorescence spectrometry employed flame atom cells, flame atomizers for atomic fluorescence are currently of very limited use, due to problems of high background emission, quenching of the fluorescence due to flame constituents (e.g., CO, CO_2 , and N_2), and the significant dilution effect of the sample by the flame gases (1). The inductively coupled plasma exhibits very high atomization efficiency and, thus, relative freedom from scatter. However, intrinsic atomic emission is produced in plasmas and can complicate the applicability of plasmas to ultra-trace metal analysis. The fact that ionization of metal atoms often occurs with high efficiency in a plasma can also be a shortcoming, although, for some metals, the monovalent ion exhibits a higher fluorescence efficiency than the neutral atom (8).

Cathodic sputtering methods for producing a metal atom population have found application for solid metallic samples, particularly metal alloys (9). A cathodic sputtering

chamber contains a sample (typically metallic, in the form of a flat specimen) which is connected as the cathode. The chamber is filled with a rare gas and a d.c. glow discharge is initiated. Positive ions striking the cathode sputter metal atoms off the surface of the sample after which the atomic fluorescence signal is measured (1). A hollow cathode glow discharge created in a hollow cathode lamp as an atomization reservoir has recently been used to obtain an extremely low detection limit for lead (1.8 ag), and offers a low quenching environment for atomic fluorescence measurements (7).

Currently, electrothermal atomization devices are the most popular atom cells in AFS, exhibiting several advantages: (a) high sampling efficiency (the atomization process is more efficient, particularly when compared to that of a flame cell), (b) the average residence time of atoms in the optical path is at least 1 s, so the viewing time is increased as compared to that of other atomization devices, (c) unusually high sensitivity is obtained for small volume samples (e.g. 5-100 μ L), (d) small amounts of analyte are required (10^{-8} - 10^{-11} g), and (e) solids can often be directly analyzed (1,2). However, electrothermal atomizers may suffer from intense background emission from the atomizer surface, but this can be circumvented if the fluorescence is measured in the uv region, where this emission is usually negligible (10). Additional shortcomings of electrothermal atomizers may be decreased precision and memory effects, possibility of scatter of the source radiation as a result of the condensation of vaporized samples in the light path, and potential matrix interferences (e.g., analyte-matrix and/or analyte-graphite surface interactions) (1). Nevertheless, it is a well-documented fact that the lowest detection limits for many metals to date have been achieved via laser-induced fluorescence with electrothermal atomization (10).

An alternative to conventional procedures for atom production in atomic fluorescence, as described above, is multiphoton ultraviolet laser photolysis. This technique, referred to as "laser-photolytic fragmentation fluorescence spectrometry" is described in detail in the following section.

2. Laser-Photolytic Fragmentation Fluorescence Spectrometry

a. Introduction

It is possible to utilize the technique of laser-photolytic fragmentation fluorescence spectrometry (LP-FFS) to convert non-fluorescent compounds into luminescent fragments, thereby extending the applicability of fluorescence spectrometry to virtually all organic and organometallic compounds of interest. This method of analysis is based on the production of atomic and/or simple molecular fragments (e.g. CH, CN, CO, C₂, Cu, Ga, Fe) via laser photolysis of a sample (11). Fluorescence is the dominant de-excitation process for many small molecules because they possess few vibrational degrees of freedom, thereby limiting competing radiationless decay pathways. Atomic fragments, produced upon laser irradiation, are the focus of the work described in this dissertation. Herein is described a project in which metal atoms are generated by the multiphoton dissociation of volatile organometallic compounds. Fluorescence spectroscopy is used to detect the production of these atoms.

The initial development of "laser photolytic atomic fluorescence spectrometry" (hereafter denoted LP-AFS) was the objective of the research described in this dissertation. LP-AFS is a special case of LP-FFS, wherein the atomic photoproducts produced upon multiphoton laser photolysis are of interest. LP-AFS should be capable of detecting metal atoms in trace quantities and serve as a useful alternative to conventional atomic spectrometric methods. The principal practical considerations are the chemical conversion of a given metal-containing sample to the corresponding organometallic compound possessing a sufficiently high vapor pressure, thereby rendering it useful for analysis via LP-AFS, the efficient photolytic conversion of that vapor-phase species to metal atoms, and efficient excitation and detection of the fluorescence of those metal atoms.

In general terms, the overall procedure involved in metal analysis via LP-AFS is outlined as follows:

(a) A suitable complexing agent must be found to convert metal analyte ion(s) in a solid or

solution sample to a species amenable to vaporization (the photolytic production of metal atoms occurs with appreciable efficiency only in the gas phase).

(b) The metal complex, thus formed, must be introduced into a vacuum chamber in the gas phase, whereby photolysis (preferably at 193 nm) of that chelate results in the production of "bare" metal atoms.

(c) Finally, the photolytically produced metal atoms must be efficiently detected via laser-induced fluorescence.

b. Potential Advantages and Disadvantages of LP-AFS

The potential advantages of LP-AFS as compared with those of conventional atomic spectrometric methods to be evaluated and considered are:

(a) Matrix effects (multiplicative interferences) should be minimized in LP-AFS due to the low pressure regime in which the atoms are produced inside a vacuum chamber and the very short time (ns) that exists between the production and excitation of metal atoms. The opportunity for collisions with other species is decreased, compared with that existing in conventional atom cells (p.5).

(b) As compared with a plasma, flame, or electrothermal atomization source, scattering of incident laser radiation should be much less severe in LP-AFS, due to the relatively low number densities of species present.

(c) Background emission derived from ligand-derived molecular fragments in LP-AFS should be present but should not cause a major interference. There are often severe background emission problems associated with conventional atom cells (especially flames and plasmas). For instance, in flame atomizers, there is often significant background emission associated with the chemiluminescence of flame species (e.g. OH, C₂, CH and CN) (2). The inductively coupled plasma (ICP) as an atom cell exhibits significant spectral background produced by the hot plasma gases. Furnaces as atomization reservoirs generally have

blackbody background emission associated with the hot atomizer surface.

(d) Common interferences should be minimal in LP-AFS. For example, as a direct result of the high temperature environment, the ionization of many elements (e.g. alkali and alkaline-earth metals) is particularly efficient when a plasma atom cell is employed (3). As another example, furnace atom cells may exhibit sample matrix/analyte interactions that result in interference.

Some disadvantages are anticipated in LP-AFS; they are summarized as follows:

(a) The chelation of the metal ion(s) in a solution or solid sample must proceed rapidly and quantitatively for an accurate correlation between atomic fluorescence intensity and original metal ion concentration to be feasible.

(b) The ligand chosen for a chelation reaction must form very volatile complexes for LP-AFS to be feasible. (Fortunately, a significant literature exists on the studies of highly volatile metal complexes). This places an important constraint on the choice of ligand.

(c) Laser-based spectroscopic measurements often are relatively complex and costly, yet the use of two lasers might be absolutely essential for trace metal determinations in LP-AFS. A photolysis laser followed by a probe laser may be required in LP-AFS to selectively detect certain metals in the presence of photolytically generated ligand background fluorescence. A probe laser could possibly enhance the metal atom fluorescence and not the ligand-derived molecular fluorescence, thereby reducing the relative contribution of the latter to the background. Also, selective detection of desired atoms against the background of other atoms with overlapping spectral lines might require the use of two lasers.

(d) A limitation to resonance atomic fluorescence transitions in pump and probe LP-AFS may arise due to the collision-free environment inside the vacuum chamber. (See p.117 for further discussion). This factor could be troublesome because of the difficulty of measuring a fluorescence signal imposed on a broad background produced by laser radiation reflected from the sample chamber or other optical surfaces.

metals in analytically-relevant samples. The extremely high volatility of many metal carbonyls is the only attribute of interest for the work described in this dissertation.

d. Multiphoton Dissociation of Beta-Diketonate Complexes

Complexes of metal ions with beta-diketonate ligands exhibit extremely high volatility and marked thermal stability, attributes which will be described further on p.18. The multiphoton photochemistry of metal beta-diketonate complexes in the gas phase has been investigated by several research groups. For example, Tyndall et al. investigated the 248 nm multiphoton dissociation (MPD) of $\text{Cr}(\text{hfa})_3$ ($\text{hfa} = 1,1,1,5,5,5\text{-hexafluoro-2,4-pentanedione}$), (arene)chromium tricarbonyls, (bis(benzene))chromium and chromocene, coupled with fluorescence detection of the resulting Cr atoms (24). The authors observed extensive atomic Cr fluorescence and the absence of any molecular fluorescence except when $\text{Cr}(\text{hfa})_3$ was photolyzed (24). It was estimated that a minimum of 2-3 photons were required to form Cr atoms due to the high bond dissociation energy of the parent $\text{Cr}(\text{hfa})_3$ complex (24). Molecular fluorescence was also observed when $\text{Cr}(\text{hfa})_3$ was photolyzed, over the wavelength range from about 220 to 550 nm, with two maxima centered at 270 and 330 nm. The origin of this fluorescence was attributed to the ligand but was not investigated further by the authors. In another study, jet-cooled $\text{Cr}(\text{acac})_3$ [where $\text{acac} = 2,4\text{-pentanedione}$] has been studied by MPD/MPI, whereby two-photon uv excitation led to the production of ground state chromium atoms (38). No fragment other than the Cr atom was detected upon photolysis of $\text{Cr}(\text{acac})_3$; the threshold energy required for Cr atom generation was reported to be 9.73 eV ($78,500\text{ cm}^{-1}$) (38).

Transition metal (Cr(III) , Mn(II) , Fe(III) , Co(II) , Ni(II)) and lanthanide (La(III) , Ce(III) , Eu(III) , Er(III)) beta-diketonate complexes were photodissociated with 266 nm laser radiation and subsequently studied with MPI/mass spectrometric detection by Morris and Johnston (17). Mass spectrometric analysis showed exclusive production of M^+ (parent metal ion) and other small ions which suggested that dissociation of the parent produced neutral fragments which

c. Photochemistry Involved in the LP-AFS Technique

LP-AFS, as used to produce metal atoms in the gas phase, is based on the following general photolytic scheme, where ML_n is an organometallic compound :



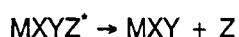
According to (A), a volatile organometallic compound (ML_n) absorbs $n \geq 1$ photons from a 193-nm ArF excimer laser, which ultimately produces neutral (M) and excited (M^*) metal atoms, as well as ligand-derived molecular photofragments. The electronically excited metal atoms can fluoresce, as indicated above in (C). In cases in which ground-state metal atoms are predominantly produced by the photolysis laser, a second (probe) laser is introduced to excite fluorescence from a specific atomic photofragment, as shown in (B) above. The final step is to relate the fluorescence signal intensity obtained to the initial concentration of the volatile organometallic compound.

The LP-AFS technique can readily be applied only to gas phase samples. In condensed phases, free metal atom generation is inhibited by the extremely high chemical reactivity of the metal atoms (12,13). In contrast, in the gas phase, ligands are readily lost, leading to the production of the bare metal atom which, once formed, should remain in residence in an atom reservoir long enough to be detected if the total pressure is sufficiently low. For LP-AFS, the original sample may be a solid or in solution form, as long as the constituent metal ions are capable of being chelated.

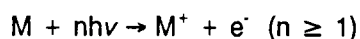
The photochemistry involved in the LP-AFS technique is generally "non-linear", meaning that the parent molecule absorbs more than one photon upon laser photolysis, resulting in a strongly non-linear dependence of fragment abundance on laser power (14). As a guide to

predicting how an organic or organometallic compound will behave when undergoing multiphoton excitation, a classification scheme has been developed by Robin and coworkers (14). Suppose that a parent molecule (MXYZ) is initially excited to a resonant state via absorption of one or more photons by the ground state, to form MXYZ^* . At this juncture, the excited parent molecule (MXYZ^*) may choose either of two paths. If the parent molecule exhibits "Class A" type behavior, it absorbs one or more additional photons, after which it is ionized to form the parent ion MXYZ^+ . Under conditions of high laser fluence, MXYZ^+ may be further excited by the absorption of one or more photons, leading to fragmentation to eventually form M^+ , X^+ , Y^+ , and Z^+ , as well as neutral fragments. This behavior is often exhibited by organic compounds (14).

The overwhelming majority of organometallic compounds follow "Class B" behavior, meaning that, after the initial excitation step to form MXYZ^* , the excited parent MXYZ^* immediately fragments, before absorption of additional photons, to form neutral species. If the products are photochemically unstable and they are one-photon resonant with the incident laser light, they may absorb additional photons, and may undergo additional fragmentation, ultimately resulting in production of atomic fragments:



If M absorbs one or more additional photons, it can be ionized :



In summary, under illumination by an intense photon beam, "Class A" molecules tend to ionize

first, followed by fragmentation, whereas the opposite is true for "Class B" type molecules. For some molecules, there is experimental evidence that supports the existence of both types of behavior, depending on the experimental conditions (14).

$\text{Cr}(\text{CO})_6$ is a representative example of the manner in which photodissociation results in the production of metal atoms, as studied by multiphoton ionization (MPI) (15). The proposed mechanism involves multiphoton absorption to a resonant dissociative state of $\text{Cr}(\text{CO})_6$, a metal-ligand charge transfer state ($^1\text{A}_{1g} \rightarrow ^1\text{T}_{1u}$ at an energy of 35800 cm^{-1} above the ground state) (15). This implies that photolysis via wavelengths $< 300 \text{ nm}$ requires one photon to reach the first dissociative state, whereas two or more photons are required if photoinduced by wavelengths $> 300 \text{ nm}$ (15). Once the dissociative state is reached, the processes of absorption and decarbonylation continue until free Cr atoms remain, which requires an overall energy of $\approx 82000 \text{ cm}^{-1}$ (15). The resulting Cr atoms then absorb 2-3 additional photons to produce Cr^+ , as detected by MPI. This is typical "Class B" behavior.

However, $\text{Cr}(\text{CO})_6$ does not indiscriminately follow "Class B" behavior in all cases, as this mechanism would tend to suggest. As an example, Fisanick et al. reported in a multiphoton dissociation (MPD) study of $\text{Cr}(\text{CO})_6$, $\text{Cr}(\text{CO})_3\text{C}_6\text{H}_6$, and $\text{Cr}(\text{C}_6\text{H}_6)_2$, whereby Cr^+ was observed in MPI-generated mass spectra in each case, that ionization followed fragmentation ("Class B" behavior) for each of these complexes at dissociation wavelengths longer than 400 nm (16). However, at dissociation wavelengths shorter than 400 nm , both Cr^+ and CrO^+ appeared in the MPI-generated mass spectra for each complex, which implied that complete dissociation to neutral fragments prior to ionization might not have occurred (16). These results suggest that, in some cases, there exists a dissociation wavelength dependence, so the Robin classification scheme (14) can be used only as a general model. Thus, the experimental conditions may dictate the nature of the photochemical processes of an organometallic compound. Nevertheless, "Class B" behavior is a useful model for understanding LP-AFS processes, whereby the production of neutral metal atoms by the multiphoton dissociation is desired.

Inasmuch as the photochemical processes involved in LP-AFS are non-linear, the copious literature on the subject of the multiphoton dissociation of organometallic compounds provides a theoretically sound basis for the implementation of this technique. Multiphoton dissociation of a wide variety of gas-phase metal complexes has been extensively studied and, upon uv or visible laser irradiation, most follow a similar photochemical route. One or more photons are absorbed by the parent compound, resulting in extensive dissociation that proceeds to the bare metal atom, which is usually produced within a picosecond time frame, even at moderate photolysis laser power (17,18). The technique of multiphoton dissociation (MPD) with multiphoton ionization (MPI) detection has shown that dissociation of organometallic compounds to ground and excited state metal atoms is very efficient as compared with competing ionization processes (19).

Organometallic compounds, especially metal carbonyls, exhibit broad, intense, absorptions, often to dissociative excited states, in both the ultraviolet and visible regions of the spectrum, so they are easily photodissociated by currently available laser sources (20). Excitation into these absorption bands results in a rapid loss of ligands; the shorter the photolysis wavelength, the more tendency there is for the loss of CO ligands from metal carbonyls (20,21). It can be inferred from these results that a 193 nm ArF excimer laser would be an efficient photolysis source for metal carbonyls as well as other organometallic compounds to be used as sources of gas-phase metal atoms. Refer to Table 1.1 [p.14] for representative examples of the successful generation of free metal atoms from metal carbonyls.

There are numerous organometallic systems other than the metal carbonyls which undergo multiphoton absorption in the uv and/or visible regions to produce metal atoms in high yield ("Class B" behavior), of which several are listed in Table 1.2 [p.15]. These examples are of interest inasmuch as metal carbonyls would not be a generally feasible choice for LP-AFS, because of the experimental difficulty in generating metal carbonyls from real metal-containing samples. Methods to generate metal carbonyls would be feasible for only a small number of

TABLE 1.1

METAL CARBONYLS FROM WHICH ATOMS HAVE BEEN PHOTOLYTICALLY GENERATED

Parent Compound(s)	λ (excitation) in nm	Detection Method	Ref.
W(CO)_6 ; Cr(CO)_6	363-585	MPI	21
Cr(CO)_6	248	fluorescence	18
Cr(CO)_6	193,248,351	fluorescence	22
$\text{Cr(CO)}_3(\text{C}_6\text{H}_6)$; $\text{Cr(CO)}_3(\text{CH}_3\text{C}_6\text{H}_5)$; $\text{Cr(CO)}_3[(n\text{-C}_3\text{H}_7)\text{C}_6\text{H}_5]$; $\text{Cr(CO)}_3[(t\text{-C}_4\text{H}_9)\text{C}_6\text{H}_5]$	248	fluorescence	23
Cr(CO)_6 ; $\text{Cr(CO)}_3\text{C}_6\text{H}_6$	355-500 ; 355	fluorescence	24
$\text{Cr(CO)}_3\text{C}_6\text{H}_6$	uv (unspecified)	MPI	25
Fe(CO)_5	uv (unspecified)	MPI	26
series of iron carbonyls	uv (unspecified)	MPI	27
Fe(CO)_5 ; Mn(CO)_{10} ; $\text{Mn(CO)}_5\text{Br}$; $\text{Fe(CO)}_3\text{C}_5\text{H}_5$	193,248	fluorescence	28
Mo(CO)_6 ; Cr(CO)_6 ; Fe(CO)_5	280	MPI	29
series of n-alkyl subst. arene chromium tricarbonyls	uv (unspecified)	MPI	30
$\text{Fe(CO)}_3\text{L}$ where $\text{L} = \text{C}_4\text{H}_6$; C_6H_6 ; C_8H_8 ; 3 isomers of C_8F_8	uv (unspecified)	MPI	31
$\text{Fe}_3(\text{CO})_{12}$; $\text{Ru}_3(\text{CO})_{12}$; $\text{Fe}_2\text{-Ru(CO)}_{12}$; $\text{FeRu}_2(\text{CO})_{12}$; $\text{Fe}_2(\text{CO})_9$; $\text{Fe}_2\text{Cp}_2(\text{CO})_4$; $\text{Fe}_2(\text{SCH}_3)_2(\text{CO})_6$	380-580	MPI	32
$\text{Mn}_2(\text{CO})_{10}$	363-585	MPI	33
Fe(CO)_5	366.5-370.0	MPI	33
Fe(CO)_5 ; $\text{Co(CO)}_3\text{NO}$; $(\text{C}_5\text{H}_5)\text{Co(CO)}_2$	uv (unspecified)	MPI/mass spec.	17

TABLE 1.2

ORGANOMETALLICS FROM WHICH ATOMS HAVE BEEN PHOTOLYTICALLY GENERATED

Parent Compound(s)	λ (excitation) in nm	Detection Method	Ref.
$\text{Ni}(\text{C}_5\text{H}_5)_2$	372.5-540.0	MPI	35
$\text{Ni}(\text{C}_5\text{H}_5)_2$; $\text{Fe}(\text{C}_5\text{H}_5)_2$	380-500	MPI	36
$\text{Fe}(\text{C}_5\text{H}_5)_2$	248 or 351 <u>and</u> 430-452	MPI	37
$\text{Pb}(\text{CH}_3)_4$; $\text{Pb}(\text{C}_2\text{H}_5)_4$; $\text{Fe}(\text{C}_5\text{H}_5)_2(\text{CH}_3)_2$	193	fluorescence	28
$\text{Zn}(\text{CH}_3)_2$	248	fluorescence	28

metals in analytically-relevant samples. The extremely high volatility of many metal carbonyls is the only attribute of interest for the work described in this dissertation.

d. Multiphoton Dissociation of Beta-Diketonate Complexes

Complexes of metal ions with beta-diketonate ligands exhibit extremely high volatility and marked thermal stability, attributes which will be described further on p.18. The multiphoton photochemistry of metal beta-diketonate complexes in the gas phase has been investigated by several research groups. For example, Tyndall et al. investigated the 248 nm multiphoton dissociation (MPD) of $\text{Cr}(\text{hfa})_3$ ($\text{hfa} = 1,1,1,5,5,5\text{-hexafluoro-2,4-pentanedione}$), (arene)chromium tricarbonyls, (bis(benzene))chromium and chromocene, coupled with fluorescence detection of the resulting Cr atoms (24). The authors observed extensive atomic Cr fluorescence and the absence of any molecular fluorescence except when $\text{Cr}(\text{hfa})_3$ was photolyzed (24). It was estimated that a minimum of 2-3 photons were required to form Cr atoms due to the high bond dissociation energy of the parent $\text{Cr}(\text{hfa})_3$ complex (24). Molecular fluorescence was also observed when $\text{Cr}(\text{hfa})_3$ was photolyzed, over the wavelength range from about 220 to 550 nm, with two maxima centered at 270 and 330 nm. The origin of this fluorescence was attributed to the ligand but was not investigated further by the authors. In another study, jet-cooled $\text{Cr}(\text{acac})_3$ [where $\text{acac} = 1,2\text{-pentanedione}$] has been studied by MPD/MPI, whereby two-photon uv excitation led to the production of ground state chromium atoms (38). No fragment other than the Cr atom was detected upon photolysis of $\text{Cr}(\text{acac})_3$; the threshold energy required for Cr atom generation was reported to be 9.73 eV ($78,500\text{ cm}^{-1}$) (38).

Transition metal (Cr(III) , Mn(II) , Fe(III) , Co(II) , Ni(II)) and lanthanide (La(III) , Ce(III) , Eu(III) , Er(III)) beta-diketonate complexes were photodissociated with 266 nm laser radiation and subsequently studied with MPI/mass spectrometric detection by Morris and Johnston (17). Mass spectrometric analysis showed exclusive production of M^+ (parent metal ion) and other small ions which suggested that dissociation of the parent produced neutral fragments which

were subsequently ionized (17). The authors estimated that the total energy required to dissociate the trivalent metal complexes and ionize the corresponding bare metal atom was 16.3 ± 1.4 eV ($131,000 \text{ cm}^{-1}$), which means that at least 4 266-nm photons were required for the dissociation/ionization process (21). The total ligand binding energy for $\text{Fe}(\text{acac})_3$ was estimated to be 8.4 ± 1.4 eV or an average binding energy of 2.8 eV per ligand (17).

"Two-color" (uv dissociation laser pulse followed by a visible ionization laser pulse) MPD/MPI-MS of jet-cooled acetylacetonato (acac) complexes of the first transition metals (Al(III), Sc(III), Mn(III), Fe(III), Co(III), Ni(II), Cu(II), Zn(II), Ga(III)) has been studied by Mikami et al. (12). The authors cited a previous paper (39) in which photodissociation of $\text{Cr}(\text{acac})_3$ using MPD/MPI with mass spectrometry was performed and it was determined that the neutral Cr atom was efficiently generated by 2-photon excitation with uv light ($\lambda = 242\text{-}258 \text{ nm}$) and, under these conditions, no other photofragments were observed (12). The threshold energy for the dissociation was reported as 9.74 eV ($78,600 \text{ cm}^{-1}$) (12). Mikami et al. found that $\text{Cu}(\text{acac})_2$ was the only compound that exhibited free metal atom generation similar to that earlier observed for $\text{Cr}(\text{acac})_3$ (12). $\text{Cu}(\text{acac})_2$ was dissociated with uv light ($\lambda = 280.5 \text{ nm}$), and the free metal atoms formed by the photolytic process were ionized with visible light. The mass spectra of the Cu(II) and Cr(III) complexes exhibited an extremely intense peak identified as the free metal ion, with few additional fragments.

In contrast, mass spectra of complexes of the other transition metals (Ga, Fe, Mn, Ni and Zn) showed a weak peak due to the free metal ion and an extensive fragmentation pattern. When the visible ionization laser was tuned to a wavelength that would be expected to induce ionization of the metal atom, one would have expected that the intensity, in the mass spectrum, of the free metal ion would have been dramatically enhanced as compared with those of other fragment ions. The Cu(II) and Cr(III) complexes exhibited such behavior, which suggests that the visible light ionized atoms which were prepared by UV photolysis. The other complexes did not exhibit this behavior; in those cases, uv radiation alone produced the metal ion and

additional fragments at the same time. It was concluded that free metal atom generation occurred in the Cu(II) and Cr(III) complexes, whereas fragmentation followed molecular ion formation in other complexes ("Class A" behavior according to the Robin classification scheme for organometallic compounds) (12).

e. Applications of LP-AFS

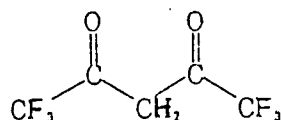
The technique of LP-AFS could be used for the determination of organometallic compounds or, in a more general way, for the generation of metal atoms for atomic fluorescence spectroscopy. As far as the latter is concerned, LP-AFS, as it applies to the detection of atomic fragments, has been reported. As an example, photofragmentation of bis-(1,1,1,5,5,5-hexafluoro-2,4-pentanedionate)Cu(II) [Cu(hfa)₂] by a KrF excimer laser ($\lambda = 248$ nm) resulted in the formation of ground state copper atoms, which were subsequently excited by a probe laser tuned to an atomic transition at 324.75 nm and detected by fluorescence (40). In another case, Oldenberg et al. have observed the atomic photofragment fluorescence generated from the photodissociation of gas-phase alkali chlorides (NaCl and KCl) (41). Atomic alkali emission was monitored at 589 nm for Na^{*} and 766 nm for K^{*}. The encouraging results reported by Oldenberg et al. for the application of LP-AFS for Na and K bodes well for the extension of this technique to many other metals.

3. Beta-diketones as Complexing Ligands in LP-AFS

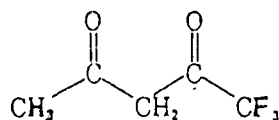
a. Chemistry of the Beta-Diketonates

Metal beta-diketonate complexes were chosen as the most feasible class of compounds for investigation via LP-AFS due to reports of unusual physical properties associated with them. It is crucial for a metal chelate as a candidate for study in the LP-AFS technique to be capable of being introduced into a vacuum chamber in the vapor phase. This criterion implies that such

a chelate possess high volatility, yet not thermally decompose at elevated temperatures that might be required to introduce it into the vacuum chamber. It is also important that the metal chelates chosen for LP-AFS be easily prepared and handled. Among the many beta-diketone ligands in existence, two were chosen for the research described in this dissertation due to reports of the exceptionally high volatility and thermal stability of their chelates with virtually all metallic elements (42). These ligands are 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfa) and 1,1,1-trifluoro-2,4-pentanedione (tfa), structures for which are given here:

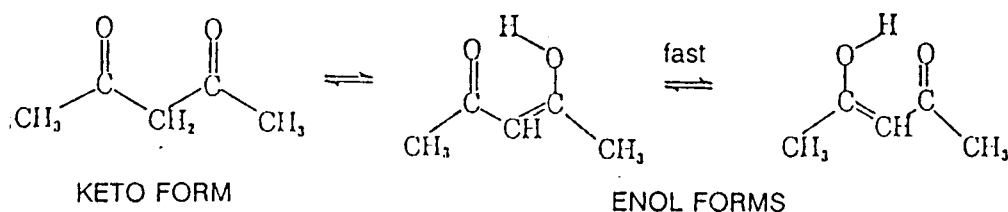


1,1,1,5,5,5-hexafluoro-2,4-pentanedione

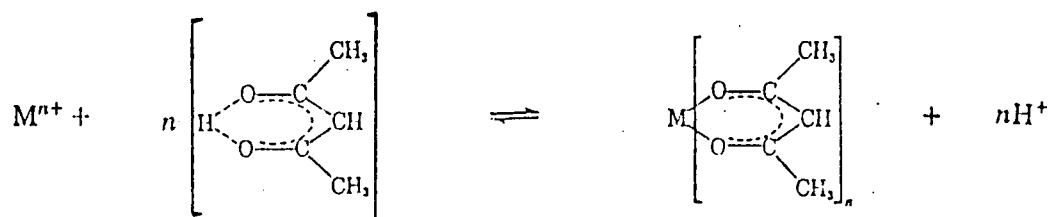


1,1,1-trifluoro-2,4-pentanedione

All beta-diketone ligands exhibit keto-enol tautomerism, which is an important characteristic, since it is the enolate ion that forms complexes with metals (43):

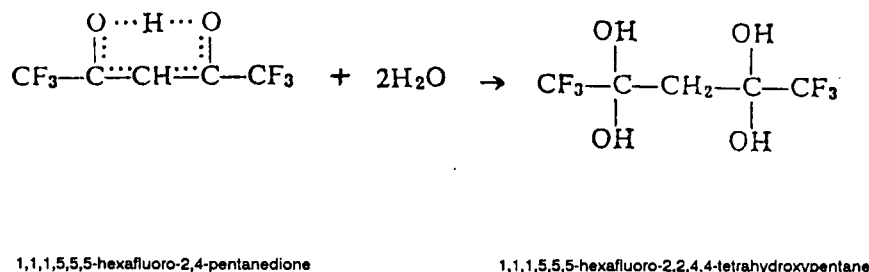


The enolic proton of the ligand can be replaced by a metal cation to form the metal chelate as shown :



The metal cation can react with $n \geq 1$ enolate ion(s) to form either a neutral or charged complex. An example of a neutral complex is $\text{Fe}(\text{hfa})_3$. An example of a complex that achieves the proper hexa-coordination by adduct formation with water is $\text{Ni}(\text{hfa})_2 \cdot 2\text{H}_2\text{O}$.

The hfa ligand, upon contact with water, forms a tetrahydroxy compound which is a poorer coordinating moiety as compared with the anhydrous enol (44,45):



Unfortunately, this situation results in experimental difficulty in quantitatively forming metal chelates in a metal-containing aqueous solution sample, as will be discussed further in Chapter 4.

The beta-diketone ligands (tfa and hfa) are known to react quantitatively with many metal cations (with high yield and purity) (46) and the synthetic procedures to form the metal chelates are straightforward, characteristics which make these ligands suitable for LP-AFS. Furthermore, beta-diketonate complexes have broad and intense ligand-metal charge transfer transitions throughout the vacuum and near-uv wavelength region (e.g. $\epsilon > 10^3$ in MeOH at $\lambda = 266$ nm for the following complexes: $\text{Cr}(\text{tfa})_3$, $\text{Fe}(\text{tfa})_3$, $\text{Co}(\text{tfa})_2$, $\text{Cr}(\text{hfa})_3$, $\text{Ni}(\text{hfa})_2$, $\text{Cr}(\text{acac})_3$, $\text{Fe}(\text{acac})_3$, $\text{Co}(\text{acac})_3$, $\text{Co}(\text{acac})_2$, $\text{Ni}(\text{acac})_2$, $\text{Eu}(\text{thd})_3$, $\text{La}(\text{thd})_3$, $\text{Ce}(\text{thd})_4$, $\text{Er}(\text{thd})_3$, and $\text{Eu}(\text{fod})_3$ where acac: 2,4-pentanedione; thd: 2,2,6,6-tetramethyl-3,5-heptanedione; fod: 6,6,7,7,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione (17)), so a 193 nm ArF excimer laser photolysis source should easily access these transitions.

b. Analytical Applications of Beta-Diketonates

Analytical applications of the beta-diketonates reported in the literature include gas chromatographic separations of metal ions (47,48) and trace metal determinations by GC/MS with isotope dilution (49). Applications involving "volatile metal chelate sampling" are of particular relevance insofar as LP-AFS is concerned. This terminology refers to the formation of a metal chelate from the reaction of a beta-diketone ligand and a metal-containing sample, its subsequent volatilization and, finally, its detection. A significant literature exists which describes the determination of metals by the formation, extraction and gas chromatographic separation of the volatile beta-diketonate chelates. For example, the quantitative determination of Cr^{3+} in blood and plasma by reaction with a trifluoroacetylacetone/benzene solution and analysis via electron capture gas chromatography has been reported by Hansen et al. (50). The hexafluoro ligand (hfa) was also employed, but its dihydrate hindered quantitative chelation of the Cr in blood and plasma. In another study performed by Wolf et al., the determination of Cr^{3+} and Be^{2+} as their trifluoroacetylacetonate derivatives at the pg level by gas chromatography with mass spectrometric detection was reported (51). Volatile hexafluoroacetylacetonates (mixed ligand complexes with hfa and neutral donors) have been introduced into a gas chromatograph (52,53). The determination of Be^{2+} in biological fluids, plant leaves and liver by gas chromatography/electron capture detection involved a chelation method with tfa/benzene, as investigated by Taylor et al. (54).

Gas chromatography (GC) coupled with non-spectroscopic detection for the analysis of beta-diketonates is not without its limitations. Electron capture detection of a gas chromatographic effluent is not specific for a given metal, depending solely on adequate chromatographic separation of the various chelates. Moreover, the fluorinated ligands can degrade detector performance (55). On-column degradation of metal chelates due to contact with the stationary phase and/or hot metal surfaces has resulted in unfavorable chromatographic characteristics for many metal chelates, of which $\text{Fe}(\text{hfa})_3$ and $\text{Fe}(\text{tfa})_3$ are

prime examples (55). Many investigators in this area have chosen to either divert the gc effluent (containing the metal chelate) into various spectroscopic detectors or to omit the separation step altogether. The latter is preferable for analysis via LP-AFS.

An example of a successful method for the introduction of volatile metal chelates into a spectroscopic detector has been reported by Black and Browner (56). The authors applied ICP-AES detection of the volatile beta-diketonate complexes of Fe(III), Cu(II), Zn(II), Al(III), Mn(II) and Cr(III) by introducing the chelate complexes (dissolved in xylene) into the spectrometer by pneumatic nebulization (56). Numerous other examples also have been described. Using volatile beta-diketonate sample introduction, the determination of Cr by AAS was successfully attempted by Castillo et al. (57). Batch injection of volatile trifluoroacetylacetonates of Al, Be, Cr, Cu and Fe into an ICP atomic emission spectrometer was studied by Fujinaga et al. (58), who found that $\text{Cu}(\text{tfa})_2$ and $\text{Fe}(\text{tfa})_3$ partially decomposed in the heated stainless steel tubing between the sample introduction device and the torch unless ligand vapor was added to the carrier gas. The determination of Be^{2+} by ICP-AES after thermal vaporization of its beta-diketonate complex (ligands = acac and tta) (59) and by gas chromatography/electron capture detection (ligand = tfa) (60) has been investigated by Measures and Edmond. Castillo et al. developed an electrically heated volatilization system for injecting, volatilizing and then detecting Cr^{3+} , Zn^{2+} and Mn^{2+} (chelating agent = acac) via AAS (61).

Chelation of a metal ion in an aqueous solution can be achieved by either of two methods. The metal ion of interest can be extracted from solution by a ligand dissolved in an appropriate water-immiscible solvent. The examples cited directly above involve this method of chelation. Alternatively, the solvent-extraction step can be eliminated by using "direct" chelation, which refers to performance of the reaction between a ligand and a metal ion by adding the ligand directly to the aqueous solution. For LP-AFS, a direct method of metal chelation is preferable in order to reduce the complexity of the analytical sampling procedure. Volatile metal chelate sampling as it applies to AFS in low temperature flames has been investigated by Rando

and Heithmar, which is one of the very few reported uses of beta-diketonates in atomic fluorescence spectrometry (62). $\text{Fe}(\text{tfa})_3$ was purged directly from aqueous samples into a flame, and detected via AFS, with a reported limit of detection of 0.10 ppb Fe (62). The successful applications of volatile metal chelate sampling bode well for the implementation of LP-AFS as an analytical tool.

Elimination of extensive sample preparation steps for solid samples (e.g. acid digestion or dry ashing) and containment of the sample in a closed atmosphere to reduce contamination are valid reasons for which a direct chelation procedure would be beneficial. For example, a method for preparing and introducing volatile beta-diketonates of Fe, Zn, Co, Mn and Cr for ICP-AE spectrometry was reported by Black and Browner (63). Direct chelation reactions (no organic solvent involved) were carried out with bovine liver, human blood serum, pure metals and/or metal salts, using the ligands hfa and tfa. The authors reported that the limitations of the technique included variable precision and a matrix and specific element dependency, difficulties in calibration caused by a need to use standard additions, the uncertainty in efficiency in the chelate/metal extraction, and the uncertain applicability to a wide variety of different metals (63). It will be necessary to address these issues in terms of their impact on the analytical utility of LP-AFS.

4. Research to be Described in This Dissertation

The possibility of analytical applications in the area of trace metal detection as a result of the multiphoton dissociation of gas-phase metal complexes are evident as described above. In this work, solid metal chelates were synthesized, and then vaporized and subjected to 193 nm photolysis, which unequivocally yielded "bare" metal atoms which were detected via atomic fluorescence spectrometry. The method was characterized by the determination of typical analytical figures of merit (e.g. limit of detection, linear dynamic range, precision, and laser power dependence). Pump and probe experiments were attempted for several of the solid

metal chelates; the pulsed photolysis laser (193 nm excimer) dissociated a volatile metal chelate into atomic and molecular fragments. Then, a probe laser pulse (delayed by a variable time interval) induced fluorescence from a resulting atomic photoproduct.

To investigate the analytical utility of LP-AFS for "real-world" samples, aqueous solutions and solid samples containing metal ions were studied. The first step involved chelation of the metals in a sample with a suitable ligand (e.g. 1,1,1,5,5,5-hexafluoro-2,4-pentanedione [hfa]). The resulting metal chelate was vaporized, subjected to 193 nm photolysis, and detected as described for the solid metal chelates. An attempt was then made to correlate the observed atomic fluorescence signal with the concentration of the metal ion in the corresponding metal-containing solid or solution sample.

CHAPTER 2

EXPERIMENTAL SECTION: SPECTROSCOPIC AND CHEMICAL PROCEDURES

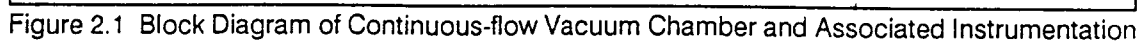
During the first phase of this research in which solid metal chelates were the subject of analysis, signal processing was handled without the aid of a laboratory computer. As research progressed into the phase in which volatile metal chelate sampling was introduced, additional instrumentation and computer interfacing became a necessity. Our research facilities expanded to include a pulsed supersonic valve sample introduction vacuum chamber. For reasons of clarity, the sections that follow will be separated into three major divisions. The first division will be devoted to a description of the instrumentation necessary to perform the high temperature metal chelate work. A continuous-flow vacuum chamber and a pulsed supersonic valve sample introduction chamber used in the course of this research will both be thoroughly described. A description of the instrumental capabilities prior and subsequent to the addition of the laboratory computer will be discussed as it applies. The second division will be devoted to a thorough description of the spectroscopic procedures employed to investigate the analytical figures of merit for the metal chelates for both one laser photolysis and two laser "pump-and-probe" experiments. A description of the chemical procedures involved in the course of this work, namely, chelate synthesis and volatile metal chelate sampling, will be discussed in the third major division.

1. Instrumentation

a. Continuous-flow Vacuum Chamber Design

A block diagram of a continuous-flow vacuum chamber and associated instrumentation can be seen in Figure 2.1 [p.27]. The fragmentation fluorescence vacuum chamber, fabricated by machine shop personnel at the University of Tennessee, consists of a stainless steel rectangular block (14 x 12.7 x 9 cm) which contains four circular ports and one o-ring sealed rectangular port (5.7 x 10.0 cm), the latter of which is well-suited for the adaptation of a variety of sample introduction devices. Three of the circular ports hold o-ring (Parker viton) sealed 2.5" o.d. fused silica windows (Grade 1000, Dynasil, Ringoes, NJ) through which the perpendicularly propagating laser beams as well as collected fluorescence can readily pass. The fourth circular port has been adapted to accommodate two pressure measuring devices : an ion gauge (Bayard-Alpert type, Huntington IK-150-SF) and a capacitance manometer (Model CMH-01S03, Vacuum General, San Diego, CA). Several ion gauges were interchanged throughout the course of this work due to deleterious effects of deposited metal films on the filaments. The filament was composed either of thoriated iridium or tungsten. The metal chelates tended to degrade the thoriated iridium filament quickly, so the tungsten filament was clearly more suitable. An ion gauge controller (Model RG-81, Veeco Instruments, Long Island, NY) was used for pressure measurement in the pressure regime of 10^{-4} to 10^{-7} torr. The capacitance manometer was controlled with a pressure readout unit (Model 80-6A, Vacuum General), useful in the higher pressure regime of 10^{-3} to 10^{-5} torr.

Interior baffles composed of stainless steel, designed to reduce laser scattering inside the chamber cavity, were installed. For the solid metal chelate work, the interior baffle dimensions for the excimer laser beam side measured 8 x 14 mm and for the probe laser beam side they were 9 x 28 mm. In contrast, the interior baffle dimensions used in the volatile metal chelate sampling work were identical (9 x 28 mm) for both sides due to a larger focal length of the photolysis laser entrance lens used in these experiments, requiring a larger beam pathway



through the chamber. For additional detailed information concerning the design of this particular chamber, refer to Schendel (64).

Toward the end of this research project, the chamber was slightly modified, as can be seen in Figure 2.2 [p.29], with respect to the laser beam entrance window ports. Stainless steel arm extensions, 6" in length, were installed on the existing laser beam window ports to reduce excessive light scattering by providing a longer laser beam path and decreasing the size of the windows to an outer diameter of 1.75".

b. Sample Introduction Devices

Several different sample introduction devices were used in the course of this work. In the early stages, solid metal chelate samples requiring the use of relatively high temperatures (~75-120°C) necessitated the sample introduction system depicted in Figure 2.3 [p.30]. This device was built in-house and consisted of a glass envelope made of two mated 1" kovar-to-glass stems (Model 7675-36, Ace Glass, Vineland, NJ) welded to a stainless steel plate which was positively sealed to high vacuum with an o-ring. A 0.75 mm i.d. length of glass-lined tubing (Scientific Instrument Services, Ringoes, NJ) was soldered to the stainless steel plug depicted in the figure. This design provided a way safely to resistively heat the glass-lined tubing through which the hot sample vapor was passing during an experiment. Approximately five grams of a solid metal chelate sample was placed in a 250 mL round-bottomed glass bulb and degassed via a rotary vane vacuum pump (Model 1405, Sargent Welch, Skokie, IL) by opening a rough pumping valve on-line. After a suitable degassing period, the sample was heated to an appropriate temperature, at which point the hot vapor was introduced into the sample chamber via a needle metering valve (Model 1315G4Y, Hoke, Cresskill, NJ). The entire sample line as pictured was wrapped in heating tape and further insulated by glass wool to provide for an even temperature distribution. The temperature of the heating mantle, controlled by a variable transformer, was always kept 10-15°C lower than that of the sample line to prevent

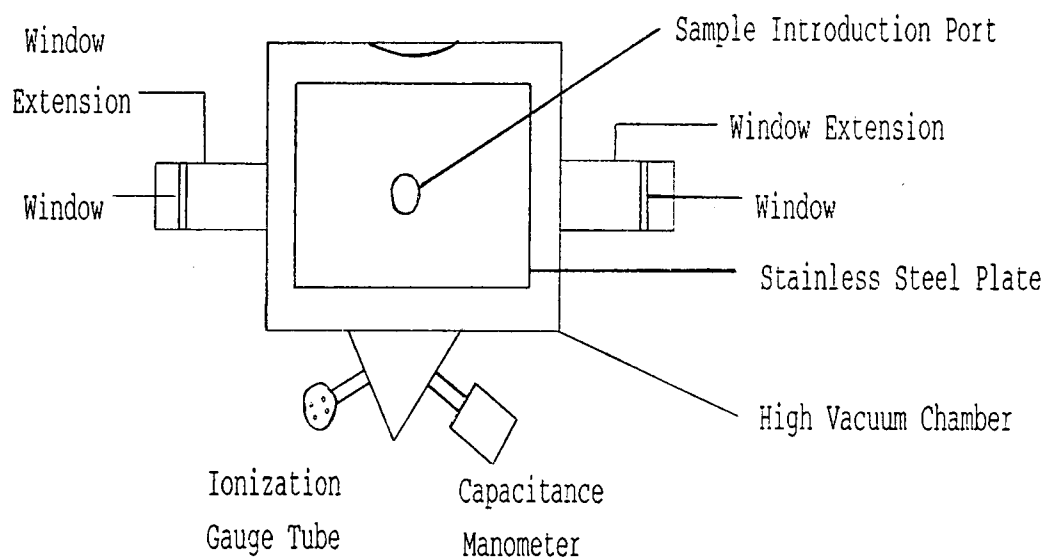


Figure 2.2 Side View of Continuous-flow Vacuum Chamber Modification Designed to Reduce Scattering

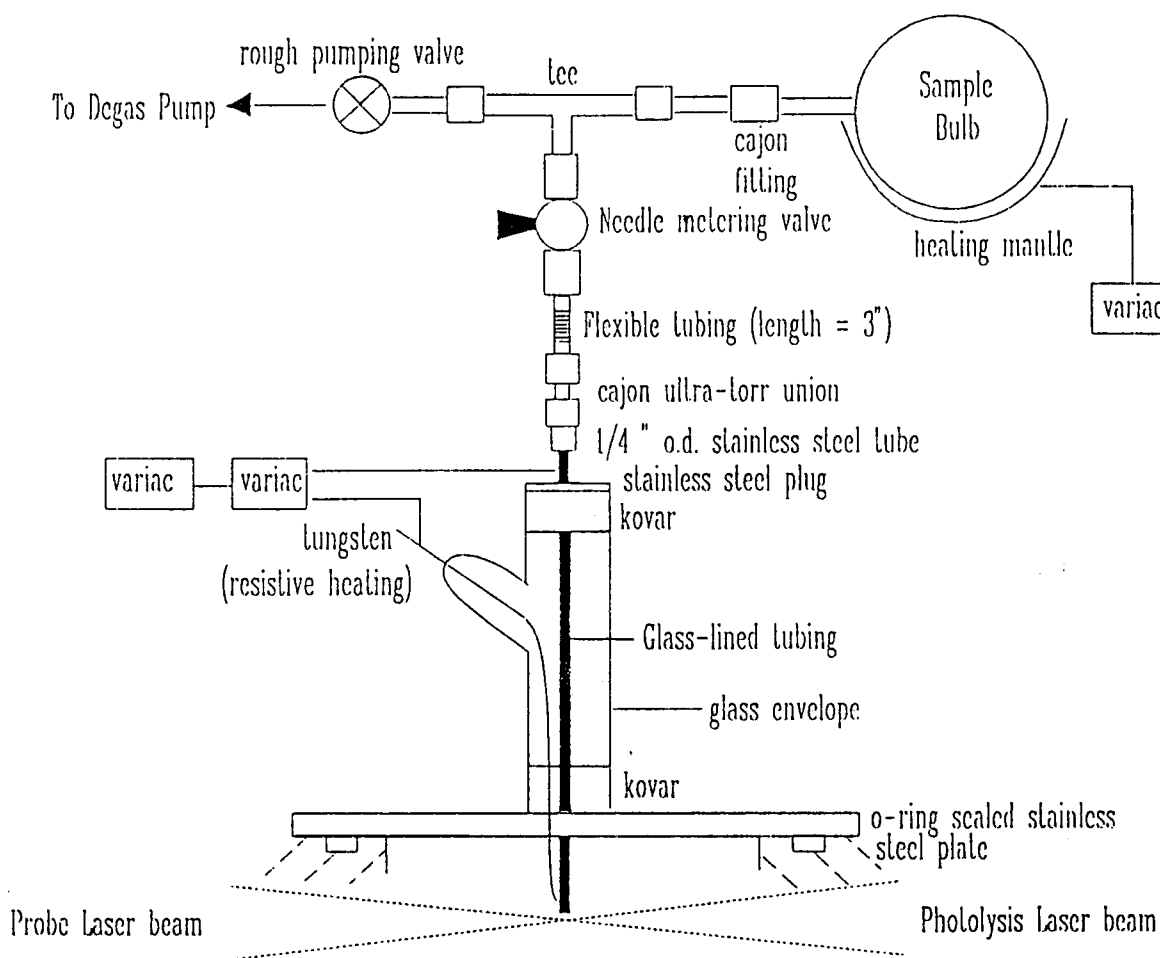


Figure 2.3 Diagram of the High Temperature Sample Introduction System used in LP-FFS

condensation of the sample in the line. A J-type thermocouple with a digital readout (Model 5TC-GG-J-30-36, Omega, Stamford, CT) was used to monitor the temperature of the sample and line throughout an experiment. The glass-lined tubing was resistively heated by using two variable transformers connected in series.

The volatile metal chelate sampling aspect of this research required a slight modification to this sample introduction device, as depicted in Figure 2.4 [p.32]. Unlike the pure metal chelates, in which case the sample size was "unlimited" and a significant vapor pressure was produced via the heating process, the solution work required a smaller sample vessel in which the chelation could take place as well as a reduction in the dead-volume in the sample introduction line. A 25 mL round-bottomed glass sample bulb equipped with a high vacuum valve was used as the "reaction vessel" in these experiments. As can be seen in Figure 2.4, a reduction in the dead volume was accomplished by a three way valve built by our glass shop personnel. A reduction in the number of fittings should also be evident by comparing Figures 2.3 and 2.4. As usual, the entire sample introduction device was wrapped in heating tape and insulated by glass wool. In Figure 2.5 [p.33], a final modification was made in an attempt to further reduce the dead volume in the sample introduction line. In this configuration, degassing of the sample was carried out off-line using an in-house built glass vacuum line equipped with a variety of different arms to which sample bulbs of varying neck sizes could be attached. Afterwards, the bulb could be sealed by the valve directly connected to the 25 mL sample bulb and placed on-line as pictured in Figure 2.5. The turbomolecular pump used for evacuating the high vacuum chamber was employed to evacuate the rest of the sample introduction line prior to the introduction of the hot sample vapor into the chamber. When solid samples (e.g., bovine liver, copper oxide, metal alloys, etc.) were directly chelated with ligand, a sample bulb (100 mL) with a larger surface area was more suitable, but in all other aspects, the sample introduction device was identical to that pictured in Figure 2.5.

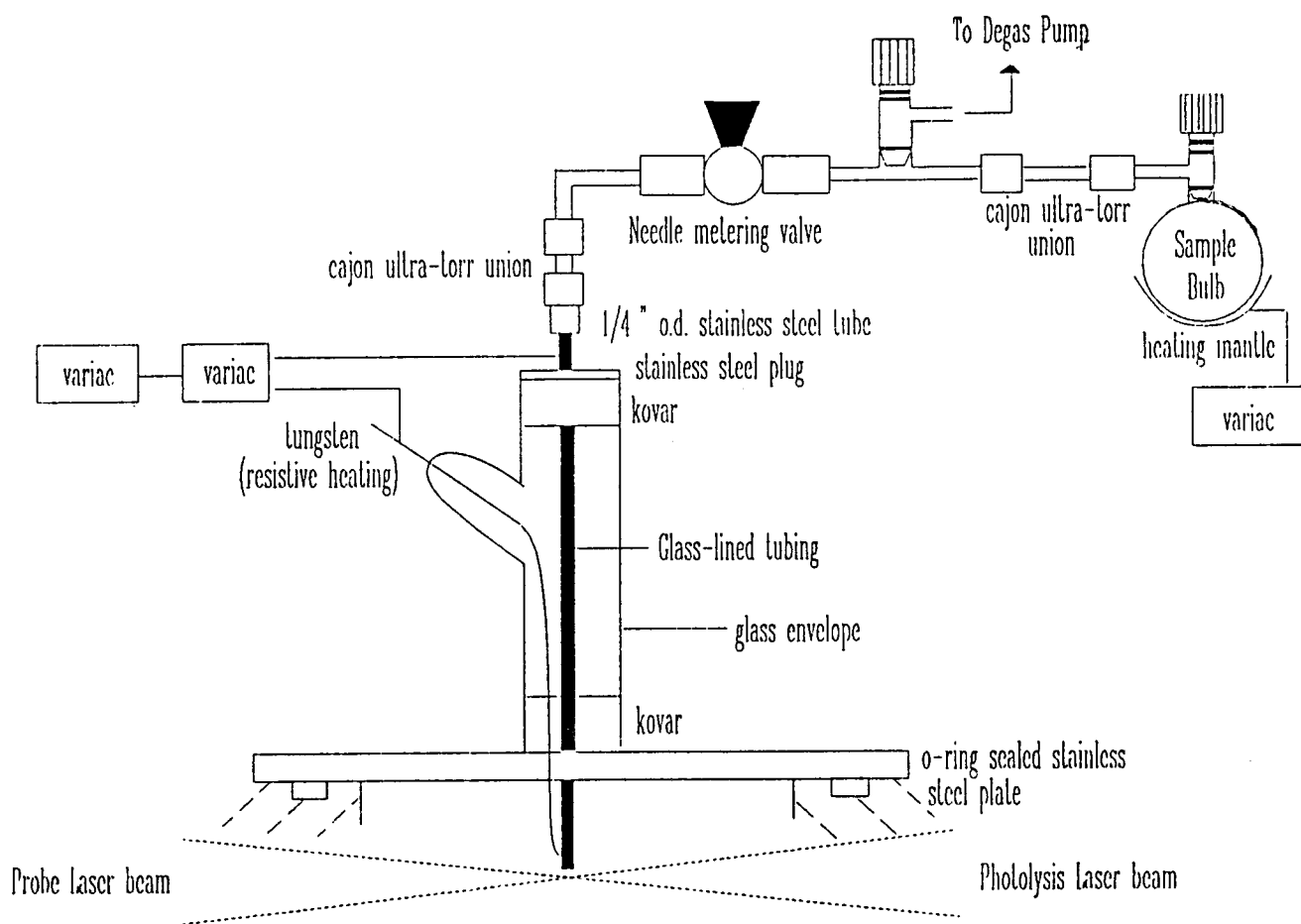


Figure 2.4 Modified Sample Introduction System for Volatile Metal Chelate Sampling

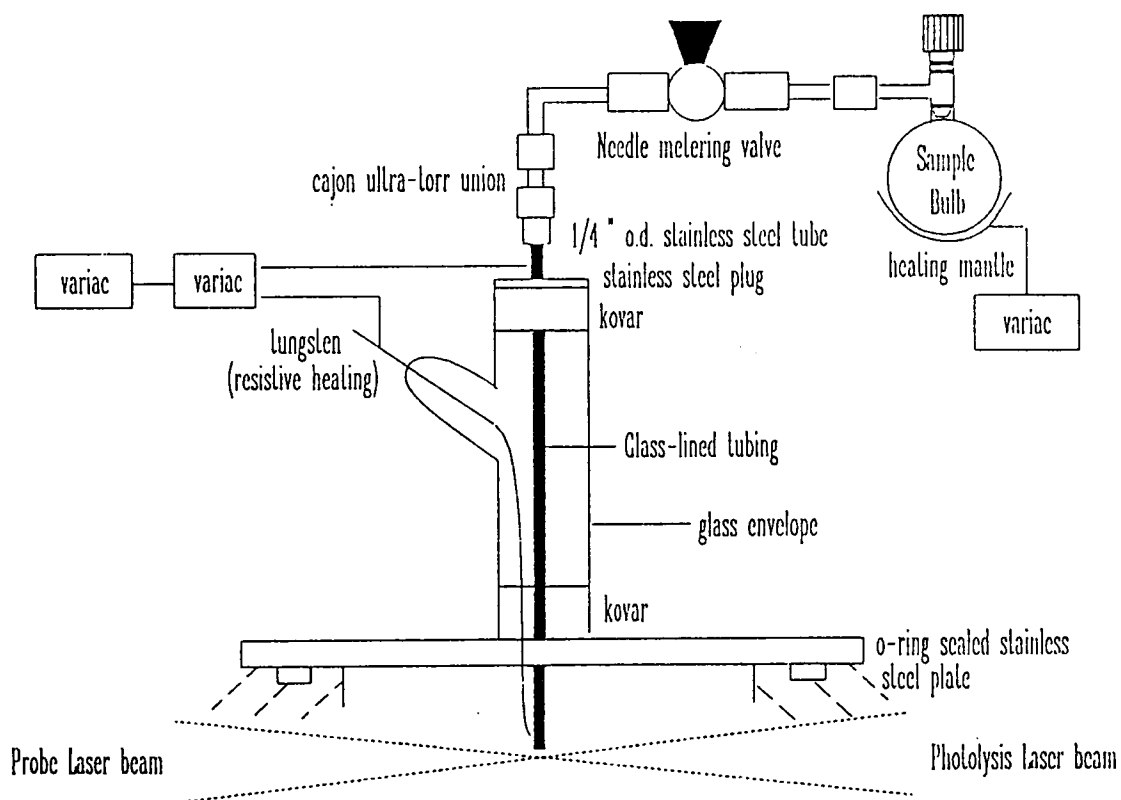
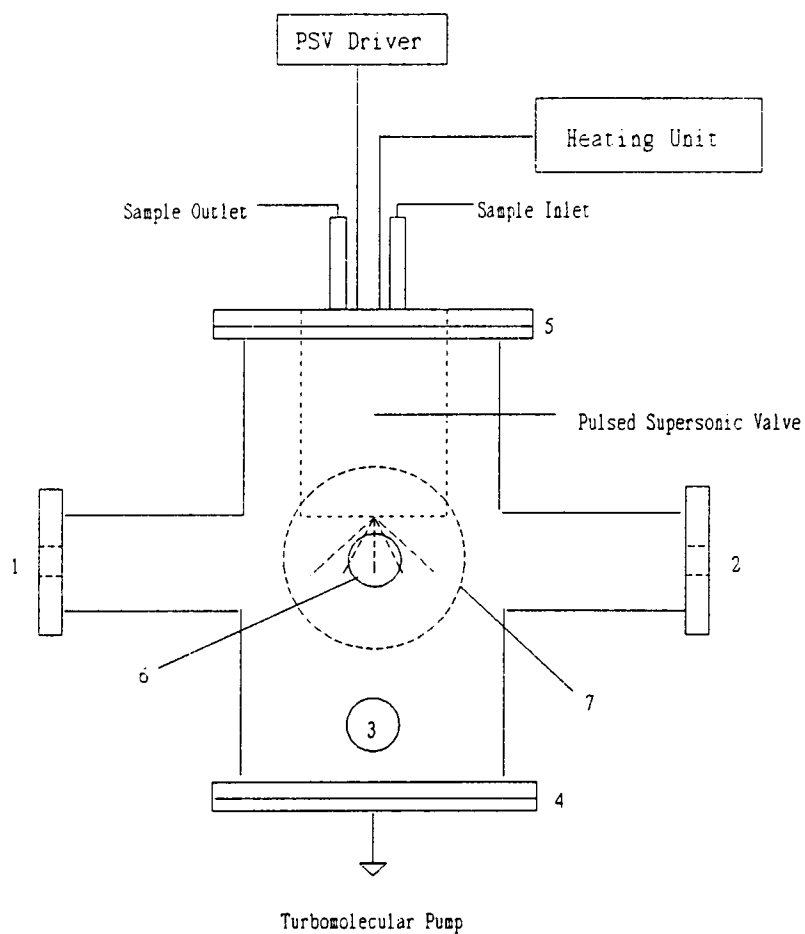


Figure 2.5 Final Modification of the Sample Introduction System used in LP-FFS

c. Pulsed Supersonic Valve Sample Introduction Vacuum Chamber Design

During the course of this research, some of the experiments were performed in a completely different vacuum chamber and sample introduction line than that which is described immediately above. A pulsed valve was used to introduce the sample under investigation to form a supersonic jet inside the vacuum chamber. The vacuum chamber used in conjunction with the pulsed valve sample introduction was fabricated from 304 stainless steel (MDC Manufacturing Inc., Hayward, CA) and consisted of a six-way cylindrical cross design that was modified in-house to incorporate seven different ports. An estimate of the chamber volume is 2.5 L. Refer to Figure 2.6 [p.35] for a diagram of this chamber. A fluorescence viewport contained a 2.75" o.d. pyrex window attached to the chamber by a 4" flange. A two-laser alignment viewport contained a window through which one could observe laser-induced fluorescence in order to optimize parameters and properly overlap the two lasers for "pump-probe" experiments. The photolysis and probe laser viewports each contained a removable 1.75" fused silica window (Grade 1000, Dynasil) that was sealed by an o-ring to a 6" flange. An ion gauge port held an ionization gauge tube (tungsten filament type) used for the measurement of pressure in the chamber, as discussed previously. An 8" flange connected the chamber to the turbomolecular pump, which was identical with the vacuum system to be discussed for the continuous-flow vacuum chamber, p.36.

The top of the chamber contained an 8" flange which held a pulsed supersonic molecular beam valve (Model C-211SS, R.M. Jordan Co., Mountain View, CA). This valve operated on the magnetic beam repulsion principle. It had a nozzle diameter of 0.5 mm and a nominal gas pulse duration (FWHM) of 60 μ s for Helium carrier gas. The valve temperature could be controlled to temperatures as high as 70°C. The temperature was continuously monitored using a J-type thermocouple gauge. The PSV control unit (Quanta-Ray design, R.M. Jordan Co.) provided power for the fan-cooled pulsed valve and other essential functions (i.e., trigger source, current adjustment, and pulse delay time). The valve was in all cases operated at



[1 = probe laser input port ; 2 = photolysis laser input port ; 3 = ion gauge port ; 4 = turbo pump flange
5 = PSV flange ; 6 = alignment viewport ; 7 = fluorescence collection port]

Figure 2.6 Diagram of the Pulsed Supersonic Valve Sample Introduction Vacuum Chamber

a frequency of 10 Hz so that synchronization with the lasers was simplified.

d. Pulsed Supersonic Valve Chamber Sample Handling Line

The inlet port of the pulsed valve was directly connected to a sample handling line made of stainless steel as depicted in Figure 2.7 [p.37]. This sample line was designed and built by Dr. Sang C. Lee, of the University of Tennessee. The 1/4" o.d. stainless steel tubing of the inlet port was connected to a needle metering valve (Model 1315G4Y, Hoke), which lead to a "4-way" cross of stainless steel tubing, as depicted in Figure 2.7. Each Hoke needle valve shown had a specific function. Carrier gas could be admitted into the vacuum chamber as needed. The sample under investigation could be introduced into the line, and subsequently into the vacuum chamber via a needle metering valve. The pressure within the sample line could be monitored via a capacitance manometer. The sample could be degassed via a freeze-thaw cycle by opening up the corresponding Hoke needle valve as depicted in Figure 2.7. Argon was used as the carrier gas and the amount introduced to pressurize the sample line was monitored with a Baratron absolute pressure gauge (Model 122A, MKS, Andover, MA), by which a pressure measurement over a full-scale range of 1000 torr could be achieved. A large (5000 mL) glass bulb with an attached valve could be used as a storage vessel for the carrier gas when necessary. The sample bulb typically used was a 25 mL glass bulb drawn out into a 1/4" o.d. stem.

e. Vacuum System

The vacuum chamber could be evacuated to a pressure of approximately 1×10^{-7} torr in the absence of sample via a turbomolecular pump (Model TSU 332, Balzers-Pfeiffer, Hudson, NH). In the presence of sample, this vacuum pump system was capable of dealing with pressures as great as 1 mtorr. A pumping speed of 370 L/s of helium could be achieved with this vacuum system.

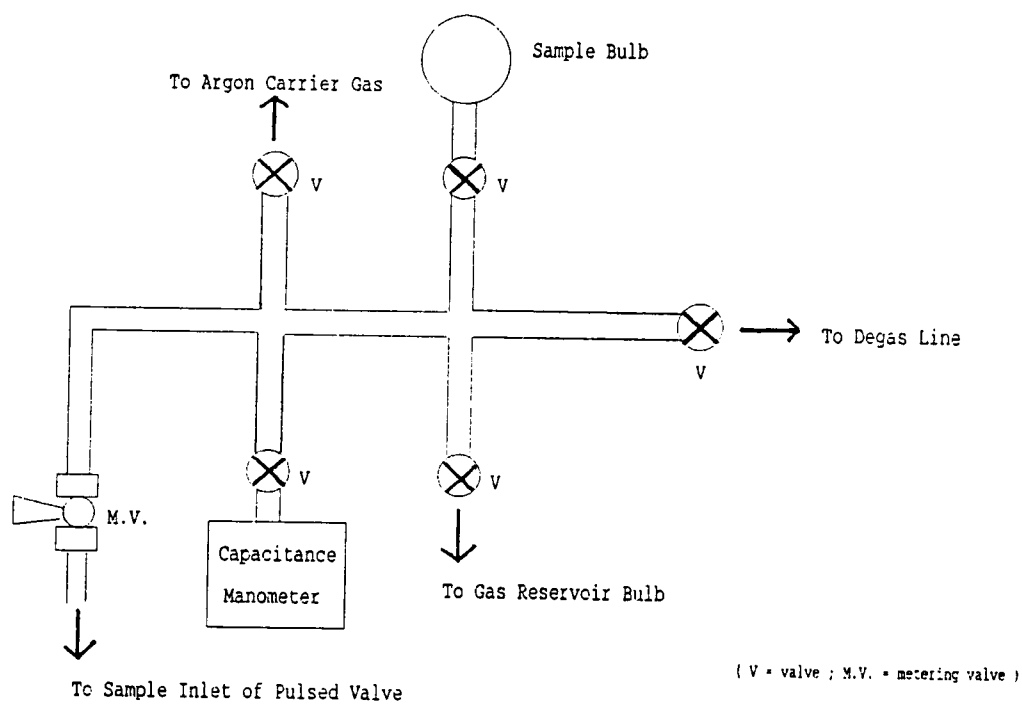


Figure 2.7 Diagram of the Sample Introduction Line used for the PSV Chamber

f. Photolysis Laser

The photolysis laser used throughout the work in this dissertation was a microprocessor-controlled argon fluoride excimer laser (Model 2210, Questek, Billerica, MA). The output radiation at 193 nm was a rectangular beam measuring 23 mm in the horizontal direction and 8 mm in the vertical direction. The temporal pulse width of the excimer laser beam was 15 ns, and the laser was operated at a pulse repetition rate of 10 Hz. The laser beam energy (in mJ/pulse) was continuously monitored by an on-board power detector, and generally could be "power-locked" in the range of 125 to 25 mJ/pulse. The photolysis laser beam was slightly cropped by an aluminum aperture to insure that only the most intense portion of the laser beam was reaching the actual sample interrogation region inside the chamber. The dimensions of this aperture measured 36 mm in the horizontal direction and 10 mm in the vertical direction. (The excimer laser beam diverged considerably by the time it had passed through the aperture, which explains why the dimensions are so large.) The photolysis laser beam was focused into the vacuum chamber via a 15 cm focal length fused silica plano-convex lens (Twardy Technology, Darien, CT), positioned approximately 14 cm from the chamber, and 67 cm from the output aperture of the photolysis laser. For the volatile metal chelate sampling work, a 20 cm focal length fused silica plano-convex lens (Twardy Technology) was used for focusing the excimer laser beam. A uv photodiode, positioned approximately 10 cm from the output shutter and in the periphery of the photolysis laser beam as depicted in Figure 2.1 [p.27], was used to trigger a gated integrator and boxcar averager.

g. Probe Beam Source : Nd:YAG Pumped Dye Laser System

During most of the work described in this dissertation, the laboratory was equipped with only one suitable probe laser, a Nd:YAG pumped dye laser system including a UV-WEX (Quanta-Ray: Division of Spectra-Physics, Mountain View, CA). The pump laser (Quanta-Ray Model DCR2A-10) produced output radiation at 1064 nm, from which the first, second, third and fourth

harmonics could be obtained using a harmonic generator. The output radiations from the harmonic generator were separated via a prism harmonic separator before entering the pulsed dye laser (Quanta-Ray Model PDL-2). Output radiation from the dye laser had a temporal pulse width of 7 ns and was tunable over a wavelength range of 380 - 920 nm, depending on the dye being used. The UV-WEX is a wavelength extender that houses both mixing and doubling crystals, allowing for overall wavelength tunability of the system in the region from 217 to 920 nm. Inside the UV-WEX, the mixed or frequency doubled uv beam entered a Pellin-Broca prism whereby the residual dye beam and/or the fundamental 1064 nm beam could be efficiently separated from the uv beam of interest.

A power meter (Model 362002, Scientech, Boulder, CO) equipped with thermopile-type laser power meter heads was used to measure the power output of the laser beam exiting the laser system. For pump beam (532 nm) and dye laser power measurements, a surface absorbing power meter head (Model 38-0101, Scientech) was used, whereas for uv beams generated in the UV-WEX, a volume absorbing power meter head (Model 36-0001, Scientech) worked well.

The probe laser beam that ultimately exited the UV-WEX had the appearance of a toroid, and had an outer diameter of approximately 0.5 cm when converged. This probe laser beam passed through an iris diaphragm so that any residual dye beam that was not separated from the uv beam by the Pellin-Broca prism inside the UV-WEX was prevented from passing into the vacuum chamber. The uv beam at this point entered two right angle turning prisms mounted on a beam steering assembly (Model 111, Daedel, Harrison City, PA) which was positioned such that the beam would travel into the chamber, thereby to achieve optical parallelism with the excimer laser beam. A smaller iris diaphragm positioned approximately 10 cm in front of the chamber window port served to limit the beam so that only the most intense well-defined portion passed into the sample interrogation region. A uv photodiode, positioned behind this small iris diaphragm and in the periphery of the probe laser beam as depicted in Figure 2.1 [p.27], was

used to trigger a gated integrator and boxcar averager during pump and probe experiments.

h. Probe Beam Source : Xenon-Chloride Excimer Pumped Dye Laser System

During the latter part of this research, our laboratory acquired an additional probe laser, a second microprocessor-controlled excimer laser (Model 2210, Questek, Billerica, MA). This laser was operated with xenon chloride to pump a dye laser; it produced output radiation at 308 nm, having a temporal pulse width of 15 ns. This laser was in all cases operated at a pulse repetition rate of 10 Hz. After exiting the pump laser, the output radiation at 308 nm entered a dye laser (Model FL-2000, Lambda-Physik, Gottingen, West Germany). The dye laser exhibited a nominal pulse width of 10-15 ns, and an overall tuning range of 330 to 950 nm could be achieved, depending on the dye being used. The dye laser output resembled a small dot, measuring 1 mm in diameter. After exiting the output aperture of the dye laser, a very small portion of the beam was detected by a uv photodiode, which was used to trigger a gated integrator and boxcar averager. Then, the beam was directed via three right angle fused-silica turning prisms into the sample interrogation region inside the vacuum chamber, and was not cropped or focused in any way. The power output of the XeCl pumped dye laser was measured using the Scientech power meter and the surface absorbing power meter head previously mentioned. The power output of the XeCl excimer laser could be monitored continuously with an on-board calibrated power detector, part of the standard microprocessor-controlled circuitry of the laser.

i. Fluorescence Collection and Dispersion

The fluorescence exiting from the chamber, perpendicular to the intersection of the photolysis and probe laser beams, impinged onto a pair of collection optics. The fluorescence was collected by a 3" diameter, 5" focal length fused silica plano-convex lens (Model 41965, Oriel, Stratford, CT) followed by a 2.5 x 2.0 ", 4" focal length fused silica cylindrical lens (Model

44045, Oriel, Stratford, CT). Both lenses were mounted on in-house built lens holders attached to Ealing Optics carriages, allowing for adjustment vertically, horizontally and laterally as they translated along an Ealing Optics optical rail. The plano-convex lens was positioned approximately 5 cm and the cylindrical lens approximately 14 cm relative to the chamber exit window.

The fluorescence image was dispersed by a 3/4 meter Czerny-Turner type grating monochromator (Model 1702, Spex, Metuchen, NJ). For efficient fluorescence collection and dispersion, this monochromator required the use of both of the aforementioned collection optics. During the latter part of this research, due to mechanical problems with the slit assembly mounted on this monochromator, it was necessary to interchange it with another monochromator. The replacement monochromator was a 1-meter Czerny-Turner type (Model HR-1000, Jobin-Yvon, France) which exhibited significantly higher resolution than the 0.75 m monochromator. This monochromator did not require the use of two collection optics for efficient fluorescence collection, so just the aforementioned plano-convex lens was employed.

Periodically, the monochromator was calibrated via mercury and neon pen lamps in conjunction with a 250 MHz Tektronix oscilloscope. The PMT signal output was directly sent to the oscilloscope, so that verification of the lamp emission lines was possible. To verify monochromator resolution, mercury emission lines at 312.6 nm and 313.2 nm were routinely checked. Linear regression analysis was applied to the data collected and a calibration plot was prepared to verify wavelength accuracy during experimentation.

j. Fluorescence Detection

The fluorescence signal was detected by a photomultiplier tube (PMT), several types of which were used during this research. Initially, an RCA Model 8850 photomultiplier tube was used, and when it ceased to function satisfactorily, an Amperex PMT (Model XP2020, Hicksville, NY) took its place. Finally, a Burle PMT (Model 8850, Lancaster, PA) was used for the

remainder of the research. In each case, the photomultiplier tube was powered by a power supply (Model 9201, EG&G Ortec, Oak Ridge, TN).

k. Signal Processing

The PMT output was directed to a gated integrator and boxcar averager module (Model SR250, Stanford Research Systems, Palo Alto, CA), a component of a Model SR280 mainframe (Stanford Research Systems). The mainframe provided power for the SRS modules and contained analog, digital and bargraph displays for monitoring the signal voltage. The average output from the gated integrator and boxcar averager was sent directly to an X-Y strip chart recorder (Model 2000, Houston, Austin, TX). A uv photodiode (Model 040BQ, EG&G Electro-Optics, Salem, MA), biased with a 9V battery to improve its response time, was placed in the periphery of a laser beam as depicted in Figure 2.1 to externally trigger the boxcar for proper timing. In the case of one-laser experiments, the uv photodiode was placed in the periphery of the excimer photolysis laser beam, whereas in the case of two-laser experiments, it was placed in the probe laser beam. Prior to any data collection, the averaged fluorescence signal from the boxcar output was always viewed on an oscilloscope to insure that optimum conditions for the collection of fluorescence were satisfied. The oscilloscope (Model 7704A, Tektronix, Beaverton, OR) is a 250 MHz system, allowing for accurate signal viewing in the 10-100 ns time regime, essential for the work performed during this research. Throughout data collection, the fluorescence signal and the boxcar gate position were continuously monitored on the oscilloscope to insure that the data being collected made sense. The characteristic "tail" of a decaying fluorescent signal could easily be distinguished from a scattered laser signal or background noise generated by the PMT. The boxcar gate was positioned such that the maximum fluorescence could be sampled by the boxcar.

For the determination of fluorescence decay time, a gate scanner module (Model SR200, Stanford Research Systems) was employed. This module allowed one to override the delay time

setting on the boxcar averager so that the user could control the gate delay. After the introduction of the computer, the need for this gate scanner module was eliminated.

I. Computer Control

During the course of this work, a laboratory computer (Model 50/Z, Personal System/2, IBM, Boca Raton, FL), was introduced into the spectrometer. At that point, the detected fluorescence signal was directed to the gated integrator and boxcar averager, and the averaged output was sent to a computer interface module (Model SR245, Stanford Research Systems, Palo Alto, CA). The interface consisted of eight analog input/output ports and two digital sync inputs. One analog input (channel one) collected each trigger (data point) it received from the averaged output of the boxcar. A second analog input (channel two) collected every fifth trigger (data point) from the averaged output of the boxcar. One of the digital sync inputs supplied the interface with a trigger, corresponding to the busy output signal of the boxcar averager, which synchronized data acquisition. The user chose the number of bins (data points) for which data could be collected during a scan. For fluorescence decay time studies, one of the analog output ports of the interface was used to override the delay time setting on the boxcar averager in order to scan the delay during a time scan. The use of the gate scanner was therefore eliminated. The software package (SR265) necessary to collect the data was obtained from Stanford Research Systems, and written specifically for use with our gated integrator and boxcar averager system. It was implemented without modification. As the data were being collected, a visual image of both channels in graphical form was produced on the computer screen in real-time. For emission or excitation spectral scans, a direct plot of signal intensity in volts versus wavelength was depicted on the computer screen for channel one and two. For fluorescence decay time studies, a plot of signal intensity in volts versus boxcar delay time could be seen on the screen. In each case, the ASCII data files obtained could be stored and used for further manipulation by other software. Spectra Calc, version Arithmetic A2.12, 1988, a software

package developed by Galactic Industries Corporation, was used to convert the ASCII files into the proper format for presentation-quality spectral plots.

m. Required Instrumentation for Timing

The synchronization of the ArF excimer photolysis laser and the Nd:YAG pumped dye laser system was accomplished by a master trigger circuit, constructed in-house. For a detailed schematic diagram, refer to Schendel (64). Basically, this circuit, which contained a ten-turn potentiometer, acted as a variable delay between the Nd:YAG output pulse and the excimer output pulse. The adjustment range via the ten-turn potentiometer allowed the excimer laser to fire at any time from $\sim 1.12 \mu\text{s}$ before the YAG laser to 700 ns after the YAG laser has fired. Since it took the Nd:YAG laser approximately 3.2 ms to produce an output pulse after it was triggered, the YAG pulse was the stable temporal reference point with respect to the photolysis laser. Verification of timing was completed using an oscilloscope system.

The synchronization of the ArF excimer photolysis laser and the XeCl pumped dye laser system required the use of two identical pulse generators (Model HP 8013B, Hewlett-Packard, Santa Clara, CA). One served as a trigger source and the other as a time delay source between the two lasers, procedures for which are discussed in the following sections.

n. Timing Methods for Two-Laser Experiments

Two-laser experiments were performed primarily to improve upon metal atom detectability over that observed with the photolysis laser alone. The photolysis laser was used for fragmentation of a metal chelate. The probe laser was used to induce fluorescence from previously unexcited ground state metal atoms generated by the photolysis laser. In the sections that follow which describe these two-laser experiments, if the second laser produced additional metal atom fluorescence, the term "probe-laser enhancement" is used to describe this effect. "Resonance enhancement" by the probe laser was used to describe a special case of probe-

laser enhancement in which $\lambda_{\text{probe}} = \lambda_{\text{emission}}$. For the research described in this dissertation, resonance enhancement was the major case of probe-laser enhancement studied for reasons which will become apparent in Chapter 3.

i. Continuous-flow Vacuum Chamber: ArF Excimer + Nd:YAG-pumped Dye

After conditions for observing one-laser induced fluorescence were deemed satisfactory, two-laser experiments were attempted. Maximum spatial overlap of the photolysis and probe laser beams was critical for success. The photolysis beam, positioned underneath the glass-lined tubing to be described on p.55, was left unchanged while the probe laser beam was adjusted via right angle turning prisms (as depicted in Figure 2.1 [p.26]) to pass through the "center" of the excimer laser beam pattern as indicated on a white business card. Due to the severity of the scattering signal intensity as the probe beam radiation directly hit the glass-lined tubing and scattered off the chamber windows, it was necessary to severely limit the diameter of the probe beam which actually entered the chamber. The probe beam was apertured down to a small dot, approximately 1 mm in diameter.

The aforementioned master trigger circuit was employed to synchronize the ArF excimer and the Nd:YAG pumped dye laser. Refer to Figure 2.8 [p.46] for a block diagram of this timing configuration. The master trigger circuit featured a 10-turn potentiometer which could be manually changed to produce both positive (probe pulse followed pump pulse) and negative (pump pulse followed probe pulse) two-laser delay times. The two laser pulses could coincide in time to within 10 ns (estimated timing jitter). The potentiometer on the master trigger circuit was previously calibrated by using a 400 MHz sampling oscilloscope where adjustments (in the number of potentiometer turns) corresponded to the delay time between the two lasers. Two photodiodes were required to calibrate the master trigger circuit. One photodiode detected the photolysis laser output pulse and a second photodiode detected the probe laser output pulse. Both photodiode outputs were viewed on the oscilloscope. The point at which both lasers

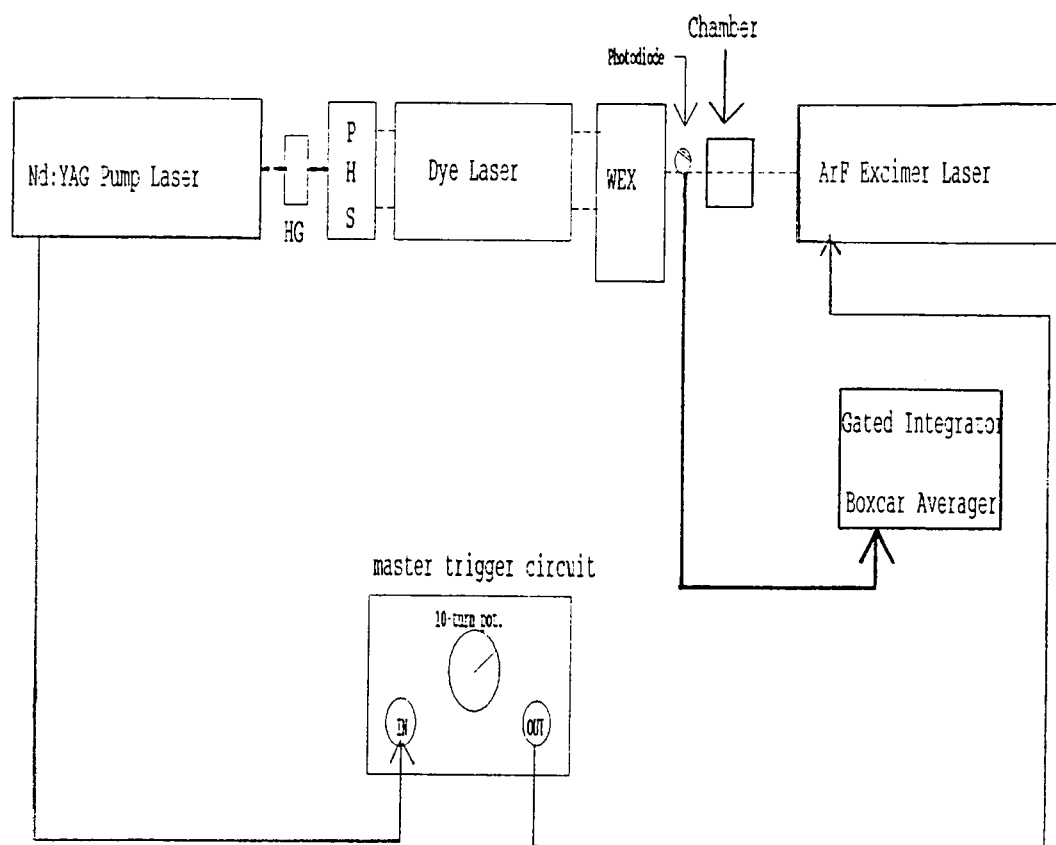


Figure 2.8 Block Diagram of the Master Trigger Circuit Timing Configuration

coincided in time was designated as approximately 0 ns. As the potentiometer on the master trigger circuit was manually turned, the time between the two photodiode outputs was observed on the oscilloscope and recorded. Refer to Table 2.1 [p.48] for these calibration data. For atomic fluorescence experiments, a "two-laser delay time" of 50 ns or less was typically chosen. Once the delay between the two lasers was adjusted, it was kept constant during data collection.

The boxcar delay time was set to maximize the two-laser induced fluorescence signal. The boxcar gate width was set to 10 ns. During experiments, the photodiode which detected the probe laser radiation triggered the boxcar.

ii. Continuous-flow Vacuum Chamber: ArF Excimer + XeCl Excimer-pumped Dye

The Nd:YAG pumped dye laser had an inherent time delay of ~ 3.2 ms between the firing of the flashlamps and the production of the YAG laser pulse, whereas the ArF excimer laser exhibited a delay between discharge and output on the order of nanoseconds. Thus, the specially designed master trigger circuit was successfully used to compensate for the difference in trigger circuits between the ArF excimer and the Nd:YAG pumped dye laser. However, to synchronize the 193 nm excimer laser with the XeCl excimer-pumped dye laser, the master trigger circuit was incapable of dealing with the short time delay between the two laser pulse outputs. Therefore, synchronization of these lasers was accomplished by the use of two pulse generators, as described on p.45. Refer to Figure 2.9 [p.49] for a block diagram of this arrangement. One pulse generator internally generated pulses at a 10 Hz repetition rate and, via a tee, was used to trigger both the XeCl excimer-pumped dye laser and a second pulse generator. The output from the second pulse generator was used to trigger the ArF excimer laser. A variable delay adjustment on the 35 ns time scale on the second pulse generator permitted the ArF excimer laser to fire at any time from ~ 600 ns before the probe laser to ~ 100 ns after the probe laser had fired. Typically, this variable delay adjustment was set so that

TABLE 2.1

CALIBRATION DATA FOR THE POTENTIOMETER ON THE MASTER TRIGGER CIRCUIT

Number of Turns (*)	t_{ns} (2-laser delay time)
3	290-300
3.25	205
3.5	150
3.75	80
4	~0-4
* starting position: potentiometer fully clockwise	

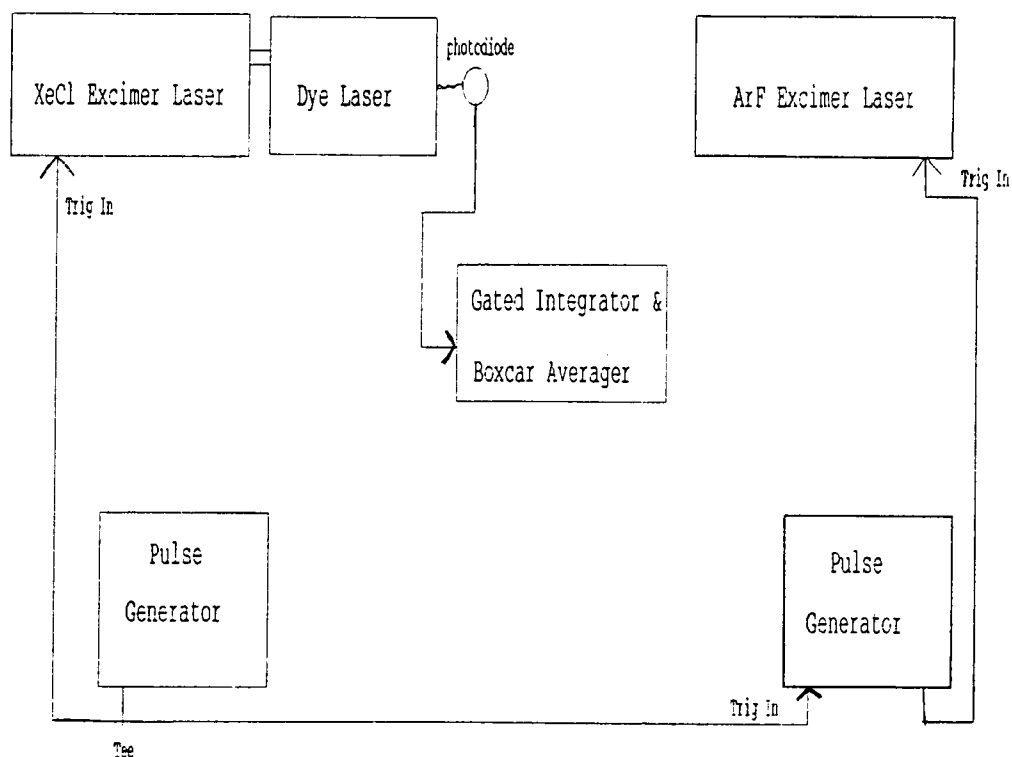


Figure 2.9 Timing Diagram for the Continuous-flow Vacuum Chamber : ArF Excimer Laser and XeCl Excimer-pumped Dye Laser

the probe laser fired ~ 35 ns after the photolysis laser so that any probe-laser induced enhancement might readily be observed on the oscilloscope. By changing the time delay between the two lasers, any contribution due to probe-laser enhancement as depicted in Figure 2.10 [p.51] could be seen on the oscilloscope. The photodiode placed in the periphery of the probe laser triggered the boxcar during data collection.

iii. Pulsed Valve Chamber: ArF Excimer + XeCl Excimer-pumped Dye Lasers

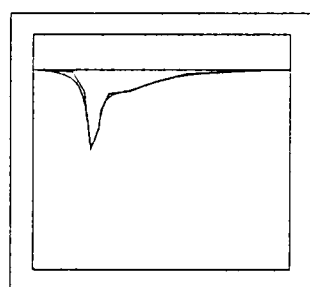
As depicted in Figure 2.11 [p.52], one pulse generator controlled the delay time between the firing of the ArF excimer and the XeCl excimer-pumped dye lasers, while an additional pulse generator controlled the delay time between the opening of the pulsed supersonic valve (PSV) and the firing of the photolysis laser. Experimentally, the current monitor output on the PSV power supply triggered one pulse generator, whose output, via a tee, triggered both the XeCl excimer-pumped dye laser and a second pulse generator. This latter pulse generator was used to externally trigger the ArF excimer laser. It was possible to adjust the variable delay on the second pulse generator, thereby changing the delay time between the two lasers. Refer to Figure 2.12 [p.53] for a schematic diagram of this timing configuration. During data collection, the XeCl-pumped dye laser beam detected by a photodiode triggered the boxcar.

2. Spectroscopic Procedures

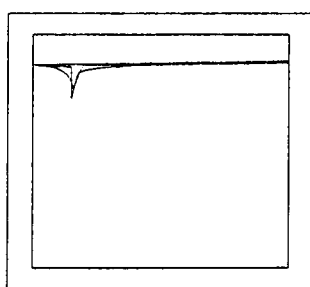
a. One-laser Analytical Figures of Merit : Collection and Analysis of Data

i. Instrumental Optimization : Continuous-flow Vacuum Chamber

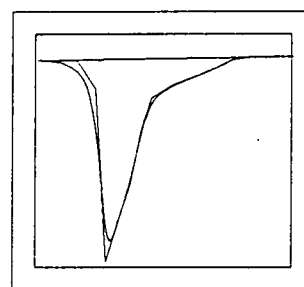
Typically, a sample to be analyzed was degassed via the auxiliary pumping system described previously (p.28), after which the sample introduction line was heated to an appropriate temperature. The sample bulb itself was then heated accordingly. Refer to Table 2.2 [p.54] for a list of sample temperatures which were used in the course of this research. Upon



OSCILLOSCOPE SCREEN
One-Laser Fluorescence



OSCILLOSCOPE SCREEN
Scattered Dye Laser
Radiation



OSCILLOSCOPE SCREEN
Two-Laser Induced Fluorescence
(2-laser induced signal superimposed
on the scattered dye laser radiation
background)

Figure 2.10 Probe-laser Enhancement Viewed Using an Oscilloscope

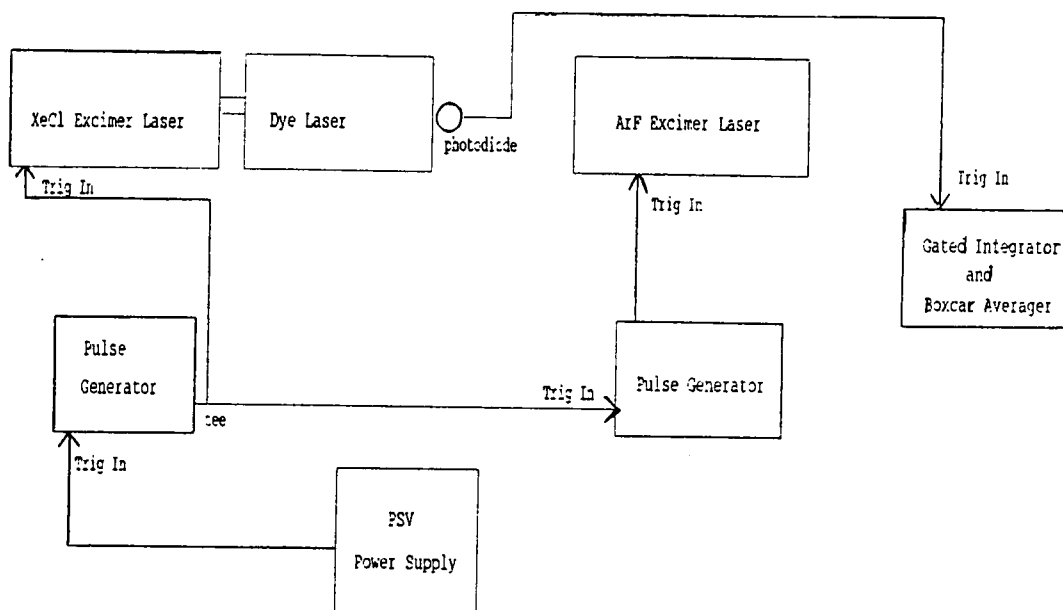


Figure 2.11 Timing Diagram for the Pulsed Supersonic Valve Sample Introduction Chamber : ArF Excimer Laser and XeCl Excimer-pumped Dye Laser

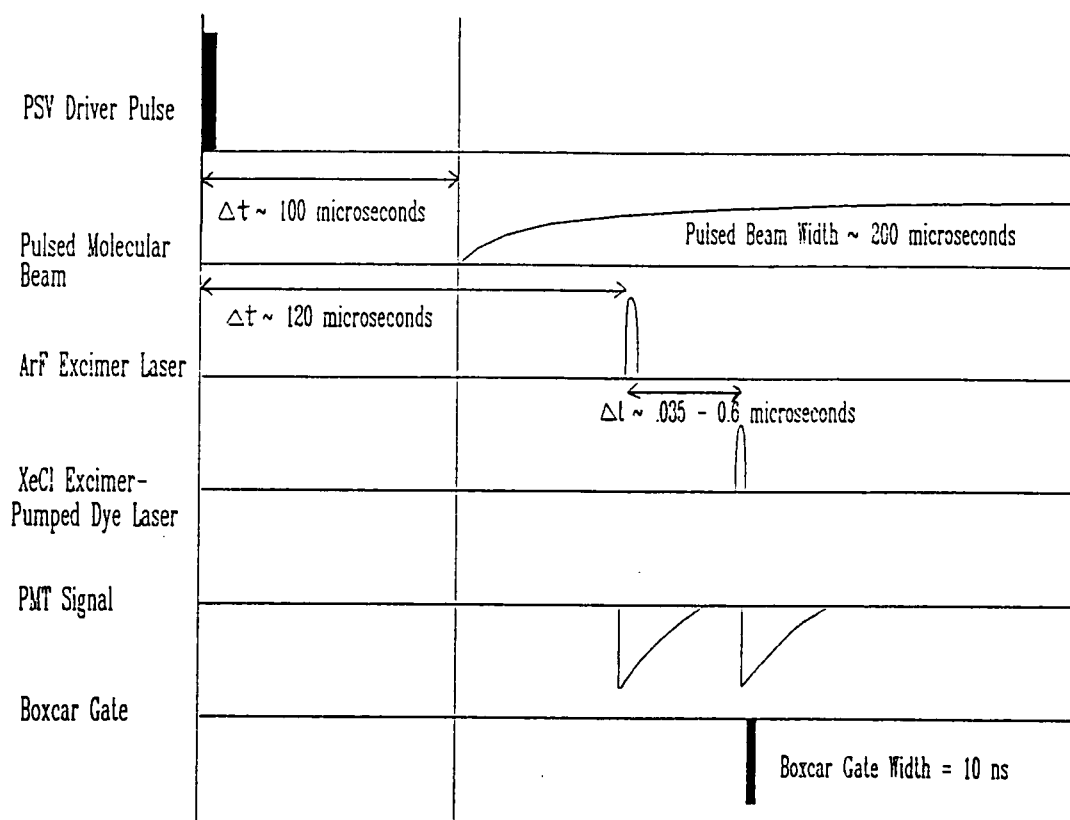


Figure 2.12 Timing Sequence for the Synchronization of the Pulsed Molecular Beam Valve, the ArF Excimer Laser and the XeCl Excimer-pumped Dye Laser

TABLE 2.2

HEATING MANTLE TEMPERATURE FOR INVESTIGATED SAMPLES

Sample	Temperature (°C)
Acrolein	25
Fe(CO) ₅	25
Co(CO) ₂ cyp	35
Bovine liver	115
SRM 855a	100
SRM 57a	100
Cu(hfa) ₂ H ₂ O	93
Cr(hfa) ₃	75
Fe(hfa) ₃	49
Ga(hfa) ₃	67
Co(hfa) ₂	100
Pb(hfa) ₂	125
Ni(hfa) ₂	110
Mn(hfa) ₂	135
Cu(II) oxide	95
Cr(tfa) ₃	123
Fe(tfa) ₃	115
Mo(CO) ₆	90

photolysis by the excimer laser, the sample, introduced into the chamber at a pressure of $\sim 1 \times 10^{-4}$ torr, produced a visible fluorescent line image inside the chamber underneath the glass-lined tubing (Figure 2.3 [p.30]). The entrance lens, which focused the ArF excimer beam onto the expanding sample vapor, was positioned such that the beam passed cleanly underneath the tubing but as close to the end as possible. This was done to insure the attainment of maximum fluorescence intensity and to reduce the possibility of 193-nm radiation scattering off the tubing and into the monochromator. It was determined that, if one positioned the beam too close to the tip of the glass-lined tubing, a signal due to second order grating diffraction of the 193 nm laser radiation was observed at 386 nm, resulting in significant background.

The monochromator slit widths were initially adjusted to $\sim 100 \mu\text{m}$ and the ArF excimer laser energy reduced to $\sim 75 \text{ mJ/pulse}$ at a repetition rate of 10 Hz. In a completely darkened laboratory, the fluorescence image could be seen passing through the collection optics with the aid of a white card. This image was centered on the entrance slit of the monochromator by first adjusting the plano-convex lens and then the cylindrical lens. The collection optics were translated along the rail and adjusted both laterally and vertically in order to achieve this condition. In cases in which the fluorescent image was barely discernible, it was helpful to introduce an organic sample into the vacuum chamber prior to the sample of interest, to aid the optimization of alignment. Organic compounds tend to readily fragment under conditions of 193 nm photolysis. Acrolein (Aldrich, 97%) was typically the organic of choice because it produced a large signal which facilitated the alignment process. Refer to Figure 2.13 [p.56] for an example 193 nm emission spectrum of acrolein and the pertinent wavelengths used for optimization. Additional common organic compounds such as acetone and toluene could also be introduced into the chamber to generate visible fluorescence which could be used to double-check operating system parameters.

At this point, the physical position of the photodiode used to trigger the boxcar was manually adjusted such that each laser pulse resulted in a clean, relatively stable trigger. The

ACROLEIN
193 NM PHOTOLYSIS

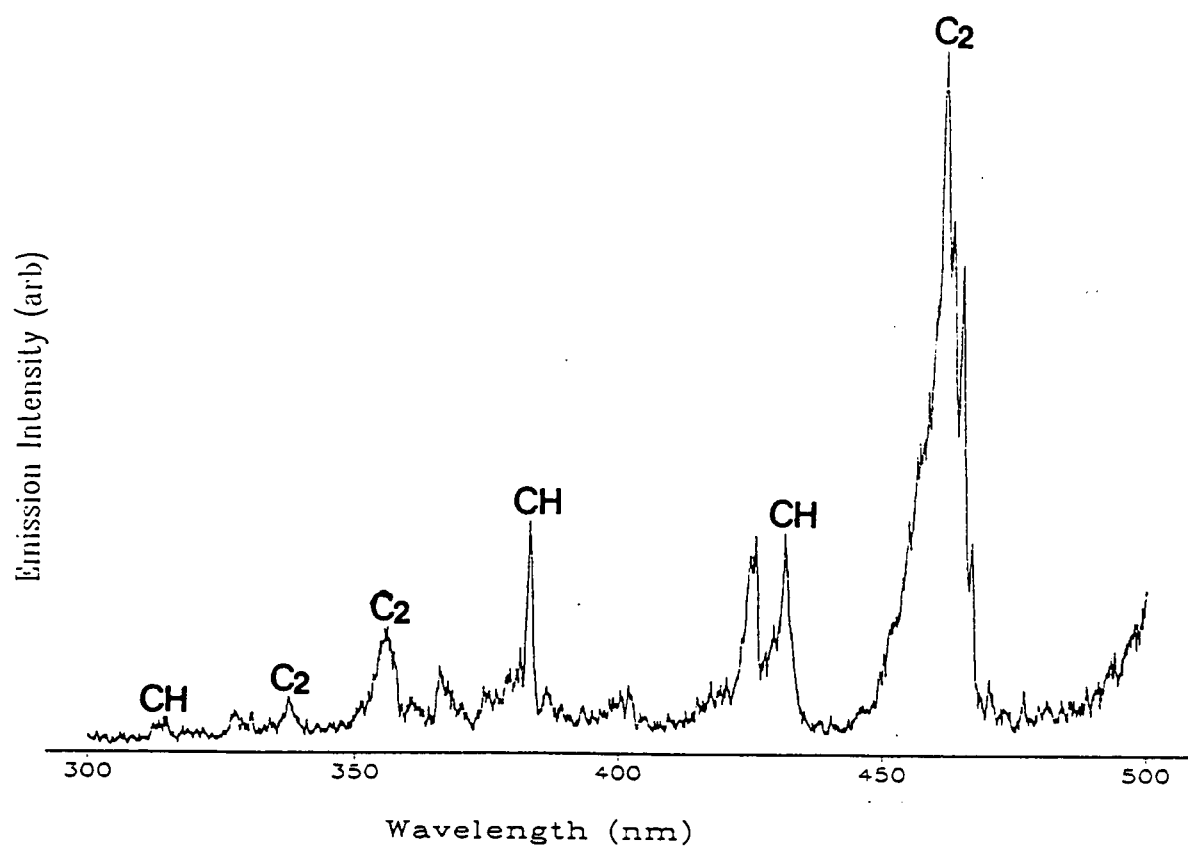


Figure 2.13 LP-FFS Emission Spectrum from the 193 nm Laser Photolysis of Acrolein

"rate adjust" feature on the boxcar module was also manually adjusted to provide for a stable trigger. Typically, the boxcar was set to a delay time of 10 ns, a gate width of 10 ns, and to collect 30-100 samples per average. A survey spectrum was then taken to determine the most analytically promising fluorescence line for further studies. As the monochromator was scanned from 300 - 500 nm, the oscilloscope monitored the detector output signal so that any fluorescence signal could be easily seen. A hard copy of each survey spectrum was obtained with the x-y chart recorder. The atomic line of choice was determined by reviewing this spectrum to see which line had the highest relative signal intensity (in volts) and the smallest spectral bandwidth. Several references were used to verify the existence of both the atomic and molecular fragments generated by 193 nm photolysis. For identification of the atomic spectral lines, Winefordner (65) and Moore (66) were used, whereas for the molecular fragments, Pearse and Gaydon (67) was the source of choice. To double-check the identity of a feature as a molecular or atomic emission peak in circumstances in which it was questionable, the gate scanner (prior to obtaining the laboratory computer) or the aforementioned SR265 software package was used to determine the fluorescence decay time of the signal of interest, which would clarify the matter. If the feature in question exhibited a fluorescence lifetime of 50 ns or less, it could generally be identified as an atomic fragment. Molecular fragments typically exhibited fluorescence lifetimes as large as 2 μ s. For the metal chelates, common "background" molecular fragments due to the photodissociation of the ligand were CH (314.3 and 431.4 nm), and C₂ (467 nm).

Once the most analytically promising atomic line was chosen, the monochromator was set to that particular wavelength and the entire procedure was repeated as above to further optimize the conditions for observing fluorescence. The boxcar gate width and delay time were adjusted using the dual-channel oscilloscope so that the maximum fluorescence signal from the averaged output of the boxcar was obtained. The exit/entrance slits were also optimized carefully to maintain adequate resolution, but at the same time, to allow as much radiation as

possible to enter the monochromator. A final survey spectrum was obtained after all these conditions were met.

ii. Measurement of Limits of Detection

The limit of detection, as defined for the work in this dissertation, is the amount of analyte introduced into the chamber that produces a signal equal to two times the standard deviation observed for an empty chamber (i.e., no sample introduced). In order to determine the limit of detection, the instrument must be operating under optimum conditions. The monochromator slits were opened as much as possible ($\sim 300 \mu\text{m}$ entrance/ $\sim 150 \mu\text{m}$ exit) but not so much so that resolution was completely sacrificed. It was necessary to make an accurate ion gauge pressure reading after the sample introduction line had been heated to the proper temperature, which corresponded to the base pressure (pressure inside the vacuum chamber prior to introduction of the sample). Typically, if the sample introduction line was at a temperature of 115°C , then the base pressure was $3\text{-}4 \times 10^{-7}$ torr. The 193 nm photolysis energy was generally "power-locked" at 85-90 mJ/pulse. The sample was then introduced at a pressure of $\sim 1 \times 10^{-6}$ torr. Then, the metering valve was quickly closed and a monochromator scan over a small wavelength range ($\sim 5 \text{ nm}$) was obtained. If the signal to noise ratio was observed to be greater than two, then the procedure was repeated, decreasing the sample pressure accordingly in steps (e.g. 9×10^{-7} torr, 8×10^{-7} torr, etc.) to the base pressure in successive increments. For instance, if a sample pressure of 5×10^{-7} torr was determined to produce a signal to noise ratio of two, several scans with and without sample were run to verify these results. Instrumental conditions were assumed to be constant throughout this procedure.

The chamber pressure which most closely approximated the limit of detection was then applied to the ideal gas law, after which the amount of analyte in units of moles could be reported as either the "chamber volume" LOD or "probe volume" LOD. The "chamber volume" LOD was calculated based on the assumption of a chamber volume of 450 cm^3 and an

assumption that the density of analyte atoms (atoms/cm³) was the same everywhere inside the chamber. The "probe volume" LOD corresponded to that amount of sample that could be detected if just the "sample interrogation" volume of 0.013 cm³ (i.e. the region of overlap of the photolysis and probe lasers) was taken into consideration.

iii. Precision

To achieve optimal reproducibility, the photolysis laser power and sample pressure must be as nearly constant as possible throughout data collection. Experimentally, the sample vapor was introduced into the chamber at a pressure of $\sim 1 \times 10^{-5}$ torr, and the photolysis laser was power-locked at 75-80 mJ/pulse. The monochromator was then scanned over a small wavelength range (~ 5 nm) such that the baseline on either side of the atomic line under investigation was clearly seen. Typically, in quick succession, 10-15 additional scans were made under identical experimental conditions. The resulting peak heights were manually measured and converted to volts, after which the standard deviation was calculated.

iv. Linear Dynamic Range

The determination of linear dynamic range required accurate sample pressure measurements over several decades. The sample pressure that most nearly corresponded to the limit of detection was chosen as a starting point. The monochromator was set to scan over a few nanometers, bracketing the analytically significant line of choice. One or two replicate scans were taken for this particular sample pressure. It was essential that the laser power remain constant throughout this entire procedure. The sample pressure was then adjusted to a value approximately a factor of 10 higher than the limit of detection, and the aforementioned procedure was repeated for at least two sample pressures within that order of magnitude. This procedure was continued, sampling at each decade, until the sample pressure reached 1×10^{-3} torr, at which point the turbomolecular pump could not tolerate a higher pressure. The resulting

peak heights above background were converted into volts, and a log-log plot of signal intensity (in volts) versus sample pressure (in mtorr) was prepared. Initially, this log-log plot was prepared manually, and linear regression analysis was subsequently applied to the part of the plot which was linear. Subsequently, Lotus 1-2-3 software was employed to carry out data analysis and preparation of calibration plots. The linear dynamic range was reported as "exhibited linearity" over a certain number of decades in sample pressure.

v. Dependence of Signal on Photolysis Laser Pulse Energy

The question addressed in a study of the dependence of the atomic fluorescence signal on the photolysis laser pulse energy was how many 193 nm photons appeared to be necessary to produce the excited bare metal atom fragment from the corresponding chelate. To perform power dependence studies on a particular fragment of interest, the photolysis laser was "power-locked" at the highest possible energy per pulse. The sample pressure was adjusted to $\sim 1 \times 10^{-5}$ torr. The monochromator was then scanned over the atomic fluorescence peak at least twice. This procedure was then repeated as the laser was "power-locked" at consecutively lower power, decreasing by 10 mJ/pulse for each step. Peak heights were measured above background, converted to volts, and a log-log plot of signal intensity (in volts) versus photolysis laser pulse energy (mJ/pulse) was prepared. The slope of the best-fit line resulting from linear regression analysis provided an estimate of the number of photons necessary to dissociate the organometallic chelate to the "bare metal atom". For example, a slope of approximately 2 in the log-log plot would imply that a minimum of two photons had to be absorbed by the metal chelate to produce the electronically excited metal atom.

vi. Instrumental Optimization : Pulsed Valve Sample Introduction Vacuum Chamber

The most critical step in the optimization of the pulsed supersonic valve (psv) instrumentation was precision in the synchronization of the opening of the pulsed valve with the firing of the photolysis laser. This was accomplished as depicted in Figure 2.14 [p.62]. The pulsed valve power supply was internally triggered at a 10 Hz repetition rate. The current monitor output on the power supply triggered a pulse generator, which in turn triggered the ArF photolysis laser. The time between the current monitor output and the photolysis laser pulse was 130 μ s. A photodiode placed in the periphery of the ArF photolysis laser beam was used to trigger the boxcar.

Typically, a sample to be analyzed was degassed and subsequently admitted into the vacuum chamber via the pulsed valve. If the sample vapor pressure was so low that visible fluorescence in the chamber was not seen even after heating the sample to the temperature limit of the valve (70°C), then the sample introduction line was used to admit argon at a backing pressure of ~ 1 atm. Otherwise, the sample was admitted without any buffer gas. Upon photolysis by the excimer laser, the sample produced a fluorescent line image inside the chamber, approximately 5 cm below the orifice of the pulsed valve. The position of the photolysis entrance lens and the time delay on the pulse generator were adjusted to maximize the "brightness" of the image. The rest of the procedure necessary to collect a survey spectrum was the same as that which was described for the continuous-flow vacuum chamber.

b. Two-Laser Experiments: Collection and Analysis of Data

i. Excitation Spectra

Once maximum spatial overlap of the pump and probe laser beams and proper timing had been achieved, the monochromator was set at the wavelength corresponding to the atomic fluorescence line in question. The Nd:YAG pumped-dye laser, under the direction of a

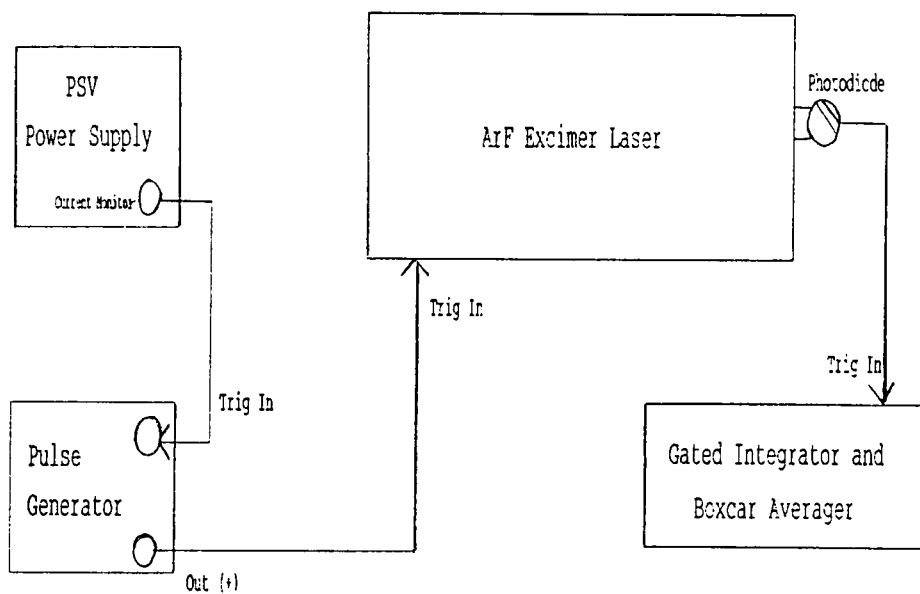


Figure 2.14 Timing Diagram for the Pulsed Supersonic Valve Sample Introduction Chamber : One-Laser Configuration

microprocessor-controlled stepping motor, was then scanned over a region of approximately 2 nm within which the atomic line was centered. If probe-laser enhancement of the atomic fluorescence was taking place, a peak of significantly narrower spectral bandwidth than that of the scattering signal due to the probe laser radiation could be seen rising above the relatively broad scatter background, when $\lambda_{\text{probe}} = \lambda_{\text{emission}}$ ("resonance enhancement"). Refer to Figure 2.15 [p.64] for an example. An excitation spectrum of signal intensity (in volts) vs. dye laser wavelength was obtained in the presence of sample vapor. In the absence of sample, the same procedure was repeated to allow inspection of the differences between the two spectra. For measurement of a fluorescence spectrum, the laser wavelength corresponding to the maximum in the excitation spectrum was used.

ii. Fluorescence Spectra

At a sample pressure of ~0.1 mtorr, a fluorescence spectrum was collected by scanning the monochromator over a wavelength region which bracketed the analytically significant atomic fluorescence line. During this procedure, the dye laser was set at the maximum wavelength for which probe-laser enhancement could be achieved. The signal which resulted corresponded to the scattered probe laser radiation plus the contribution (if any) due to probe-laser enhancement of the atomic fluorescence. Under the same conditions, a second fluorescence spectrum was obtained in the presence of sample, but without using the probe laser. The observed signal in this case was due to one-laser induced fluorescence. A third and final fluorescence spectrum was collected in the absence of sample, but with both lasers firing, which produced a peak due solely to the scattered probe radiation. This entire procedure was repeated at least once to check reproducibility.

Once these three spectra were collected, then the peak height of the signal in each of the three collected spectra was manually measured and converted to volts. The contribution due to probe-laser enhancement was determined by subtracting both the signal (in volts) due to

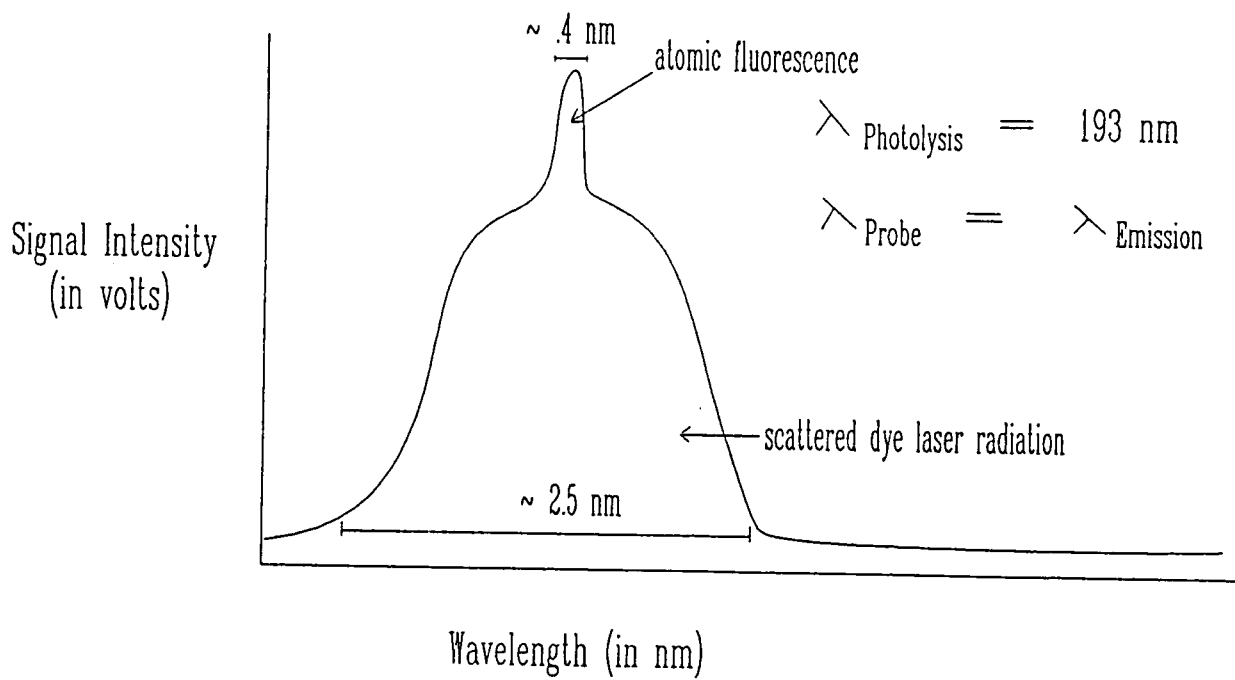


Figure 2.15 Example of an Excitation Spectrum

the scattered probe signal and the signal due to one-laser fluorescence from the two-laser induced signal.

iii. Analytical Figures of Merit: Two-Laser Experiments

In addition to excitation and emission spectra, several other two-laser studies were undertaken. The dependence of the emission signal on probe laser power, dependence of the atomic fluorescence signal on sample pressure, and precision of two-laser atomic fluorescence signals were all performed to evaluate the effect of the probe laser. The procedures implemented were analogous to those described for the one-laser experiments (see p.60).

3. Chemical Procedures

a. Beta-Diketonate Chelates

i. Ligands

The ligand 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, hereafter denoted as "hfa", was purchased from Aldrich (99%) and used without further purification. It was stored in a 250 mL round-bottomed flask fitted with a high-vacuum, o-ring sealed, bakeable valve in a cold room to prevent its deterioration into the tetrahydroxypentane derivative (44,45).

The ligand 1,1,1-trifluoro-2,4-pentanedione, hereafter denoted as "tfa", was purchased from Aldrich (99%) and used without further purification. No special storage precautions were used.

ii. Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedione) diaquo copper (II)

Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedione) diaquo copper (II) [$\text{Cu}(\text{hfa})_2 \cdot 2\text{H}_2\text{O}$] was synthesized according to the procedure outlined by Berg and Truemper (68). Approximately 0.240 moles of copper (II) acetate monohydrate (Fischer Scientific, reagent grade) was dissolved

in 450 mL of distilled water and subsequently heated to 90°C for ~15 min. After this mixture was cooled to room temperature, 100 g of hfa, dissolved in 40 mL of ethanol, was added to the copper (II) solution. Precipitation of the product was instantaneous, and continued as the mixture was cooled to 0°C. After vacuum filtration and washing with ~ 200 mL of distilled water, the product was dried in a vacuum desiccator. The final product consisted of small crystals, the color of green grass. The product was stored in a desiccator in the dark in a capped and parafilm glass container.

iii. Tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedione) gallium (III)

The general procedure for the synthesis of tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedione) gallium (III) [Ga(hfa)₃] outlined by Morris, Moshier and Sievers (69) was followed. Due to the extremely hygroscopic nature of anhydrous gallium chloride, this synthesis was carried out in a glove bag purged with nitrogen. Approximately 0.088 moles of anhydrous gallium chloride (Aesar-Johnson/Matthey) was added to 350 mL of carbon tetrachloride (dried with calcium chloride) in a 1-L round-bottomed distillation flask. This flask was fitted with a water cooled reflux condenser and was equipped with a side arm which allowed for a slow purge of the system with nitrogen. While the flask was manually shaken, 0.24 mol (50 g) of hfa was added drop by drop to the existing mixture. This action resulted in a vigorous release of HCl fumes as evidenced by pH paper and effervescence in the mineral oil bubbler at the receiving end of the condenser. The reaction solution turned pale-orange in color. After the evolution of HCl subsided, the flask containing the reaction mixture was placed on a heater/stirrer and fitted with the water-cooled reflux condenser. The mixture was allowed to reflux for 2.5 h at 98°C. After this time, the hot solution was quickly filtered under vacuum and evaporated to dryness in a crystallization dish under a stream of dry air. The resulting solid was dissolved in ~ 160 mL of boiling carbon tetrachloride (b.p. = 77°C) and immediately gravity filtered. The filtrate was put in a cold room at 0°C overnight. The following morning, the small amount of carbon

tetrachloride that remained was evaporated under a stream of dry air. The remaining cold mixture was filtered under vacuum and the solid in the funnel was washed with 50 mL of cold carbon tetrachloride. The solid product (pale orange needles) was allowed to air dry, after which it was stored in a desiccator.

iv. Tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedione) iron (III)

Tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedione) iron (III) [$\text{Fe}(\text{hfa})_3$] was synthesized according to a procedure similar to that followed for the gallium chelate (69). Approximately 7.25 g of anhydrous iron (III) chloride (CERAC, C/P # I-1034) was added to 175 mL of carbon tetrachloride in a 1-L round-bottomed distillation flask fitted with a water-cooled reflux condenser. Approximately 25 g of hfa was added slowly to the flask. HCl vapor was released continuously. The flask was fitted to a water-cooled reflux condenser and refluxed for 3.5 h at 96°C. The hot mixture was then gravity filtered and the excess solvent evaporated under a stream of dry air. The remaining crystals (blood-red in color) were redissolved in 90 mL of boiling carbon tetrachloride. This solution was again gravity filtered and allowed to stand overnight in a cold room at 0°C. Most of the carbon tetrachloride was then evaporated under a stream of dry air. The solution was filtered by vacuum filtration and washed with 25 mL of cold carbon tetrachloride. The solid product consisted of blood-red plate crystals, and was stored in a desiccator.

v. Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedione) lead (II)

The synthetic procedure followed was outlined by Schweitzer et al. (70). Approximately 175 mL of toluene dried over phosphorous pentoxide was added to a 1-L round-bottomed distillation flask connected to a water-cooled reflux condenser. Approximately 25 g (0.12 mol) of hfa was added to the toluene and slowly mixed. An excess of lead powder (Aldrich, 99.999 % , 100-mesh) was added also, after which a slow reflux at 90°C was commenced. The solution

immediately turned a pale yellow-green color. A clear crystalline film formed on the upper portion of the distillation flask, presumably due to the excess amount of ligand. After 6.5 h of slow refluxing, the hot solution was gravity filtered to remove the excess lead powder and then allowed to stand overnight at 0°C. Purification via recrystallization in toluene was performed the following morning. Pale yellow needle-like crystals were produced in low yield and stored in a desiccator.

vi. Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedione) cobalt (II)

Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedione) cobalt (II) [Co(hfa)₂] was synthesized according to a procedure similar to that used for the iron and gallium chelates (69). To 175 mL of carbon tetrachloride in a 1-L round-bottomed distillation flask fitted with a water-cooled reflux condenser were added 25 g (0.12 mol) of hfa and 7.8 g (0.06 mol) of anhydrous cobalt (II) chloride (Aldrich, 97 %). No immediate color change was observed. Refluxing was initiated and evidence of the evolution of HCl could be seen in a mineral oil bubbler attached to the receiving end of the reflux condenser. After 2 hours of refluxing at 98°C, the solution turned a pale brown-orange color. The mixture was gravity filtered to remove the excess cobalt (II) chloride, and the excess solvent was evaporated under a stream of dry air. The resulting orange product was redissolved in 90 mL of boiling carbon tetrachloride after which the solution was gravity filtered and placed in a cold room at 0°C overnight. The following morning, the product was filtered under vacuum and washed with 25 mL of cold carbon tetrachloride. The product consisted of a rust-orange powder obtained in relatively low yield.

vii. Commercially Available Beta-diketonate Chelates

Some metal beta-diketonate chelates became commercially available during the latter part of this work, including bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedione) manganese (II), bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedione) nickel (II) and bis(1,1,1,5,5,5-hexafluoro-2,4-

pentanedione) cobalt (II). These chelates were purchased from Aldrich and used without further purification.

b. Other Chemicals Used in this Work

Several metal complexes other than the beta-diketonate chelates were used in the course of this work. Iron pentacarbonyl (Strem Chemicals Inc., Newburyport, MA, Lot # 123278-S), cobalt cyclopentadienyl dicarbonyl (Strem Chemicals Inc.) and molybdenum hexacarbonyl (Aldrich) were each employed to aid in identification of metal fluorescence spectra.

A variety of standard reference materials was used in the course of this research. Bovine liver (SRM 1577a, National Institute of Standards and Technology [NIST], Gaithersburg, MD), silicon metal (SRM 57a, NIST), and an aluminum casting alloy-356 (SRM 855a, NIST) were all employed for verifying the applicability of this technique for solid samples. In addition, a copper oxide sample (Thorn Smith) which contained 4.55% Cu and an iron (III) ammonium sulfate sample (Thorn Smith) which contained 2.18 % Fe were used to verify appropriate conditions for laser photolysis.

c. Volatile Metal Chelate Sampling : On-line Synthesis

After the establishment of LP-FFS as a viable technique for metal detection as evidenced by success with the solid metal chelates, it was decided to investigate the applicability of the technique to "real-world" samples. Aqueous solutions containing metal ions and solid samples such as agricultural specimens were targeted as the next approach in extending this method of analysis to "real-world" samples.

For aqueous solution work, 0.01 M metal nitrate solutions were prepared and serially diluted to successively lower concentrations (down to 1×10^{-6} M). The 0.01 M metal nitrate solutions (iron (III), cobalt (II), nickel (II), chromium (III), and copper (II)) were stored in a cold room after preparation and removed when needed to prepare the dilutions. Dilutions were made

immediately prior to analysis. The ligand hfa was first chosen to effect complexation due to its high volatility. Also, it had been the ligand of choice for the preparation of the pure metal chelates, and evidence of a successful reaction was easily detected via observing the color of the chelate as it was formed.

The sample introduction systems depicted in Figures 2.4 [p.32] and 2.5 [p.33] were used in this aspect of the research. The aqueous metal solution to be analyzed (5 mL volume) was quantitatively transferred to the sample bulb ("reaction vessel") shown in Figure 2.4 [p.32], typically 25 mL in volume. To this solution was added one mL of neat hfa through a stopcock at the top of the vessel. For aqueous samples of high concentration (greater than 1×10^{-4} M), color formation was immediately apparent and resembled a "bubble" at the bottom of the flask. Shaking the vessel with the valve closed intensified the color. The sample was then placed in the sample introduction line after which it was frozen by immersion of the flask in liquid nitrogen, degassed and then thawed. The thawed sample was heated to an appropriate temperature (typically 90 - 100°C). These steps were necessary because, if the sample were not degassed and was then inserted into the high vacuum chamber through the needle metering valve (Figure 2.4 [p.32]) the chamber pressure would not be an accurate assessment of the amount of sample that actually entered the chamber, because air would have been trapped in the sample bulb.

It was determined after a considerable amount of trial and error that this "on-line synthesis" was far more effective if either sonication or heating in a temperature-controlled oven to effect the reaction, instead of merely shaking the vessel, preceded the freeze-thaw cycle. Different metal solutions tended to favorably respond to either sonication [e.g. Cu (II)] or heating in the oven [e.g. Cr (III)], as discussed in detail in Chapter 4.

d. Solid Samples

For work with solid samples (e.g. standard reference materials), each sample was dried via vacuum desiccation (in the case of bovine liver) or in an oven (all other solid samples), after

which ca. 250 mg was weighed into the sample bulb depicted in Figure 2.4 [p.32]. An excess of hfa was added, the valve attached to the reaction vessel was closed and the sample was allowed to sonicate for a period as long as 4 hours, and if no color observation validating the formation of the metal chelate occurred, then the sample was subsequently heated in an oven held at a temperature of 100 - 150 °C. The amount of time the sample remained in the oven ranged from one hour to overnight, depending on the nature of the sample, details of which will be discussed in Chapter 4. Then, the sample was transferred to the sample introduction line (Figure 2.4 [p.32]) and degassed as discussed on p. 28 prior to its introduction into the vacuum chamber.

CHAPTER 3

LP-FFS OF METAL BETA-DIKETONATES AND METAL CARBONYLS

There are two major divisions in this chapter. In the first division, analytical figures of merit (limit of detection, linear dynamic range, power dependence and precision) are reported for the 193 nm photolysis of several solid metal beta-diketonates and metal carbonyls in one-laser experiments. The overall objective was to investigate the analytical utility of LP-AFS via the use of pure solid samples prior to the use of "real" solid or solution samples. It was essential to determine if "bare" metal atoms could be formed in high yield by ultraviolet laser photolysis of gas-phase metal beta-diketonates, and if so, to determine the feasibility of applying LP-AFS to "real" analytical samples.

In the second division, two-laser pump and probe experimental results for the solid metal beta-diketonates and a metal carbonyl will be thoroughly discussed. The objective was to determine if resonance laser-induced fluorescence (LIF) detection of the photolytically generated metal atoms from the original sample could significantly improve the sensitivity of the LP-AFS technique, thereby rendering it a feasible alternative to conventional methods of trace metal detection.

1. One-laser Analytical Figures of Merit

Unless otherwise stated, the sample introduction system employed in the experiments to be described here is depicted in Figure 2.3 [p.30] for continuous-flow sample introduction into a vacuum chamber. The sample handling system used for pulsed valve sample introduction is depicted in Figure 2.7 [p.37]. Two metal beta-diketonate complexes $[\text{Fe}(\text{hfa})_3]$ and $[\text{Ga}(\text{hfa})_3]$ were chosen for a complete investigation in light of prior research reported by Schendel (64), in

which further study of these two chelates was suggested, due to the possibility of obtaining excellent quantitative results. Two metal carbonyls $[\text{Fe}(\text{CO})_5]$ and $[\text{Mo}(\text{CO})_6]$ were chosen for investigation to determine what effect (if any) the ligand might have on the quantitative production of excited metal atoms upon 193 nm photolysis of a particular metal complex.

a. $\text{Ga}(\text{hfa})_3$

i. Laser Photolysis Survey Spectrum

A fluorescence spectrum was obtained (as described previously on p.57) for the 193 nm photolysis of $\text{Ga}(\text{hfa})_3$, shown in Figure 3.1 [p.74]. Atomic gallium fluorescence at 403.3 nm and 417.2 nm originating from the 193 nm photolysis of $\text{Ga}(\text{hfa})_3$ dominates the spectrum; the peak with the highest relative signal magnitude (417.2 nm) was chosen for further analytical quantitative studies. All other fluorescence seen in Figure 3.1 appears to originate from ligand-derived molecular fragments of C_2 (360.7, 468.5, 469.8, 471.5 and 473.7 nm) and CH (314.3, 387.1 and 431.4 nm). Solid $\text{Ga}(\text{hfa})_3$ showed evidence of thermal degradation in the sample bulb, as indicated by the eventual (after ca. 2 hrs continual heating) transformation from the original pale peach crystals to a pale yellow semi-solid residue, accompanied by a decrease in the atomic fluorescence signal.

ii. Limit of Detection Study

The limit of detection (LOD) for a particular metal chelate was determined as described on p.59. For $\text{Ga}(\text{hfa})_3$, gallium fluorescence at 417.2 nm was chosen for the determination of the limit of detection. The base pressure in the continuous-flow vacuum chamber prior to the introduction of chelate vapor and after heating the sample introduction line was 3.5×10^{-7} torr, as measured by an ion gauge. The gallium chelate vapor was admitted into the vacuum chamber via a needle metering valve until the ion gauge pressure stabilized at 1.3×10^{-6} torr. At this point, the monochromator was scanned over the range 415 to 420 nm, over

Gallium Hexafluoroacetylacetonate
193 NM PHOTOLYSIS

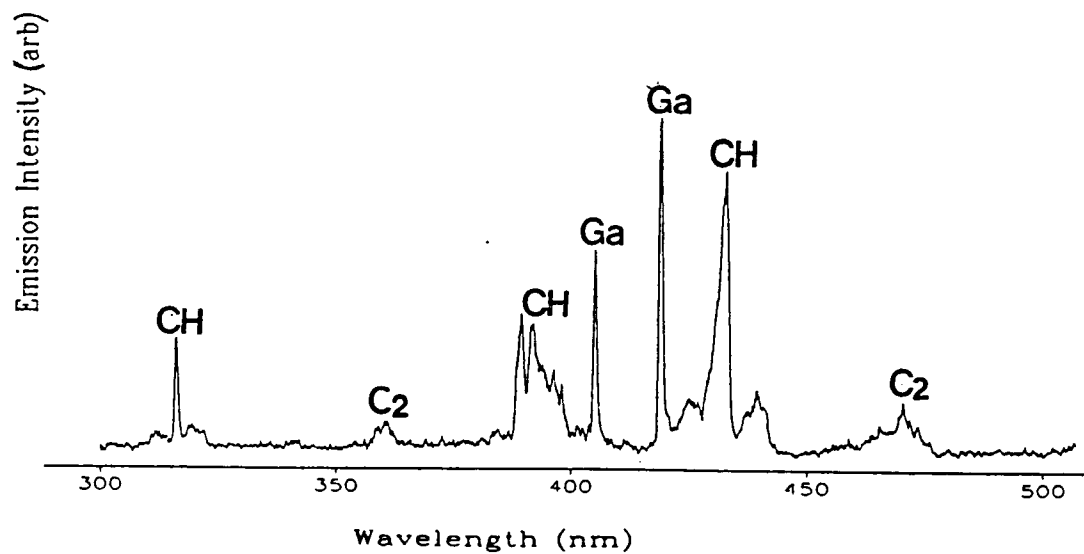


Figure 3.1 Survey Spectrum for the 193 nm Photolysis of Ga(hfa)₃

experimental conditions: sample pressure in the chamber = 1×10^{-4} torr;
sample temperature = 67°C; entrance/exit slits = 175 μm /75 μm ; boxcar
gate width = 10 ns; boxcar delay time = 24 ns; excimer laser photolysis energy
= 100 mJ/pulse at a repetition rate of 10 Hz

which gallium fluorescence at 417.2 nm was observed. Another scan over the same wavelength range was made in the absence of sample to obtain an estimate of the background noise level. During this scan, all other experimental conditions were held constant. The signal magnitude arising from fluorescence at 417.21 nm was measured above the background, and the signal to noise ratio was determined to be ca. 8, so the sample pressure was reduced (via the metering valve) to successively lower pressures in increments down to 4×10^{-7} torr. At 4×10^{-7} torr, the fluorescence was barely detectable above the noise. However, at 5×10^{-7} torr, a signal to noise ratio of ca. 2 was observed, which most closely approximated the limit of detection. Several additional scans were obtained with and without sample at a pressure of 5×10^{-7} torr to verify this observation. Since the base pressure was 3.5×10^{-7} torr, the pressure reading as a result of sample vapor was assumed to be 1.5×10^{-7} torr. The ideal gas law was applied accordingly to determine the amount of analyte which could be detected, in units of moles:

$$\begin{aligned} \text{molecular density (moles/L)} = P &= \frac{(1.5 \times 10^{-7} \text{ torr}) (1 \text{ atm}/760 \text{ torr})}{(0.082057 \text{ l-atm/mole-K}) (296.15 \text{ K})} \\ &= 8.12 \times 10^{-12} \text{ mol/L} \end{aligned}$$

Assuming a chamber volume of 450 cm^3 (0.45 L) and that the density of analyte atoms (atoms/cm^3) was the same everywhere within the vacuum chamber, then an approximate limit of detection can be determined as follows:

$$(8.12 \times 10^{-12} \text{ mol/L}) (0.45 \text{ L}) = 3.65 \times 10^{-12} \text{ moles}$$

$$(3.65 \times 10^{-12} \text{ mol}) (690.684 \text{ g/mol}) = 2.52 \times 10^{-9} \text{ g (2.5 ng chelate)}$$

$$(3.65 \times 10^{-12} \text{ mol}) (69.72 \text{ g/mol}) = 2.54 \times 10^{-10} \text{ g (250 pg analyte atoms)}$$

The assumption that the analyte atoms are distributed uniformly within the vacuum chamber is conservative. It is most probable that the number density of analyte atoms in the interrogation region is larger than the number density of analyte averaged over the entire photolysis chamber.

Accordingly, a "best case" limit of detection based on a sample interrogation volume of 0.013 cm³ (this estimate of the "probe" volume was determined by J.S. Schendel (64), p. 113) can be determined. The "probe" volume LOD can be estimated as follows:

$$(8.12 \times 10^{-12} \text{ mol/L}) (1.3 \times 10^{-5} \text{ L}) = 1.06 \times 10^{-16} \text{ moles}$$

$$(1.06 \times 10^{-16} \text{ mol}) (690.684 \text{ g/mol}) = 7.32 \times 10^{-14} \text{ g (73 fg chelate)}$$

$$(1.06 \times 10^{-16} \text{ mol}) (69.72 \text{ g/mol}) = 7.39 \times 10^{-15} \text{ g (7 fg analyte atoms)}$$

This low limit of detection for Ga(hfa)₃ was very encouraging.

iii. Precision Study

As described on p.59, a reproducibility study was performed for the gallium atomic fluorescence from the 193 nm photolysis of Ga(hfa)₃. Thirteen consecutive spectral scans over the atomic Ga fluorescence at 417.2 nm were obtained under the following conditions: sample pressure in the vacuum chamber = 1.5×10^{-5} torr; sample temperature = 67°C; entrance/exit monochromator slits = 210 μm; boxcar gate width = 10 ns; boxcar delay time = 40.2 ns; and excimer laser photolysis energy = 87.5 mJ/pulse at a repetition rate of 10 Hz. The relative standard deviation in the signal magnitude was calculated to be 5.5%.

The major source of imprecision in LP-AFS, as well as most other spectroscopic methods that use pulsed laser sources, is pulse to pulse amplitude fluctuation of the laser output. Even though the ArF excimer laser could be "power-locked" at a particular energy output and monitored via an on-board energy detector, intensity fluctuations directly affected the collected fluorescence data, as is evidenced by the results of the precision studies. Although methods do exist to normalize fluorescence signals for laser fluctuations, no attempt was made to do so in this work. Another source of imprecision was a gradual buildup of ligand-derived products and, eventually, formation of a metallic deposit on the surface of the window through

which the focused excimer laser beam passed. This experimental problem was reduced via the use of interior baffles and window extensions, as described on p. 28, but never fully eliminated. It was necessary to change both chamber windows frequently (after ~ 15 hr of use) to insure the best possible analytical results. Excimer laser photolysis is an extremely efficient technique for generating bare metal atoms which, unfortunately, manifests itself in this manner, an observation which has been reported by other workers (39,71).

iv. Linear Dynamic Range Study

The determination of linear dynamic range was performed for Ga(hfa)_3 as described on p.59. Ga(hfa)_3 vapor was admitted into the vacuum chamber at a pressure of 1.8×10^{-6} torr, and the monochromator was scanned over the 417.2 nm atomic fluorescence peak. At this same pressure, an additional scan was recorded under conditions as nearly constant as possible. The sample pressure was then adjusted to a greater value, and the procedure repeated. Overall, the sample pressure in the chamber was varied from 1.8×10^{-6} to 1.5×10^{-4} torr. The results of this study are shown in Figure 3.2 [p.78], in which the best fit linear regression line is drawn through the data points. The gallium atomic fluorescence signal is linear over the sample pressure range studied, which is approximately three orders of magnitude.

v. Dependence of Signal on Photolysis Laser Pulse Energy

The general procedure followed for the determination of the dependence of signal on the photolysis laser pulse energy was described on p.61. For Ga(hfa)_3 , the sample pressure was adjusted to 1×10^{-5} torr. The monochromator was scanned over the atomic fluorescence peak at 417.2 nm several times, at each laser pulse energy sampled. This procedure was repeated for nine different laser pulse energies within the range 10 - 97.5 mJ/pulse (laser fluence range = 3.7×10^{17} - 3.6×10^{18} photons/cm²). The results are displayed graphically in Figure 3.3 [p.79]. The best fit linear regression line is drawn through the data points. The slope of this line is 1.37,

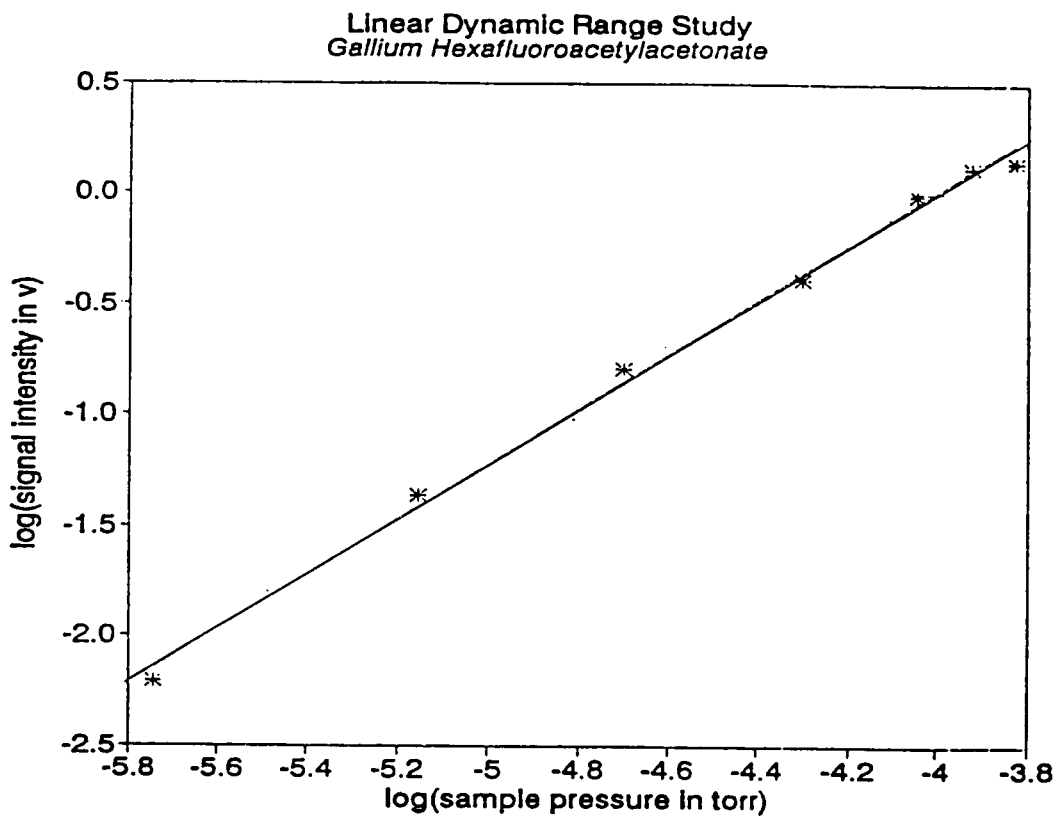


Figure 3.2 Linear Dynamic Range Study for Ga(hfa)_3

experimental conditions: entrance/exit monochromator slits = $300\mu\text{m}/300\mu\text{m}$;
boxcar gate width = 10 ns; boxcar delay time = 0 ns; excimer laser
photolysis energy = 82.5 mJ/pulse at a repetition rate of 10 Hz

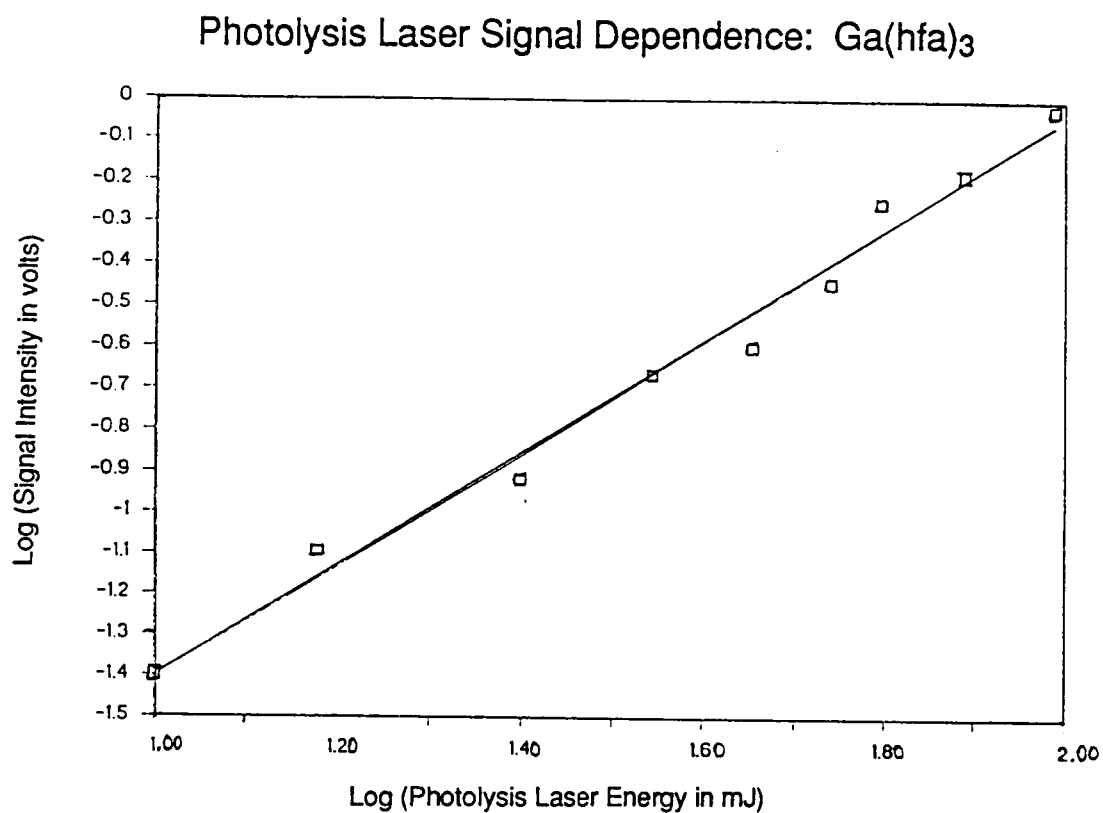


Figure 3.3 Dependence of Signal (417.2 nm Ga Fluorescence) on Photolysis Laser Pulse Energy

experimental conditions: boxcar delay time = 17.8 ns; boxcar gate width = 10 ns;
entrance/exit monochromator slits = $200\mu\text{m}/200\mu\text{m}$

which indicates a somewhat greater than linear dependence of the Ga fluorescence signal upon photolysis laser pulse energy. This nonintegral result implies partial saturation of at least one absorption transition in the multiphoton process by which excited gallium atoms are produced. It can be concluded that at least two 193 nm photons were required to produce electronically excited gallium atoms.

b. Fe(hfa)_3

i. Laser Photolysis Survey Spectrum

The fluorescence spectrum for the 193 nm laser photolysis of Fe(hfa)_3 is depicted in Figure 3.4 [p.81]. In Figure 3.4, it is immediately apparent that atomic iron fluorescence at 358.12 nm and 373.49 nm dominates the spectrum, so these two lines were chosen for further analytical investigation. Although no fewer than 20 atomic fluorescence peaks due to iron are present in the spectrum from a wavelength range of 300 to 500 nm, five of the most prominent (344.06, 358.12, 371.99, 373.49 and 374.95 nm, respectively) are labeled in Figure 3.4.

Fluorescence apparently originating from a ligand-derived molecular photofragment (CH) at 314.3 nm and 387.1 nm is present in Figure 3.4. The solid Fe(hfa)_3 sample showed evidence of very mild decomposition, when heated at an elevated temperature ($> 49^\circ\text{C}$ = melting point of Fe(hfa)_3), as evidenced by a trace of yellow residue in the sample bulb.

ii. Limit of Detection Study

It was experimentally determined that the limit of detection was lowest for iron fluorescence at 358.1 nm (not 373.5 nm) for Fe(hfa)_3 . The base pressure in the continuous-flow vacuum chamber (after heating) was measured via an ion gauge as 4×10^{-7} torr. The chelate vapor was first introduced into the vacuum chamber at a pressure of 1×10^{-6} torr, after which the monochromator was scanned from 357 to 360 nm, thereby bracketing the iron fluorescence signal at 358.1 nm. The signal magnitude arising from 358.1 nm fluorescence was found to

Iron Hexafluoroacetylacetonate
193 NM PHOTOLYSIS

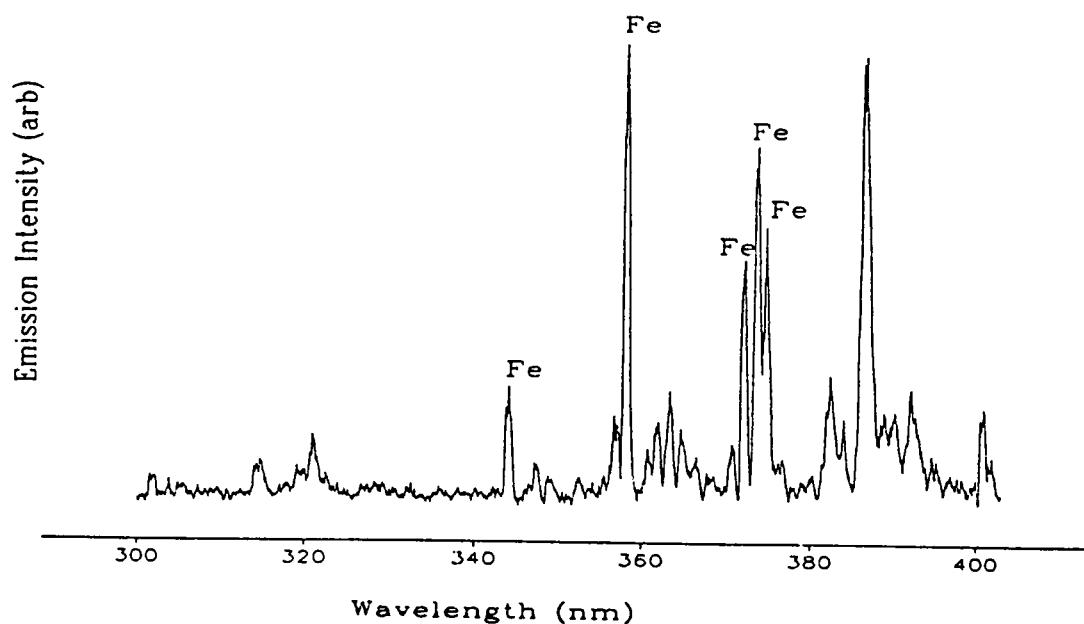


Figure 3.4 Survey Spectrum for the 193 nm Photolysis of $\text{Fe}(\text{hfa})_3$

experimental conditions: sample pressure in the chamber = 1×10^{-4} torr;
sample temperature = 49°C ; entrance/exit monochromator slits = $100\mu\text{m}/50\mu\text{m}$;
boxcar gate width = 10 ns; boxcar delay time = 12.8 ns; excimer laser
photolysis energy = 85 mJ/pulse at a repetition rate of 10 Hz

produce a signal to noise ratio much greater than 2, so, as with $\text{Ga}(\text{hfa})_3$, the sample pressure was reduced in increments down to 5×10^{-7} torr, which resulted in a signal to noise ratio of 2:1. This procedure was repeated several times with and without sample for the purpose of validation. Since the base pressure was 4×10^{-7} torr, the pressure reading as a result of the sample vapor alone was assumed to be 1×10^{-7} torr. Calculations similar to those on page 79 reveal a molecular density of 5.41×10^{-12} mol/l, resulting in a limit of detection of 1.6 ng (chelate) and 130 pg (analyte atoms). The "probe volume" LOD (assuming a "probe volume" of 0.013 cm^3) was calculated to be 47 fg (chelate) and 4 fg (analyte atoms).

iii. Precision Study

As described on p.60, a reproducibility study was performed for the atomic fluorescence from $\text{Fe}(\text{hfa})_3$. Fifteen consecutive spectral scans over the atomic Fe fluorescence at 358.1 nm were obtained under these conditions : sample pressure in the vacuum chamber = 2.5×10^{-5} torr; sample temperature = 49°C ; entrance/exit monochromator slits = $200 \mu\text{m}/100 \mu\text{m}$; boxcar gate width = 10 ns; boxcar delay time = 28 ns; and excimer laser photolysis energy = 72.5 mJ/pulse. The relative standard deviation in the signal magnitude was calculated to be 4.8%.

iv. Linear Dynamic Range Study

A determination of linear dynamic range was performed for $\text{Fe}(\text{hfa})_3$ in which the 358.1 nm iron fluorescence was monitored. The pressure range sampled for $\text{Fe}(\text{hfa})_3$ was 5×10^{-6} to 1×10^{-4} torr. The results of this study are depicted in Figure 3.5 [p.83]. The best fit linear regression line is drawn through the data points. The atomic iron fluorescence signal is relatively linear over the sample pressure range studied, which comprised approximately three orders of magnitude.

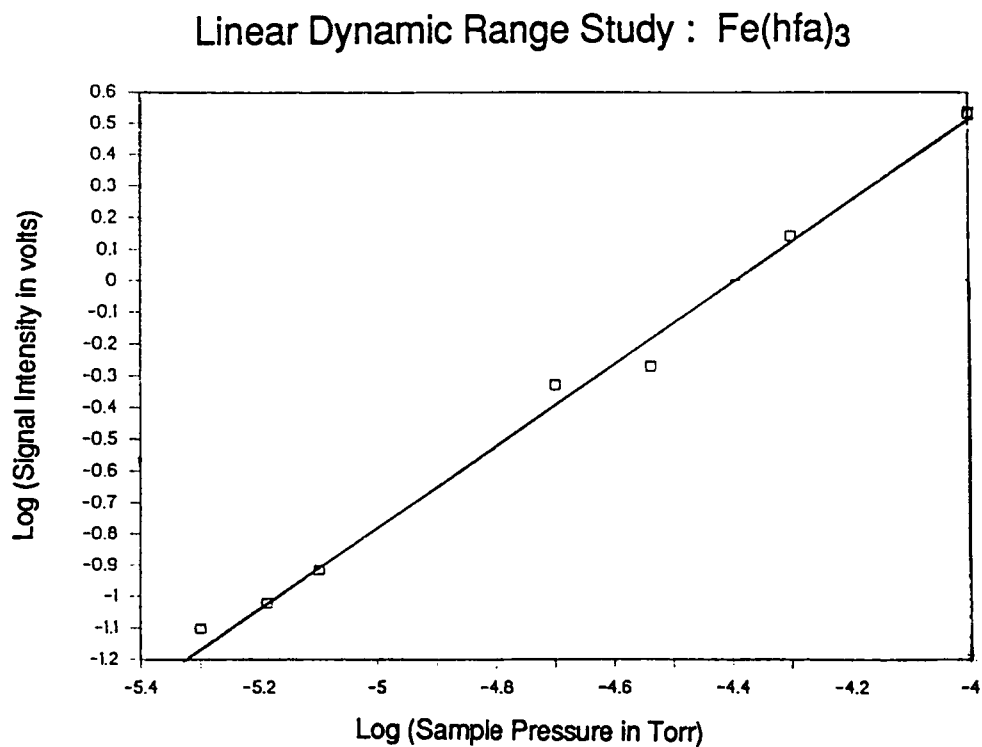


Figure 3.5 Linear Dynamic Range Study for Fe(hfa)_3

experimental conditions: excimer laser photolysis energy= 90 mJ/pulse at a repetition rate of 10 Hz; boxcar delay time= 38 ns; boxcar gate width= 30 ns; entrance/exit monochromator slits= $250\mu\text{m}/250\mu\text{m}$

v. Dependence of Signal on Photolysis Laser Pulse Energy

The general procedure followed is described on p.60. For Fe(hfa)_3 , the sample pressure was adjusted to 8×10^{-5} torr. Spectral scans for five different laser pulse energies within the range 17.5 - 80 mJ/pulse (laser fluence range = 6.5×10^{17} - 3.0×10^{18} photons/cm²) were recorded. The signal dependence on photolysis laser pulse energy for the atomic Fe line at 373.5 nm was investigated, results from which are depicted in Figure 3.6 [p.85]. The slope of the best-fit linear regression line is 1.97, which indicates a greater than linear dependence of the Fe atomic fluorescence signal upon photolysis laser pulse energy. It can be concluded that at least two 193 nm photons were needed to produce electronically excited iron atoms.

In both cases [for Fe(hfa)_3 and Ga(hfa)_3], partial saturation of one or more of the absorption steps to produce the electronically excited metal atoms is most likely involved. Due to high laser fluences employed in these studies, it is possible that more 193 nm photons are involved in the absorption process than is indicated by the slopes of Figures 3.3 and 3.6.

c. Fe(CO)_5

i. Laser Photolysis Survey Spectrum

Iron pentacarbonyl (Fe(CO)_5) introduced at room temperature into the continuous-flow vacuum chamber was efficiently photolyzed by 193 nm radiation, and a survey fluorescence spectrum was recorded to use as a comparison with that obtained for Fe(hfa)_3 . The spectrum of Fe(CO)_5 presented in Figure 3.7 [p.86] was recorded at a sample pressure of 7×10^{-5} torr. A complex spectrum of atomic Fe lines was observed. A comparison between the atomic fluorescence spectrum for both complexes indicates a difference in relative peak heights, but in general, the same atomic iron lines are present. Iron pentacarbonyl was particularly useful as an aid for preliminary signal optimization due to the intense spectral brightness of the visible fluorescent line image (mentioned on p.55) inside the vacuum chamber.

The one-laser system for pulsed valve sample introduction into a vacuum chamber was

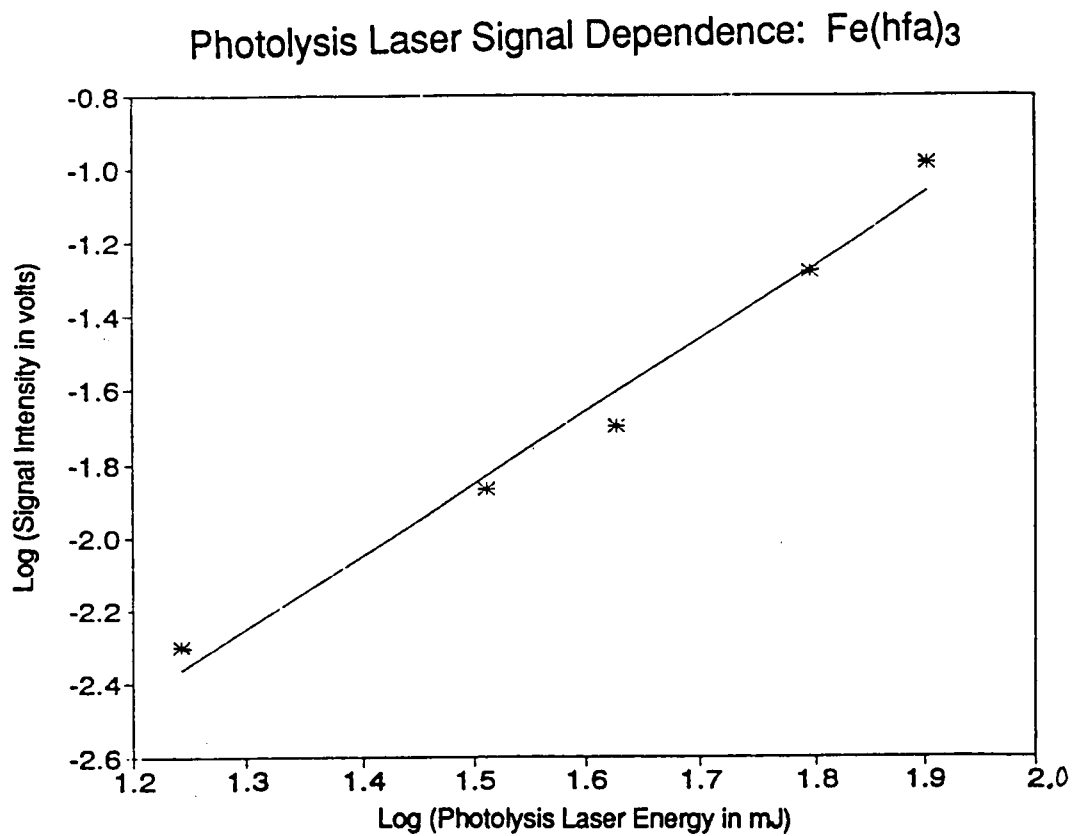


Figure 3.6 Dependence of Signal on Photolysis Laser Pulse Energy for Fe(hfa)_3
experimental conditions: boxcar delay time = 28 ns; boxcar gate width = 10 ns;
entrance/exit monochromator slits = $250\mu\text{m}/200\mu\text{m}$

Iron Pentacarbonyl – Continuous-Flow Sample Introduction
193 NM PHOTOLYSIS

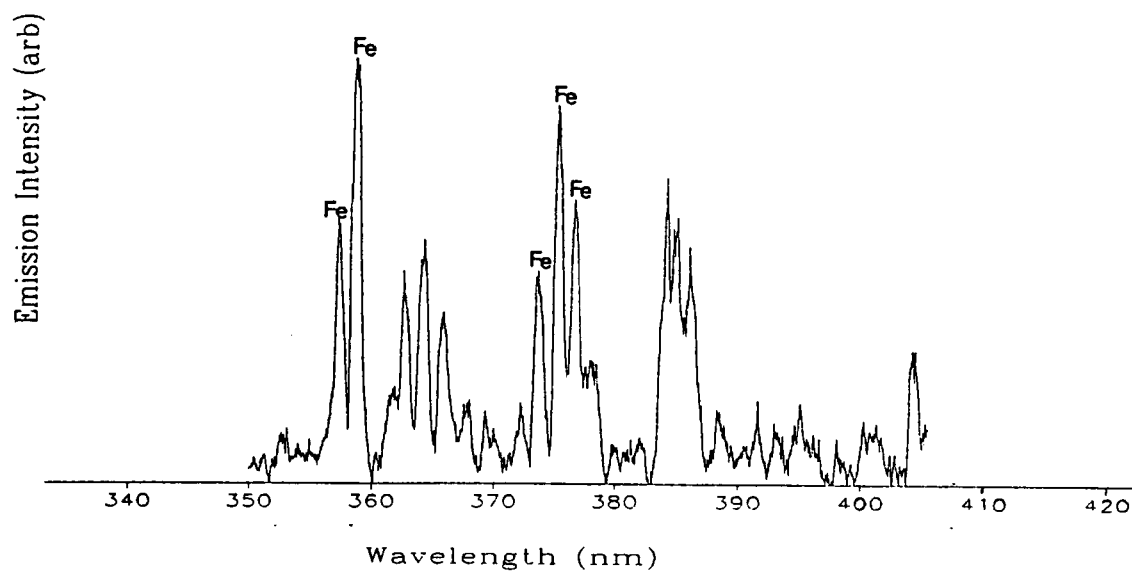


Figure 3.7 Survey Spectrum of the 193 nm Photolysis of $\text{Fe}(\text{CO})_5$

experimental conditions: sample pressure in the chamber = 7×10^{-5} torr; boxcar delay time = 16 ns; boxcar gate width = 10 ns; entrance/exit monochromator slits = $150\mu\text{m}/100\mu\text{m}$; excimer laser photolysis energy = 70 mJ/pulse at a repetition rate of 10 Hz

configured as described on p.62. Iron pentacarbonyl, held at room temperature, was introduced neat (without the addition of buffer gas) at a pressure of ca. 5 torr. The atomic fluorescence spectrum produced was identical to that which was generated in the continuous-flow chamber (Figure 3.7), except that the molecular fragment fluorescence was more cleanly resolved when pulsed valve sample introduction was employed.

ii. Limit of Detection Study

The limit of detection for $\text{Fe}(\text{CO})_5$ was determined as described on p.58. The base pressure in the continuous-flow vacuum chamber was measured via an ion gauge as 7×10^{-7} torr. Heating the sample introduction line was unnecessary due to the adequate vapor pressure achieved when $\text{Fe}(\text{CO})_5$ vapor (at room temperature) was introduced into the vacuum chamber. Initially, the sample vapor was introduced into the vacuum chamber at a pressure of 2.5×10^{-6} torr, after which the monochromator was scanned from 356 to 360 nm, thereby bracketing the iron fluorescence signal at 358.1 nm. An additional scan over the same wavelength range was made in the absence of sample to estimate the background noise level. The signal magnitude arising from iron fluorescence at 358.1 nm was determined to be ca.10 at this pressure, so the sample pressure was reduced to successively lower pressures in increments down to 9×10^{-7} torr. At 8×10^{-7} torr, (base pressure = 7×10^{-7} torr, so the sample pressure = 1×10^{-7} torr), the S/N ratio was determined to be less than 2. At 9×10^{-7} torr, (base pressure = 7×10^{-7} torr, so the sample pressure = 2×10^{-7} torr), a S/N ratio of ca. 1.9 was found. At 1×10^{-6} torr, (base pressure = 7×10^{-7} torr, so the sample pressure = 3×10^{-7} torr), a S/N ratio of ca. 2.9 was found. Two additional scans over the 358.1 nm fluorescence at this same sample pressure (3×10^{-7} torr) were obtained. From these results, a sample pressure of ca. 3×10^{-7} torr most closely approximates the limit of detection. Calculations similar to those on p.77 reveal a molecular density of 1.62×10^{11} mol/L, resulting in an LOD of 1.4 ng(carbonyl) and 400 pg(analyte atoms). The "probe volume" LOD (assuming a "probe volume" of 0.013 cm^3) was calculated to be 41

fg(carbonyl) and 11 fg(analyte atoms). The limit of detection for iron pentacarbonyl is virtually equal to that of iron hexafluoroacetylacetonate (see p.82), implying that the efficiency of photolytic conversion of the original metal complex to electronically excited iron atoms is virtually the same for Fe(hfa)_3 and Fe(CO)_5 .

iii. Precision Study

Twenty consecutive fluorescence decay scans were obtained for iron fluorescence at 358.1 nm from the 193 nm photolysis of Fe(CO)_5 . For this precision study, the boxcar gate was scanned from 0 - 125 ns, with the monochromator set to transmit radiation at 358.1 nm. The experimental conditions employed during data collection were: sample pressure in the pulsed valve sample introduction chamber = 9×10^{-5} torr [8 Torr Fe(CO)_5 diluted in 510 Torr Argon]; entrance/exit monochromator slits = 150 μm /100 μm ; boxcar gate width = 10 ns and excimer laser photolysis energy = 75/80 mJ/pulse at a repetition rate of 10 Hz. The signal magnitude at a boxcar delay time of 15 ns (fluorescence decay maximum) was obtained from each of the twenty scans as collected by the computer data acquisition program (SR265). The relative standard deviation in the signal magnitude was calculated to be 7.2 %. This value is somewhat higher than that reported for the precision studies for the metal beta-diketonates above, yet still analytically acceptable. The pulsed valve sample introduction chamber was used for this experiment for reasons of convenience. Fluorescence decay scans (rather than wavelength scans) were recorded because it was more convenient to do so, and because the experimental conditions (e.g. photolysis laser energy pulse energy) remained constant for a longer period of time.

iv. Linear Dynamic Range Study

To determine the linear dynamic range, iron fluorescence at 357.1 and 358.1 nm from Fe(CO)_5 was monitored. The pressure range sampled for Fe(CO)_5 in the continuous-flow

vacuum chamber was 6×10^{-6} to 1.2×10^{-4} torr. The results of the LDR study for Fe fluorescence at 357.1 nm are depicted in Figure 3.8 [p.90]. For iron fluorescence at 358.1 nm, the results of the LDR study are depicted in Figure 3.9 [p.91]. In each Figure, the best fit linear regression line is drawn through the data points. The atomic iron fluorescence signal (in each case) is linear over three orders of magnitude (for 357.1 nm: slope = 1.09 ± 0.02 and for 358.1 nm: slope = 1.07 ± 0.06).

v. Dependence of Signal on Photolysis Laser Pulse Energy

This dependence was measured in both the continuous-flow and the pulsed valve sample introduction chambers to determine if consistent results could be obtained, irrespective of which sample introduction method was employed during a particular experiment. First, in the continuous-flow vacuum chamber, $\text{Fe}(\text{CO})_5$ vapor was introduced at a pressure of 6×10^{-5} torr. Spectral scans over iron fluorescence at 358.1 nm for five different laser pulse energies within the range 5 - 70 mJ/pulse (laser fluence range = 1.87×10^{17} - 2.62×10^{18} photons/cm²) were obtained. The signal dependence on photolysis laser pulse energy for the iron atomic fluorescence at 358.1 nm was investigated, results from which are depicted in Figure 3.10 [p.92]. The slope of the best-fit linear regression line is drawn through the data points and is calculated to be 0.27 ± 0.03 . This result indicates a non-integral dependence of signal on photolysis laser pulse energy. Apparently, a high degree of laser saturation of at least one absorption transition in the multiphoton process by which excited iron atoms are produced from $\text{Fe}(\text{CO})_5$ exists at the high laser fluences employed in this study.

In the pulsed valve sample introduction chamber, the sample pressure was adjusted to 7×10^{-5} torr [40 Torr $\text{Fe}(\text{CO})_5$ diluted in 400 Torr Argon]. Spectral scans over the iron fluorescence at 358.1 nm for seven different laser pulse energies within the range 12.5 - 107.5 mJ/pulse (laser fluence range = 4.7×10^{17} - 4.0×10^{18} photons/cm²) were recorded. The results are depicted in Figure 3.11 [p.93]. The slope of the best-fit linear regression line is calculated to

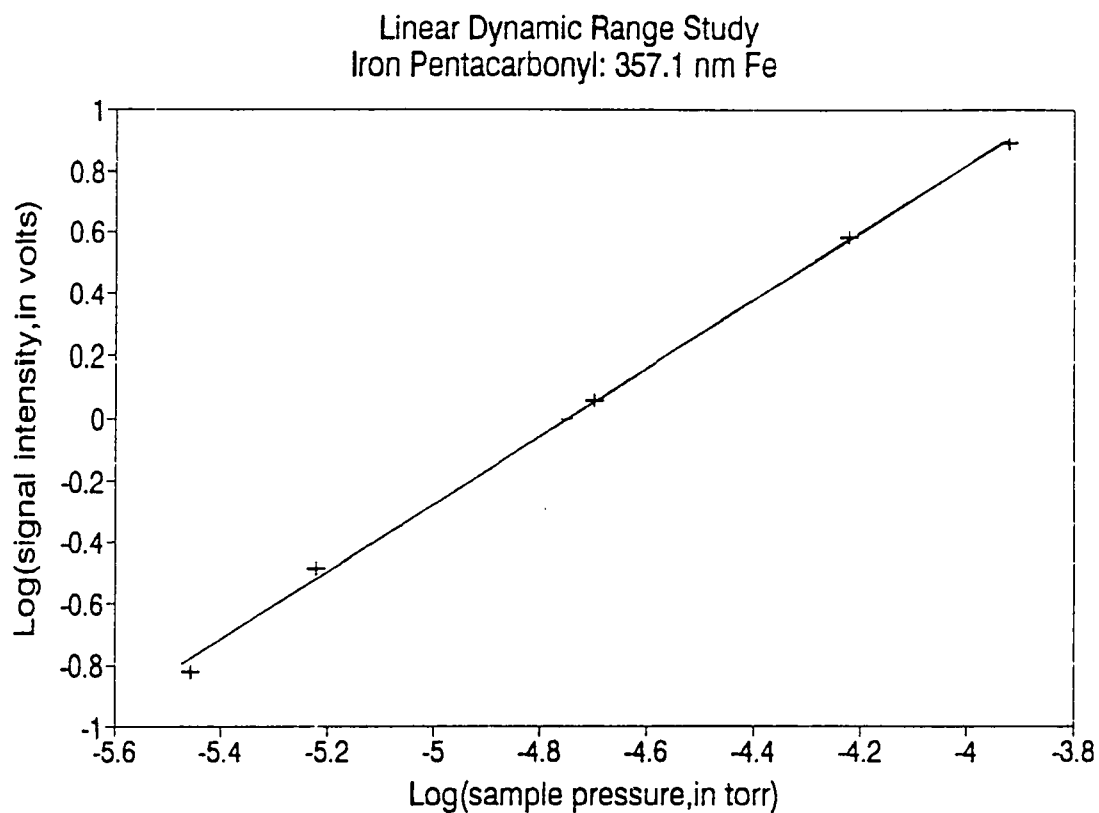


Figure 3.8 Linear Dynamic Range Study of Iron Pentacarbonyl: (357.1 nm)

experimental conditions: entrance/exit monochromator slits = $140\mu\text{m}/52\mu\text{m}$; boxcar gate width = 10 ns; boxcar delay time = 16 ns; excimer laser photolysis energy = 70 mJ/pulse at a repetition rate of 10 Hz

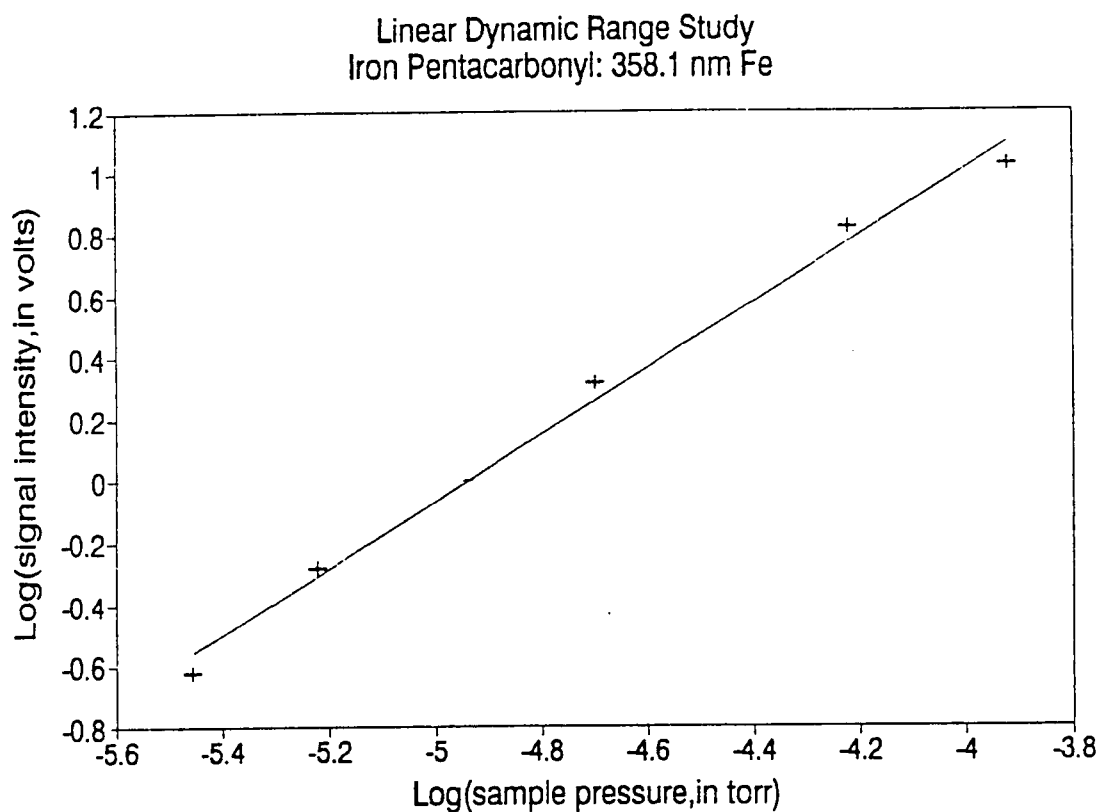


Figure 3.9 Linear Dynamic Range Study of Iron Pentacarbonyl: (358.1 nm)

experimental conditions: entrance/exit monochromator slits= $140\mu\text{m}/52\mu\text{m}$; boxcar gate width= 10 ns; boxcar delay time= 16 ns; excimer laser photolysis energy= 70 mJ/pulse at a repetition rate of 10 Hz

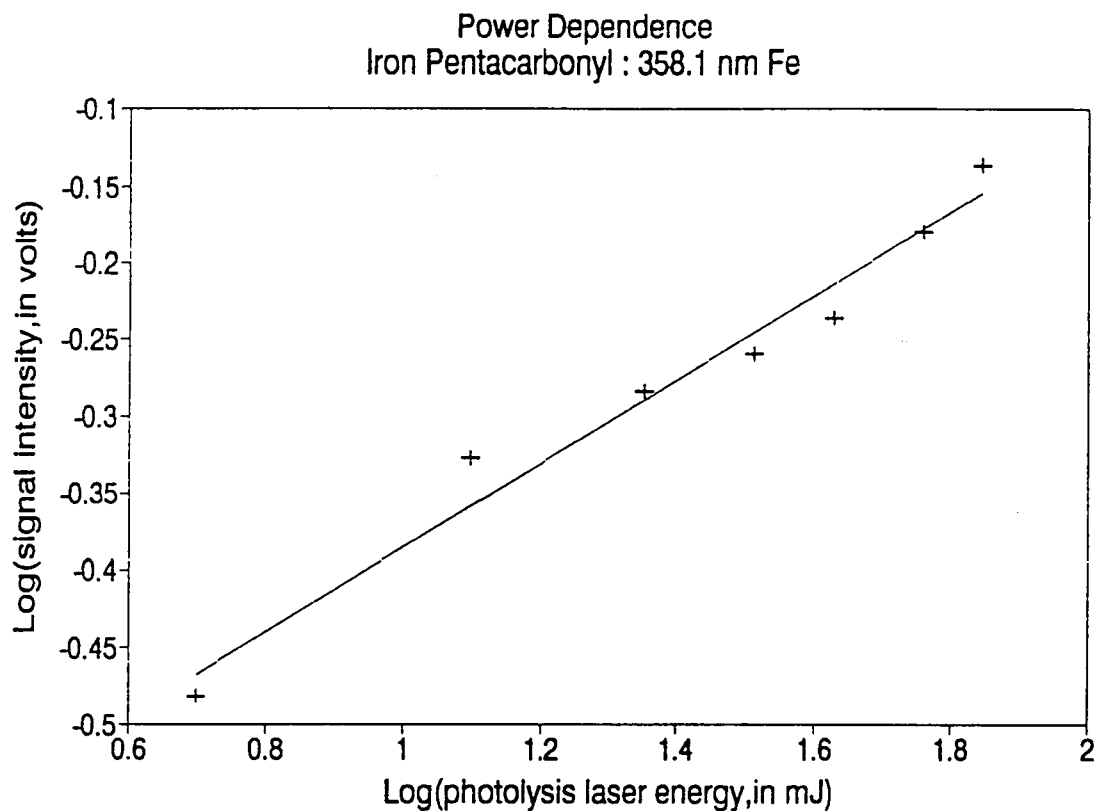


Figure 3.10 Dependence of Signal on Photolysis Laser Pulse Energy for Iron Pentacarbonyl in the Continuous-flow Sample Chamber

experimental conditions: boxcar delay time = 10 ns; boxcar gate width = 10 ns;
entrance/exit monochromator slits = 150 μ m/100 μ m

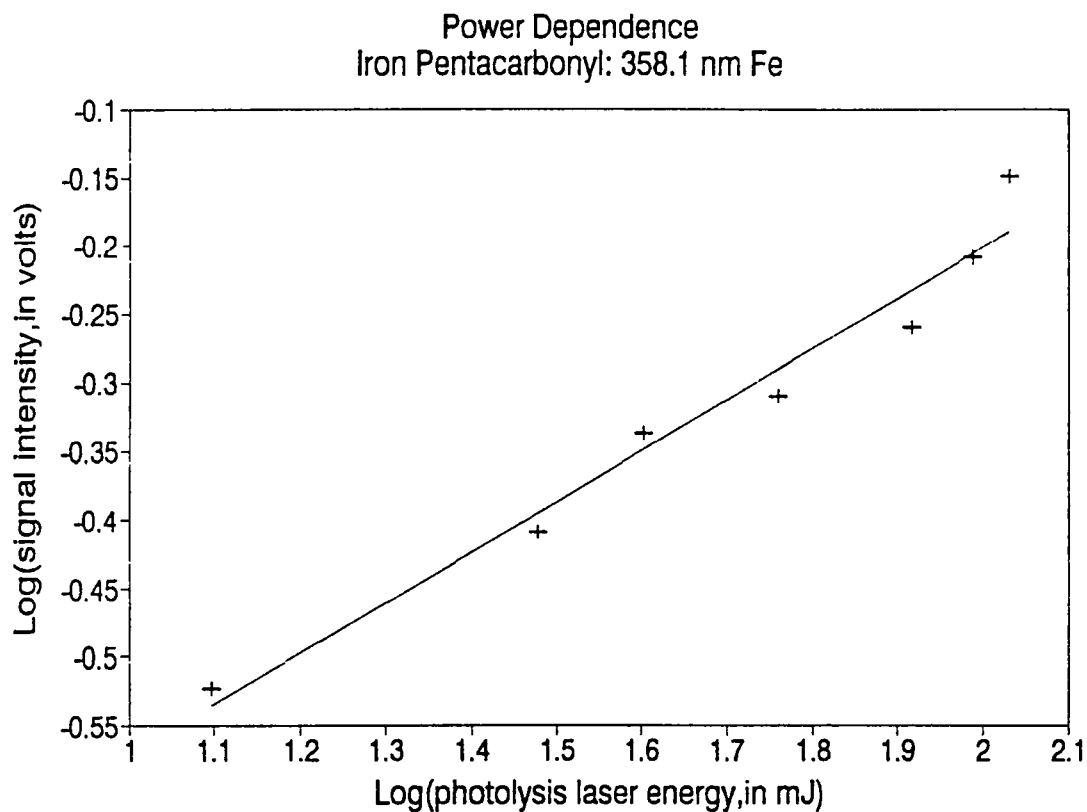


Figure 3.11 Dependence of Signal on Photolysis Laser Pulse Energy for Iron Pentacarbonyl in the Pulsed Valve Sample Chamber

experimental conditions: boxcar delay time = 10 ns; boxcar gate width = 10 ns;
entrance/exit monochromator slits = 150 μ m/100 μ m

be 0.37 ± 0.03 . Again, this result indicates a non-integral power dependence. Consistent results can apparently be obtained from the two chambers.

d. Mo(CO)_6

i. Laser Photolysis Survey Spectrum

Molybdenum hexacarbonyl [Mo(CO)_6], introduced into the continuous-flow vacuum chamber at a sample pressure of 5.5×10^{-5} torr and a temperature of 90°C , was photolyzed by 193 nm radiation, and a survey spectrum was collected as shown in Figure 3.12 [p.95]. The most prominent features are due to the atomic fluorescence of molybdenum at 379.8, 386.4 and 390.3 nm. The additional lines are assumed to be due to CO fragments. Atomic fluorescence at 386.4 nm was chosen for further study. This sample showed evidence of thermal degradation, even at low heating mantle temperatures, as evidenced by the plating out of molybdenum metal in the sample bulb and in the sample introduction line prior to being introduced into the vacuum chamber. After photolysis, molybdenum metal rapidly (< 15 min) deposited on both windows on the vacuum chamber through which the 193 nm laser beam and the fluorescence passed. Collecting data required replacing the damaged windows after each sample run.

ii. Limit of Detection Study

The limit of detection for Mo(CO)_6 was determined as described on p.58. The base pressure in the continuous-flow vacuum chamber was measured via an ion gauge as 8.0×10^{-7} torr. The sample introduction line was heated to 90°C and the sample was introduced into the chamber at a pressure of 3.0×10^{-5} torr, after which the monochromator was scanned over the 386.4 nm. An additional scan over this same wavelength range was recorded in the absence of sample. This procedure was repeated, carefully decreasing the sample pressure in increments down to 9×10^{-7} torr. At this sample pressure (9×10^{-7} torr), a signal to noise ratio of 3 was

MOLYBDENUM HEXACARBONYL
193 NM PHOTOLYSIS

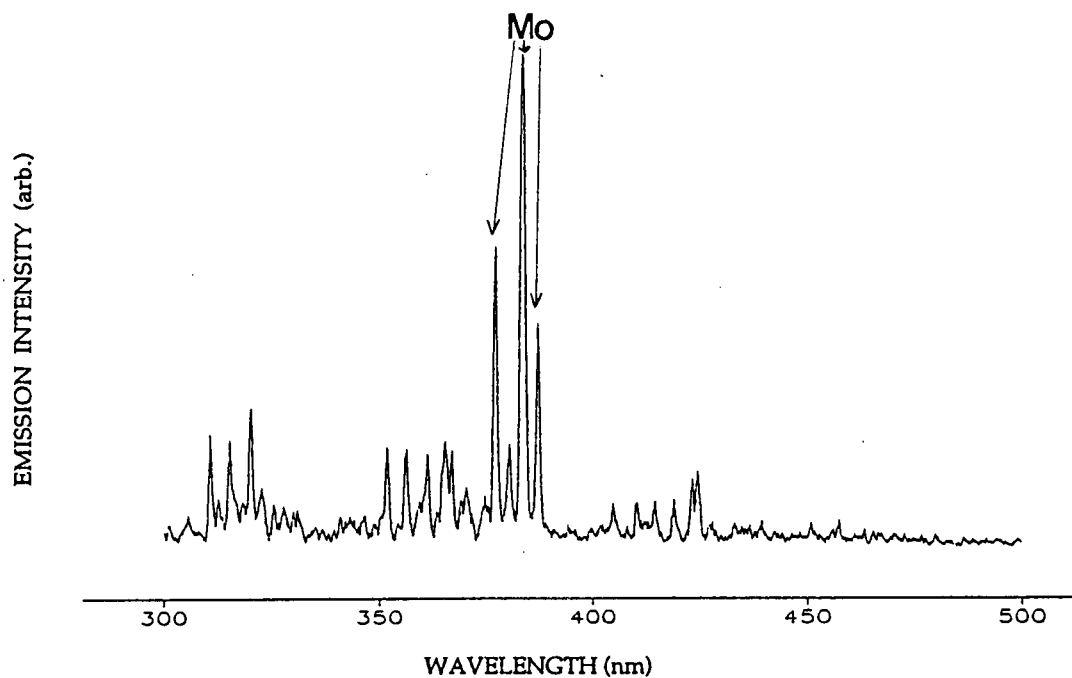


Figure 3.12 Survey Spectrum for the 193 nm Photolysis of Mo(CO)_6

experimental conditions: sample pressure in the chamber = 1×10^{-4} torr; sample temperature = 60°C ; entrance/exit monochromator slits = $230\mu\text{m}/38\mu\text{m}$; boxcar gate width = 10 ns; boxcar delay time = 34 ns; excimer laser photolysis energy = 60 mJ/pulse at a repetition rate of 10 Hz

observed. Attempts to accurately decrease the sample pressure were difficult because the base pressure in the absence of sample was 8×10^{-7} torr. Thus, based on the observed signal to noise ratio of 3, the pressure as a result of sample vapor alone was actually 1×10^{-7} torr. Calculations similar to those on p.77 reveal a molecular density of 5.41×10^{-12} mol/L, resulting in a limit of detection of 460 pg (carbonyl) and 230 pg (analyte atoms). The "probe volume" limit of detection was calculated to be 14 fg (carbonyl) and 7 fg (analyte atoms).

iii. Precision Study

Twelve consecutive fluorescence decay scans were recorded for molybdenum fluorescence at 386.4 nm. The boxcar gate was scanned from 0 to 125 ns, with the monochromator set to transmit radiation at 386.4 nm. The experimental conditions during data collection were : sample pressure in the continuous-flow chamber = 8×10^{-5} torr; entrance/exit monochromator slit widths = $194\mu\text{m}/290\mu\text{m}$; boxcar gate width = 10 ns and excimer laser photolysis energy = 55/60 mJ/pulse. The signal magnitude at a boxcar delay time of 32 ns (fluorescence decay maximum) was obtained from each of the twelve scans. The relative standard deviation in the signal magnitude was calculated to be 11.0 %, the poorest precision observed in this work, presumably due to a rapid deposition of molybdenum metal on the windows of the vacuum chamber, leading to a decrease in photon flux reaching the sample vapor and of fluorescence reaching the monochromator.

iv. Linear Dynamic Range Study

To determine the linear dynamic range, molybdenum fluorescence at 386.4 nm was monitored. The pressure range sampled in the continuous-flow vacuum chamber was 2.3×10^{-6} to 4×10^{-4} torr. The excimer laser photolysis energy was recorded as 75 mJ/pulse. The results of this study are depicted in Figure 3.13 [p.97], from which it can be concluded that the molybdenum atomic fluorescence signal is linear over at least two orders of magnitude, and

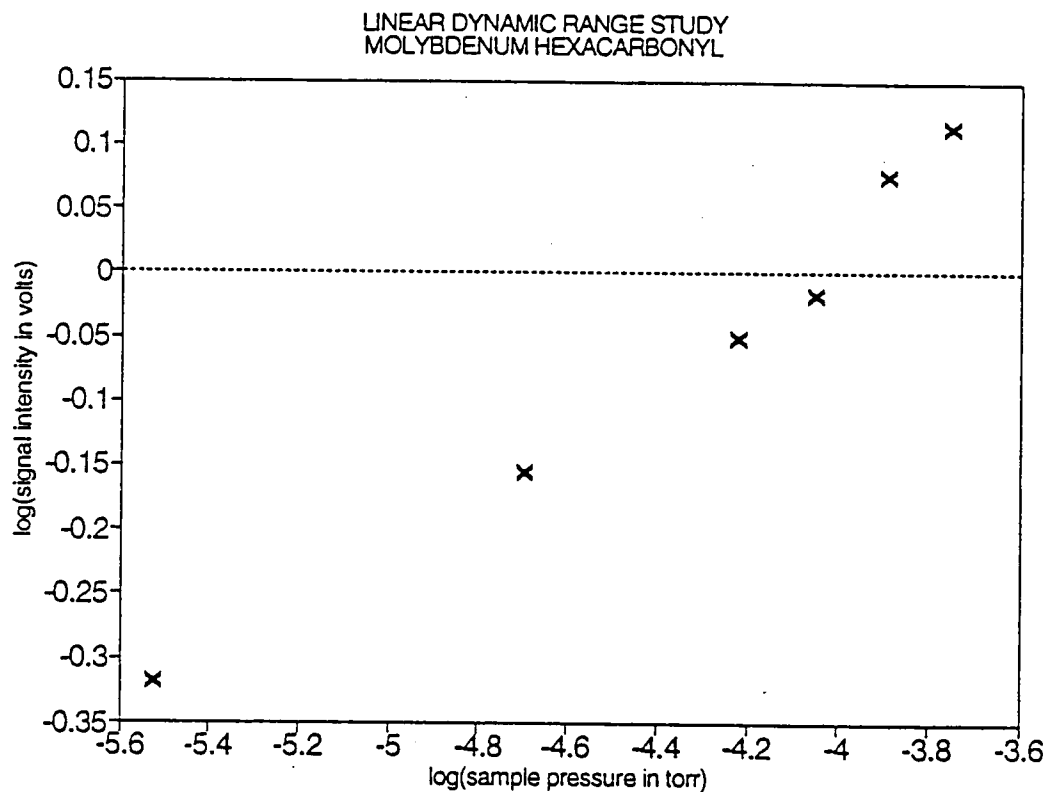


Figure 3.13 Linear Dynamic Range Study of Molybdenum Hexacarbonyl: (386.4 nm)

experimental conditions: entrance/exit monochromator slits = $155\mu\text{m}/62\mu\text{m}$; boxcar gate width = 10 ns; boxcar delay time = 22 ns; excimer laser photolysis energy = 75 mJ/pulse at a repetition rate of 10 Hz

possibly three. As can be seen in the figure, at higher sample pressures ($\sim 10^{-4}$ torr), the signal intensity is somewhat higher than expected, as evidenced by the slight curvature observed in the plot under these conditions.

v. Dependence of Signal on Photolysis Laser Pulse Energy

Mo(CO)_6 sample vapor was introduced at a pressure of 8×10^{-5} torr, after which spectral scans were collected over the molybdenum fluorescence line at 386.4 nm for eight different laser pulse energies within the range 5 - 75 mJ/pulse (laser fluence range = 1.87×10^{17} - 2.80×10^{18} photons/cm²). The results of this study are depicted in Figure 3.14 [p.99]. The slope of the best -fit linear regression line is drawn through the data points and was calculated to be 0.76 ± 0.02 . This result indicates a non-integral dependence of signal on photolysis laser pulse energy, similar to that which was observed for Fe(CO)_5 . Laser saturation of the multiphoton steps involved in this process would tend to result in a slope of <1 .

e. Additional Metal Complexes Investigated

i. Survey Atomic Fluorescence Spectra

Attempts to obtain survey atomic fluorescence spectra upon 193 nm laser photolysis were made for the following metal beta-diketonates: bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedione) lead (II), bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedione)cobalt (II), bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedione)manganese (II) and bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedione)nickel (II). All were heated to temperatures in excess of 135 °C, at which point ligand-derived molecular fragments (CH, C₂ and CO) were observed, but no atomic fluorescence was detected. It is possible that a low fragmentation efficiency at 193 nm exists for these chelates, particularly for the lead(II) and nickel (II) beta-diketonates. A comparison of the relative signal intensities of the atomic spectral lines indicates that, of the metal beta-diketonates studied here, only Co^{2+} and Mn^{2+} show strong

Dependence of Mo Fluorescence Signal Photolysis Laser Pulse Energy

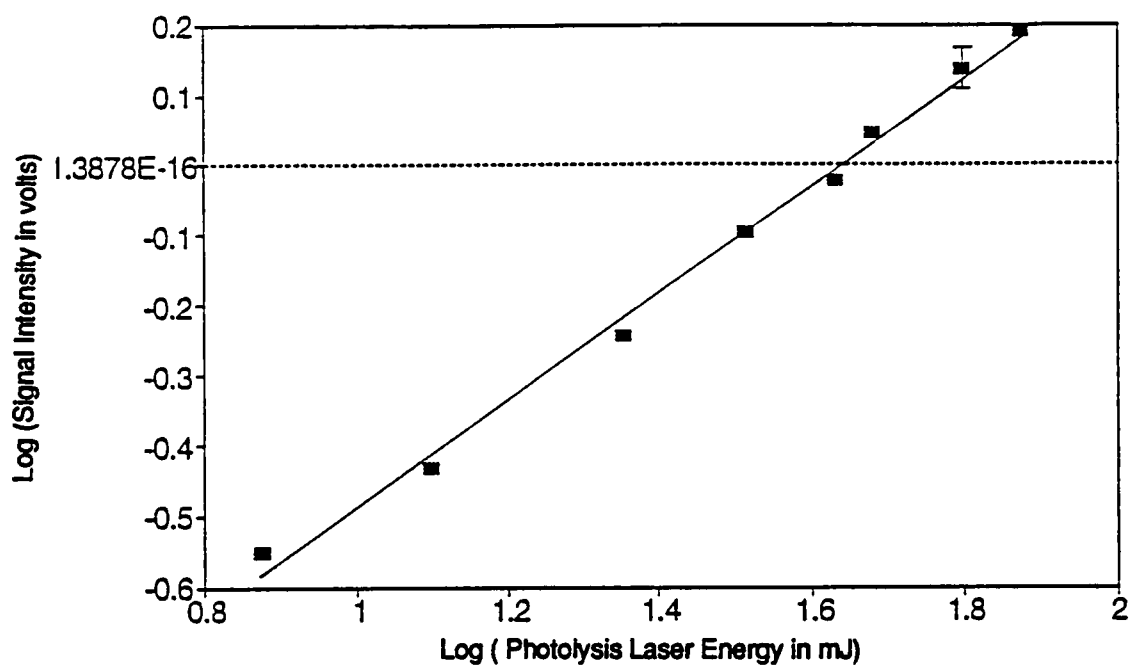


Figure 3.14 Dependence of Signal (386.4 nm Mo Fluorescence) on Photolysis Laser Pulse Energy

experimental conditions: boxcar delay time = 22 ns; boxcar gate width = 10 ns;
entrance/exit monochromator slits = 200 μ m/150 μ m

absorption at 193 nm (72). Thus, it was expected that atomic fluorescence might be generated by the 193 nm photolysis of Co(hfa)_2 and Mn(hfa)_2 , but not necessarily from Ni(hfa)_2 or Pb(hfa)_2 .

Since the 193 nm photolysis of Co(hfa)_2 in the continuous-flow chamber previously resulted only in molecular fragments, it was decided to introduce a more volatile cobalt-containing sample through the pulsed valve to determine which cobalt atomic lines were most likely to be observed (if any) upon 193 nm laser photolysis. Cyclopentadienylcobalt dicarbonyl [$\text{C}_5\text{H}_5\text{Co(CO)}_2$] was chosen due to the high susceptibility of metal carbonyl complexes to fragmentation when photolyzed by 193 nm radiation. Cyclopentadienylcobalt dicarbonyl, held at room temperature, was introduced into the pulsed valve chamber at a sample pressure of approximately 8×10^{-5} torr and an atomic fluorescence spectrum for cobalt was recorded as shown in Figure 3.15 [p.101]. Since cobalt fluorescence was observed for this sample, it is possible that the fragmentation efficiency at 193 nm for Co(hfa)_3 is small when compared to that of $\text{C}_5\text{H}_5\text{Co(CO)}_2$, which may have contributed to a lack of observed atomic fluorescence for the former. The upper temperature limit of the pulsed valve is 70°C, so Co(hfa)_3 could not be introduced into this chamber.

It should be noted that, in addition to the work reported in this dissertation, Schendel obtained survey atomic fluorescence spectra upon 193 nm photolysis for the following metal beta-diketonates: hfa derivatives [Fe,Cr,Al,Cu,Ga] and tfa derivative [Cu], which clearly indicates that atomic fluorescence signals can be attained from a wide variety of metal beta-diketonates (64).

f. Conclusions

Three metal beta-diketonates [Cu(hfa)_2 (64), Ga(hfa)_3 and Fe(hfa)_3] and two metal carbonyls [Fe(CO)_5 and Mo(CO)_6] have now been analytically characterized by the laser photofragmentation fluorescence method. Low limits of detection, relatively high analytical precision and an extended linear dynamic range have been observed in each case. At this point

Cobalt cyclopentadienyl dicarbonyl
193 NM PHOTOLYSIS

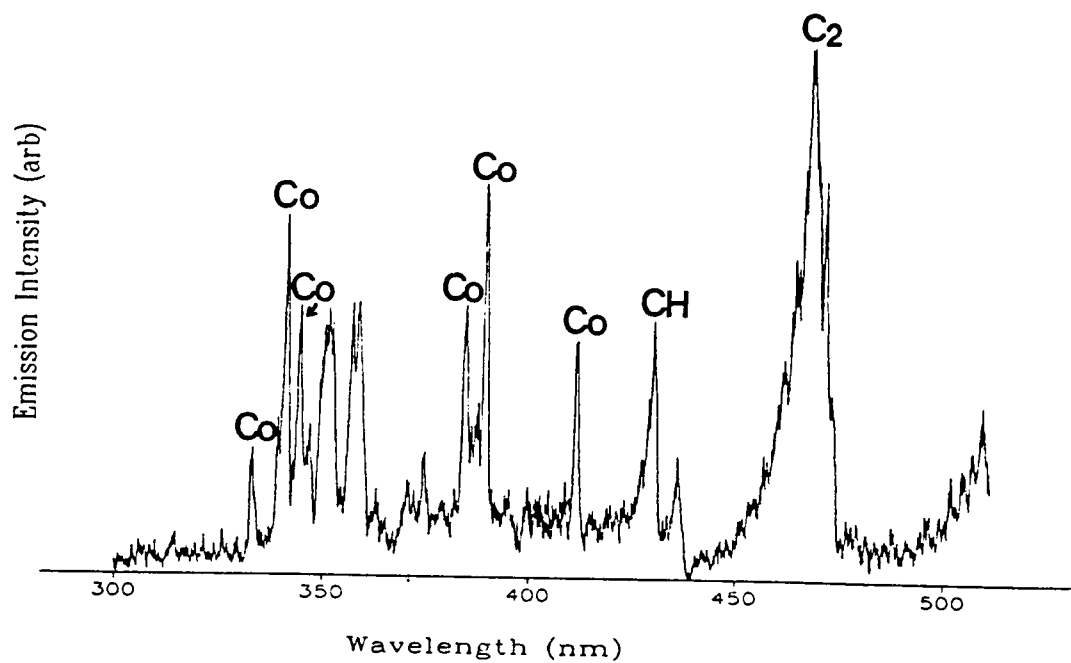


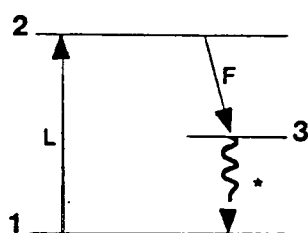
Figure 3.15 Fluorescence Survey Spectrum of the 193 nm Photolysis of $C_5H_5Co(CO)_2$ using Pulsed Valve Sample Introduction

in the research, it was necessary to determine if resonance laser induced fluorescence (a 2-laser experiment) could further improve the limits of detection. Then, LP-AFS could be applied with confidence to "real" analytical samples. The first of these objectives is addressed in the following sections. The second objective is discussed in Chapter 4.

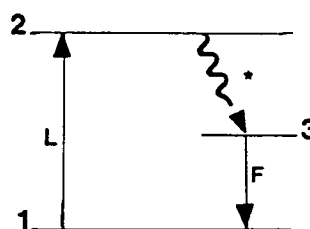
2. Laser-induced Fluorescence of the Metal Atom

a. LIF of Cu from the Laser Photolysis of Cu(hfa)_2

Two primary types of atomic fluorescence transitions are possible: resonance and non-resonance. In a resonance fluorescence transition, a photon having an energy and wavelength identical to that absorbed is emitted. This process is experimentally undesirable (but in many cases unavoidable), because it is difficult to discriminate between the fluorescence signal and the scattered radiation from the laser source. A much more desirable situation involves non-resonance fluorescence transitions. In this case, the emitted photon has an energy and wavelength different from that absorbed. The net result is enhanced selectivity, because the scattered laser radiation into the monochromator-detector apparatus can be largely rejected. The two most observed types of non-resonance atomic fluorescence transitions are "direct-line" and "stepwise-line" fluorescence (3,8), both of which are diagrammed below:



Direct-Line



Stepwise-Line

In both of these non-resonance atomic fluorescence transitions, a collisionally-induced radiationless event (denoted by a wavy arrow) is involved, and the atomic fluorescence occurs at lower energy (longer wavelength) than the laser excitation radiation. Either of these processes

may occur, depending on the particular atom being studied.

Since few collisions occur in our vacuum chamber under conditions of low sample pressure, the probability of observing "non-resonance" is presumed to be low in the research described here. Experiments described on p.117 are consistent with the presumption that non-resonance laser-induced fluorescence is difficult or impossible to observe under the current experimental conditions. Thus, resonance LIF experiments were performed, using selected metal beta-diketonates.

Although the 193 nm excimer laser photolysis of Cu(hfa)_2 coupled with laser-induced fluorescence (LIF) of photolytically generated Cu atoms at 324.75 nm has already been reported (64), these studies were duplicated as described here for two reasons. First, it was necessary to insure that experimental conditions were optimized to produce LIF by a probe laser and, secondly, it was desired to determine if a "clean" atomic fluorescence spectrum (devoid of ligand-derived molecular fragments) could be obtained as a result of LIF enhancement of the metal atom fluorescence.

To begin, the 193 nm laser photolyzed Cu(hfa)_2 to produce bare Cu atoms, which were subsequently excited by 324.75 nm photons from the WEX output of a Nd:YAG pumped dye laser. The output of DCM dye was doubled in the WEX to deliver ~ 4.5 mJ/pulse at 324.75 nm, a wavelength which corresponded to the $\text{Cu}(^2\text{P}_{3/2}^0 \rightarrow ^2\text{S}_{1/2})$ absorption transition. The timing and spatial overlap between the 193 nm photolysis laser and the probe laser were performed as described on p.45. The delay time between the two lasers was set to approximately 22 ns, so that the two laser pulses coincided in time. A scan of scattered probe laser light versus gated integrator delay time was recorded with the aid of a gate scanner (as mentioned previously on p.42). The maximum peak of this scan corresponded to 21 ns, so the boxcar delay time was set at approximately 25 ns. The photodiode which detected the probe laser radiation was set to trigger the boxcar. The monochromator was set to transmit radiation at 324.75 nm. Cu(hfa)_2 vapor at a temperature of 94°C and a pressure of 9×10^{-5} torr was admitted into the vacuum

chamber and the dye laser was scanned over a wavelength range of 325.4 - 324.15 nm to produce the excitation spectrum in Figure 3.16 [p.105]. The procedure was repeated over the same wavelength range in the absence of sample, which represented just the probe laser scattering signal, as seen in Figure 3.16. The peak with the narrow spectral bandwidth rising above the broad, scattered background is due to the LIF of Cu at 324.75 nm.

The dye laser was set at the maximum wavelength for which probe-laser enhancement was achieved (as measured from Figure 3.16). Fluorescence spectra were then collected (as described on p.64) for three cases: (a) photolysis + probe beams, sample present (b) photolysis beam only, sample present and (c) photolysis + probe beams, sample absent. The results are shown in Figure 3.17 [p.106]. The sample pressure was held at 8×10^{-5} torr for cases (a) and (b). The signal magnitude of the spectrum in case (c) subtracted from that of the spectrum in case (a) gave an estimate of the actual probe-laser induced Cu fluorescence signal. In case (c), the signal magnitude observed was due solely to scattered probe laser light. The signal due to Cu fluorescence at 324.75 nm from the pump laser alone was not detectable above the baseline under these conditions because of the low boxcar amplification setting that was used to obtain these data (by increasing the boxcar amplification, one-laser Cu fluorescence was readily observed).

From Figure 3.17, an estimate of the degree of probe-laser induced enhancement [defined as case (a) - case (c) / case (b)] was calculated to be ca.100. This "factor of enhancement" value provides an estimate of the degree of signal improvement over that obtained when only the photolysis laser was used. From these results, it can be inferred that a significant improvement in the limit of detection for Cu could be achieved by using a probe laser beam to excite ground-state Cu atoms formed by the 193-nm photolysis of Cu(hfa)_2 .

In Figure 3.18 [p.107], a two-laser extended wavelength fluorescence spectrum is shown. The experimental conditions under which this spectrum was obtained are identical to that of Figure 3.17, except that, in Figure 3.18, the monochromator was scanned from 300 - 450

LIF EXCITATION SPECTRUM OF Cu FROM LASER PHOTOLYSIS OF
 Cu(hfa)_2

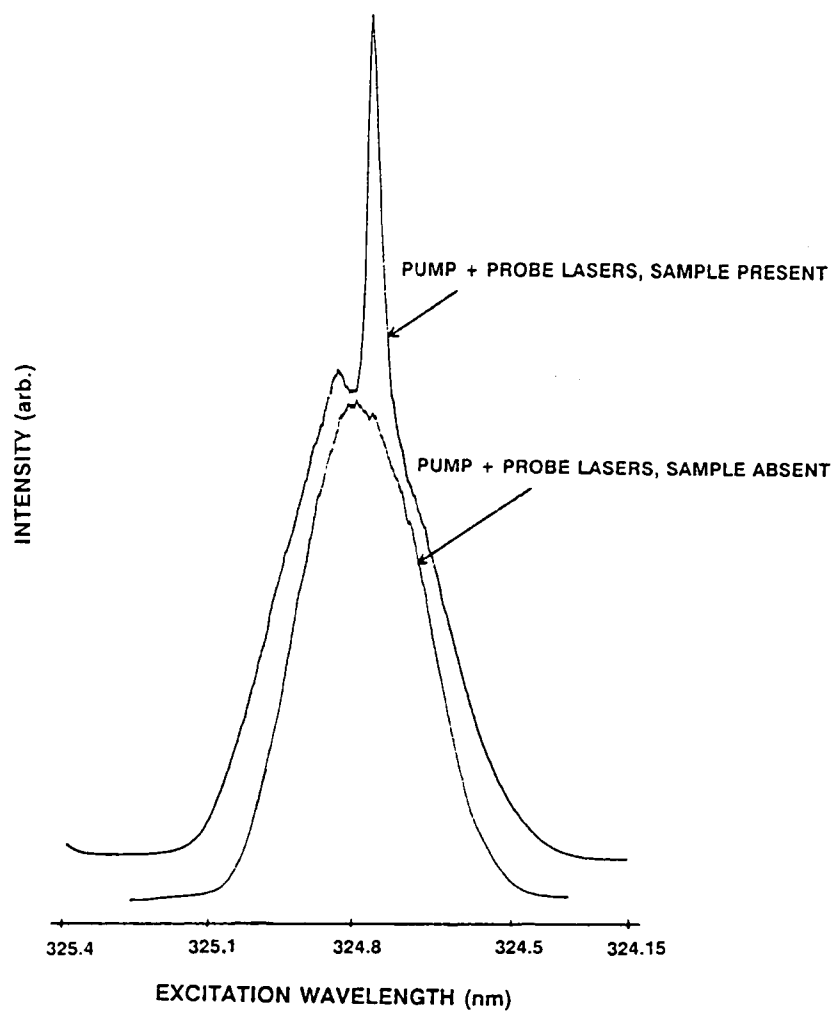


Figure 3.16 LIF Excitation Spectrum of Cu from Cu(hfa)_2

LIF SPECTRUM OF Cu FROM 193 NM LASER PHOTOLYSIS OF
 Cu(hfa)_2

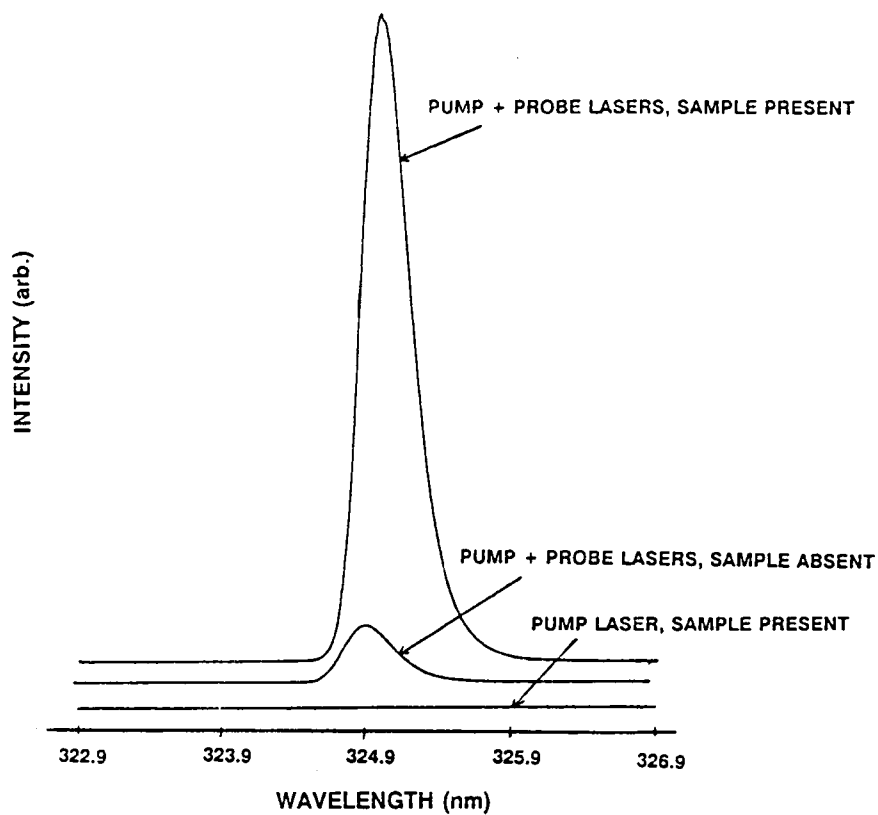


Figure 3.17 LIF Emission Spectrum of Cu from the 193 nm Laser Photolysis of Cu(hfa)_2

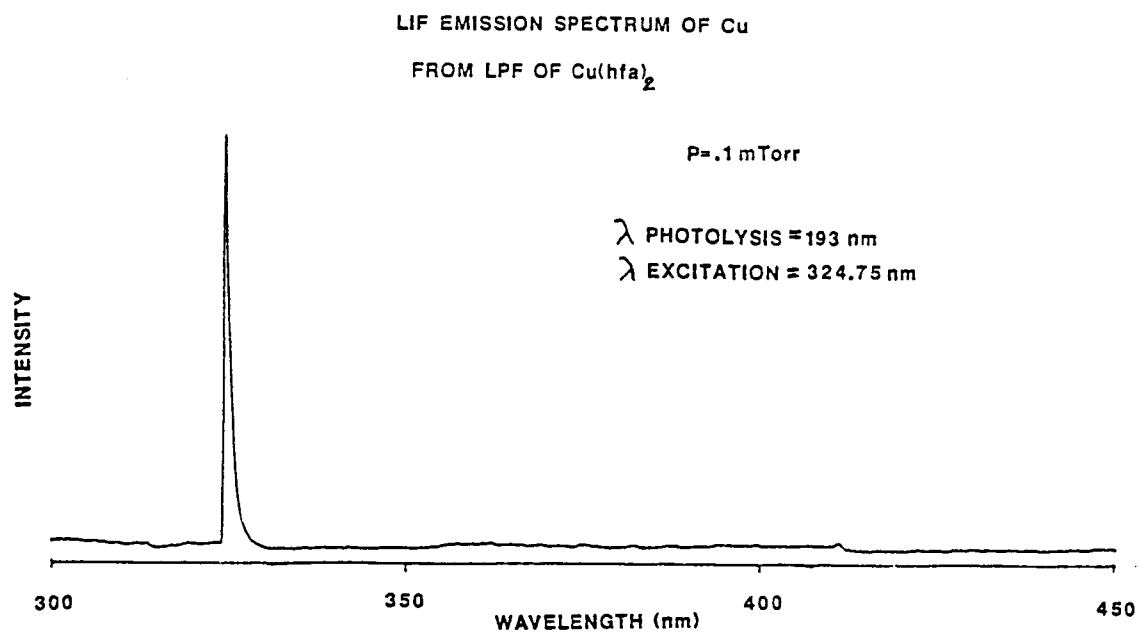


Figure 3.18 Extended Wavelength LIF Emission Spectrum of Cu from the 193 nm Laser Photolysis of Cu(hfa)_2

nm. The single intense feature is LIF of Cu at 324.75 nm. An exceedingly clean fluorescence spectrum resulted. The fluorescence due to ligand-derived molecular fragments is barely discernible above the baseline. This is a significant result when compared to the cluttered atomic spectra typically obtained by conventional atomic fluorescence and ICP-AES methods, a point which was discussed on p.9.

b. LIF of Ga from the Laser Photolysis of Ga(hfa)₃

Due to the success of LIF enhancement of Cu from Cu(hfa)₂, an analogous study was undertaken for Ga(hfa)₃. The 193 nm excimer laser photolyzed Ga(hfa)₃ to produce bare Ga atoms, which were subsequently excited by 417.2 nm photons from the WEX output of a Nd:YAG pumped dye laser, a wavelength which corresponded to the Ga(5s ²S_{1/2} → 4p ²P_{3/2}) absorption transition. The output of laser dye LDS-698 was mixed with 1064 nm in the WEX to deliver 3.9 mJ/pulse at 417.2 nm. The timing and spatial overlap between the two laser beams was optimized. The delay time between the two lasers was set at approximately 35 ns, in order to easily detect any probe-laser induced fluorescence from the short-lived (experimentally determined to be ~ 36 ns) Ga atomic fragment. A spectral scan of scattered probe laser light vs. gated integrator delay time revealed a peak maximum of 32 ns, so the boxcar was set at a delay time of 38 ns. The photodiode which detected the probe laser radiation was set to trigger the boxcar. Ga(hfa)₃ vapor (T = 73°C) held at a pressure of 5 × 10⁻⁵ torr was admitted into the vacuum chamber. The monochromator was set to transmit radiation at 417.2 nm. The dye laser was then scanned at a rate of 0.01 nm/s over a wavelength range of 417.65 - 416.90 nm to produce the excitation spectrum in Figure 3.19 [p.109]. The same procedure was repeated in the absence of sample to produce the spectrum also shown in Figure 3.19. Unlike the excitation spectrum for the LIF of Cu from Cu(hfa)₂, a small peak of relatively narrow bandwidth was seen in the current spectrum with Ga(hfa)₃. This particular experiment was performed three additional times after re-optimizing experimental parameters (e.g. 2-laser delay time, spatial overlap of the

LIF EXCITATION SPECTRUM OF Ga FROM LASER PHOTOLYSIS OF $\text{Ga}(\text{hfa})_3$

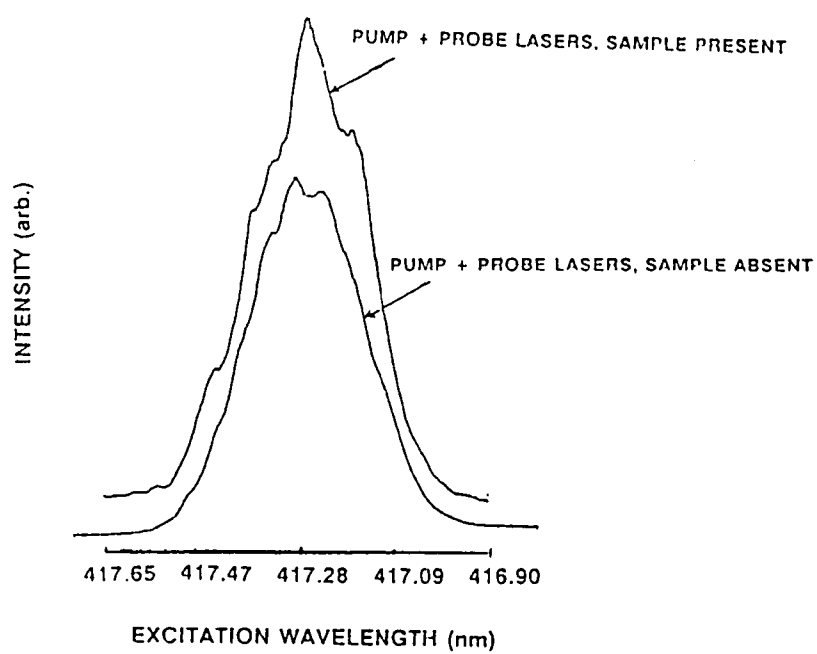


Figure 3.19 LIF Excitation Spectrum of Ga from $\text{Ga}(\text{hfa})_3$

laser beams, boxcar delay time) in an attempt to improve the signal magnitude. Although no significant improvement ensued, it was assumed that probe laser induced enhancement was taking place, but not nearly to the extent to which was observed for Cu(hfa)_2 .

The probe laser was set to the peak maximum obtained from the excitation spectrum, which most nearly corresponded to 417.2 nm, and the monochromator was scanned over the 417.2 nm fluorescence peak for three separate cases : (a) pump + probe beams, sample present (b) pump beam, sample present and (c) pump + probe beams, sample absent. The sample pressure was held constant in cases (a) and (b) and was measured as 5×10^{-5} torr. Representative fluorescence spectra from each of the three cases above are depicted in Figure 3.20 [p.111]. As compared to the fluorescence spectra collected for the LIF of Cu from $\text{Cu(hfa)}_2 \cdot 2\text{H}_2\text{O}$, the ratio of the LIF signal to that of the one-laser signal is small (factor of enhancement = 5 as estimated from Figure 3.20).

Experimentally, it was difficult to reduce the magnitude of the probe laser scattering signal to a manageable level. The probe beam was severely apertured by an iris diaphragm and the monochromator entrance and exit slits were closed as much as possible to reduce the scattering level. Temporal discrimination was attempted, but the short lifetime of the atomic fluorescence prohibited effective means to distinguish between the scattering signal (temporally instantaneous) and the fluorescence signal.

The reason(s) why the probe laser appears to produce a much smaller increase in sensitivity for Ga from Ga(hfa)_3 than for Cu from Cu(hfa)_2 are not clear. For Ga(hfa)_3 , it is possible that a higher proportion of excited gallium atoms (rather than ground state atoms) resulted from the 193 nm photofragmentation of the sample. However, regardless of the small LIF signal for Ga at 417.2 nm, three separate experiments analogous to those described for the one-laser experiments were performed as discussed in the following sections.

LIF SPECTRA OF Ga FROM 193 NM LASER PHOTOLYSIS OF
 $\text{Ga}(\text{hfa})_3$

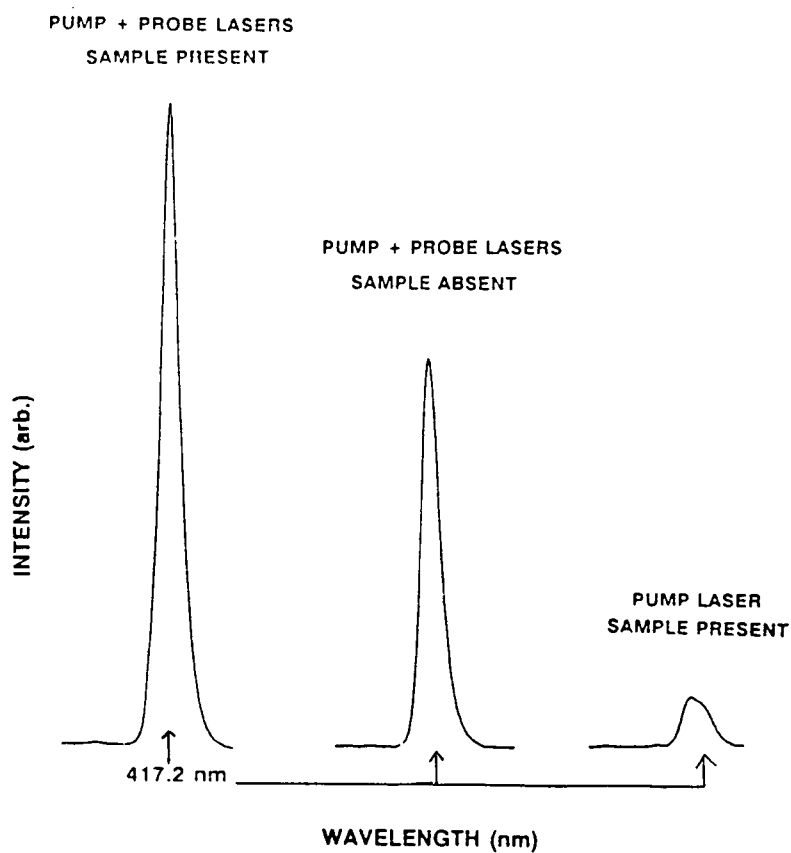


Figure 3.20 LIF Emission Spectra of Ga from the 193 nm Laser Photolysis of $\text{Ga}(\text{hfa})_3$

i. Dependence of Ga LIF Signal on Sample Pressure

Laser-induced fluorescence spectra of Ga from Ga(hfa)_3 were recorded at six different sample pressures, from a range of 4×10^{-6} to 1.1×10^{-4} torr. At each pressure, three spectra were recorded as the monochromator was scanned over the Ga fluorescence signal at 417.2 nm: (a) pump + probe beams, sample present; (b) pump beam only, sample present; and (c) pump + probe beams, sample absent. An estimate of the signal due to LIF by the probe laser could be obtained by subtracting the LIF signal with the sample absent from the LIF signal with the sample present. In addition, the factor of enhancement (relative signal improvement by bringing in the probe laser) could be obtained by dividing the LIF signal magnitude [case (a) - case (c)] by the fluorescence signal using only the photolysis laser [case (b)].

In Figure 3.21 [p.113], two curves are shown. The lower curve represents the linear dependence of the fluorescence signal (only the photolysis laser) on sample pressure, and the best-fit linear regression line is drawn through the data points (slope = 1.0). The data presented here agree well with the data reported in Figure 3.3 [p.79]. The top curve represents the dependence of the LIF signal on sample pressure; the shape of this curve is not well understood. This curve was verified two additional times. It is believed that, because the LIF signal magnitude is so small (irrespective of sample pressure), that distinguishing between the actual LIF signal and the background due to the probe laser presents a problem, and that what is actually measured is predominantly scatter of the probe laser beam rather than Ga LIF.

In Figure 3.22 [p.114], the apparent factor of enhancement of the Ga atomic fluorescence signal produced by the probe laser is plotted vs. the sample pressure. At the lowest pressure sampled (4×10^{-6} torr), the extent of enhancement was the largest (14.2). As the sample pressure increased, the apparent factor of probe-laser enhancement decreased. The general observations and shape of this plot were also observed for Cu(hfa)_2 under similar experimental conditions (64). However, for Cu, the observed probe-laser enhancement of the atomic fluorescence signal was much larger than that observed for Ga. In the case of Ga(hfa)_3 ,

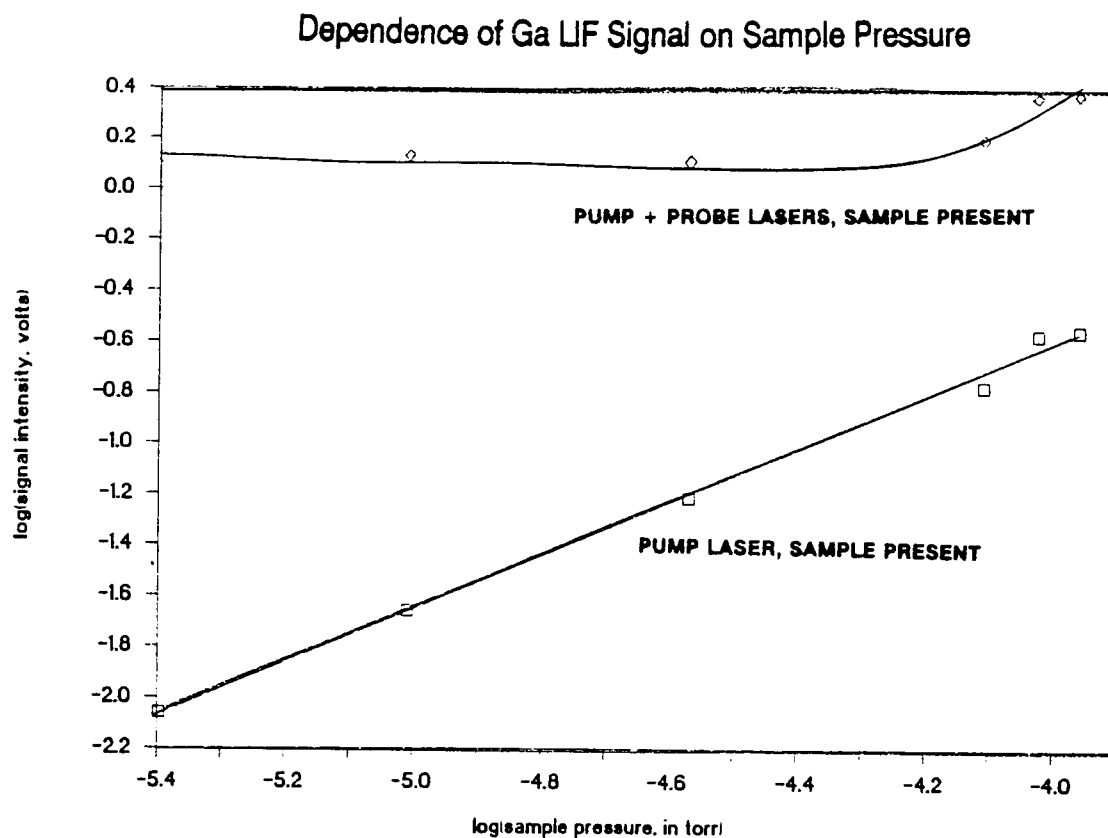


Figure 3.21 Dependence of Ga LIF Signal on Sample Pressure

bottom: pump laser only; top: both pump and probe lasers

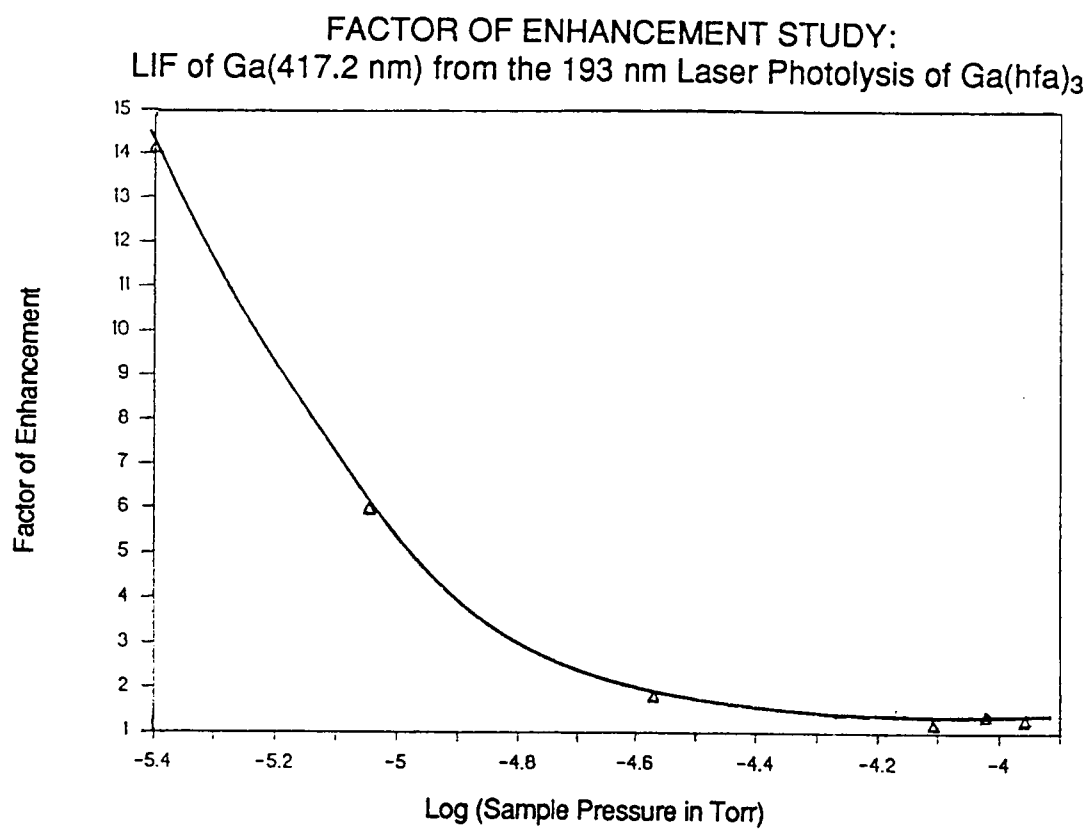


Figure 3.22 Factor of Enhancement Study for Ga(hfa)₃

it can be concluded that use of the probe laser does not effect any practical improvement in the limit of detection, at least under these experimental conditions.

ii. Dependence of Ga LIF Signal on Photolysis Laser Pulse Energy

This dependence was studied at a sample pressure of 5.5×10^{-5} torr ($T = 73^\circ\text{C}$). Six different photolysis laser pulse energies within the range 47.5 - 122.5 mJ/pulse (laser fluence = 1.78×10^{18} - 4.58×10^{18} photons/cm²) were recorded. For each laser pulse energy sampled, two spectra were recorded : (a) pump + probe laser beams, sample present and (b) pump + probe laser beams with sample absent. In each case, the peak due to the scattering signal (b) was subtracted from the peak for the spectrum in which the sample was present. This difference was assumed to represent the magnitude of the LIF signal at 417.2 nm. The results are displayed graphically in Figure 3.23 [p.116], and the best-fit linear regression line is drawn through the data points. The slope of the line was calculated to be 2.34. This indicates a greater than quadratic dependence of the LIF signal on photolysis laser pulse energy. However, the one-laser study reported earlier (Figure 3.3) of log(fluorescence signal due to photolysis laser) vs. log(laser pulse energy) exhibited a slope of 1.37.

These results are inconsistent with the data from earlier published results for an analogous study for Cu(hfa)_2 (64). In that study, it was found that the dependence of the LIF signal of Cu from the 193 nm photolysis on the photolysis laser pulse energy of Cu(hfa)_2 was 2.3 in a one-laser experiment and 1.3 in a two-laser experiment. It was assumed that this difference in 193 nm pulse-energy dependence for Cu(hfa)_2 meant that the probe laser provided the photon necessary to excite ground state copper atoms generated by the photolysis laser. Clearly, no such rationalization pertains to the Ga(hfa)_3 data. It is possible for Ga(hfa)_3 that the probe laser is responsible for some photolytic processes which are not presently understood; similar results have been noted in two-laser LP-FFS experiments of organic molecules (73). Alternatively, the data for the two-laser experiment for Ga(hfa)_3 may be virtually meaningless, due to the very

DEPENDENCE OF Ga LIF SIGNAL ON PHOTOLYSIS LASER PULSE ENERGY

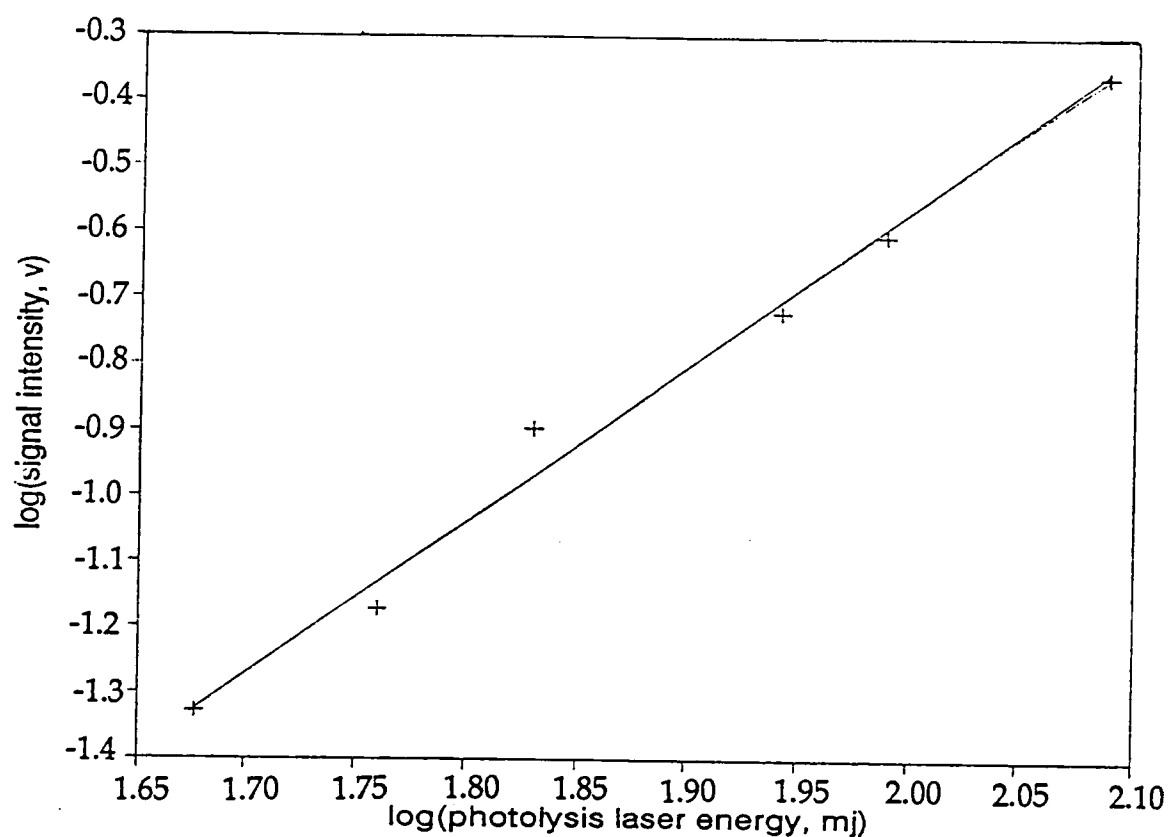


Figure 3.23 Dependence of Ga LIF Signal on Photolysis Laser Pulse Energy

small LIF signal observed for Ga(hfa)_3 .

iii. Precision of Ga LIF Signal

Eleven consecutive LIF spectral scans over the Ga fluorescence peak at 417.2 nm were recorded under the following conditions: boxcar delay time = 40.5 ns; sample pressure = 7×10^{-5} torr at 63°C; estimated 2-laser delay time = 20 ns; photolysis laser energy = 75 mJ/pulse at 10 Hz; and probe laser pulse energy = 3.9 mJ/pulse at 417.2 nm. Peak heights above the scattering background were measured, and the relative standard deviation in the signal magnitude was calculated to be 3.3 %. The precision is somewhat better than that observed when only the photolysis laser is used (%RSD = 5.5). These results are consistent with the observations reported for an analogous study with Cu(hfa)_2 (64), in which the precision of the Cu AF signal was higher in a two laser experiment than in a one-laser experiment.

c. LIF of Fe from the Laser Photolysis of Fe(hfa)_3

To decrease the deleterious effects of the severe Rayleigh scattering background at the probe laser wavelength observed in the pump-probe resonance LIF experiments described above for Ga(hfa)_3 , non-resonance ($\lambda_{\text{probe}} \neq \lambda_{\text{fluorescence}}$) experiments were attempted with the Fe(hfa)_3 chelate. Bolshov and coworkers described a graphite furnace atomization atomic fluorescence experiment in which excitation at 296.7 nm ($a^5D_4 - y^5F^0_5$) resulted in the observation of Fe atomic fluorescence at 373.5 nm ($y^5F^0_5 - a^5F_5$), an example of direct-line non-resonance fluorescence (74). A similar experiment was attempted here using our system. A Nd:YAG pumped dye laser was used as the probe laser. The output of a 50/50 methanol/water - Kiton Red 620 laser dye mix was doubled in the WEX, which produced ~ 2 mJ/pulse at a wavelength of 296.7 nm. After the timing and spatial overlap had been achieved for both lasers (p.46), the monochromator was set to the desired Fe fluorescence wavelength (373.5 nm). Fe(hfa)_3 sample vapor was introduced at a pressure of 1×10^{-4} torr. The excimer laser energy

was 75 mJ/pulse and the probe laser energy was 2 mJ/pulse.

A dye laser excitation scan over 296.7 nm revealed that no appreciable Fe LIF signal at 373.5 nm was observed under these conditions. Focusing the probe beam (296.7 nm) with a 1"dia. 6 cm f.l. plano-convex lens to provide a higher probe photon flux resulted in no improvement in the signal. The photolysis laser energy was reduced to 20 mJ/pulse while the probe laser output was kept at a maximum (~2 mJ/pulse) in an attempt to provide an avenue for additional excitation by the probe laser. The sample pressure was varied from 1×10^{-4} torr down to 1×10^{-6} torr. In no case was there evidence of probe-laser excitation taking place. Finally, the photolysis laser beam was blocked and the dye laser was set at the calculated output to produce 296.7 nm in the WEX (which was verified by the monochromator set at 296.7 nm). This probe beam was focused with a 6 cm f.l. plano-convex lens, Fe(hfa)_3 sample vapor was admitted, and the monochromator was scanned from 319.39 - 463.5 nm. Focused 296.7 nm probe laser radiation was capable of fragmenting the chelate, which resulted in broadened peaks presumably due to iron fluorescence at 344, 358, 372, 373.5 and 375 nm. However, when the photolysis laser was used in conjunction with the focused probe laser beam at 296.7 nm, Fe atomic fluorescence was observed as the monochromator was scanned, but the signal magnitudes of these peaks were essentially the same as that observed with the photolysis laser alone. It is thus concluded that no detectable excitation of Fe direct-line non-resonance fluorescence at 373.5 nm by probe-laser radiation at 296.7 nm occurs under our experimental conditions. The lack of non-resonance LIF in these experiments is not necessarily surprising (see discussion on p.102).

It was therefore decided to proceed to resonance LIF experiments for Fe(hfa)_3 . From this point on, two-laser data collection was controlled by a laboratory computer (as described on p.43). The 193 nm excimer laser photolyzed Fe(hfa)_3 to produce bare iron atoms, which were subsequently excited by 358.1 nm photons from an excimer-pumped dye laser. The XeCl excimer laser (used to pump the dye laser) output was 75 mJ/pulse and the ArF excimer laser

output was 75 mJ/pulse. The dye laser contained DMQ dye dissolved in p-dioxane, which delivered 4 mJ/pulse at 358.1 nm. The timing and spatial overlap between the photolysis and probe lasers was set up as described on p.47. From an oscilloscope trace, it was determined that the probe laser followed the photolysis laser by ~ 25 ns. Fe(hfa)_3 sample vapor was admitted into the chamber at a pressure of 1×10^{-4} torr. With the monochromator set to transmit radiation at 358.1 nm, the dye laser was scanned from 355.6 to 359.7 nm. An additional dye laser scan over this same wavelength range was obtained in the absence of sample. Both excitation spectra can be seen in Figure 3.24 [p.120]. In the presence of sample, a peak of narrow bandwidth was observed, presumably due to the LIF of Fe at 358.1 nm.

The dye laser wavelength was then set to that of the maximum of the peak presumed to be due to the LIF enhancement of Fe from the excitation spectrum. With both lasers running, Fe(hfa)_3 vapor at a sample pressure of 1×10^{-4} torr was introduced into the chamber. The monochromator was scanned from 346 - 382 nm. Refer to Figure 3.25 [p.121] for fluorescence spectra recorded for case (a) probe + pump beams, sample present; (b) pump beam, sample present; and (c) probe beam only, sample absent. In cases (a) and (b), the sample pressure was kept constant at 1×10^{-4} torr. From Figure 3.25, it appears that resonance LIF at 358.1 nm as well as minimal non-resonance LIF at 372, 373.5 and 375 nm is taking place. The degree of enhancement of the Fe fluorescence signal over that obtained in the one-laser measurement for the resonance case (factor of enhancement: ~ 5) is larger than that for non-resonance fluorescence (factor of enhancement at 372: ~ 2 , at 373.5 nm: ~ 2 and at 375 nm: ~ 2), as expected.

The tuning curve for DMQ laser dye pumped by the XeCl excimer laser at 308 nm extends over the wavelength range 346 - 377 nm, so resonance LIF enhancement for the Fe atomic fluorescence line at 373.5 nm was attempted under the same conditions as above. With the monochromator tuned to 373.5 nm, an excitation scan was obtained in the presence of Fe(hfa)_3 as the dye laser was scanned from 371.7 - 375.7 nm. An additional scan was recorded

Iron Hexafluoroacetylacetonate : Excitation Spectra
193 nm Photolysis/ 358.1 nm Probe

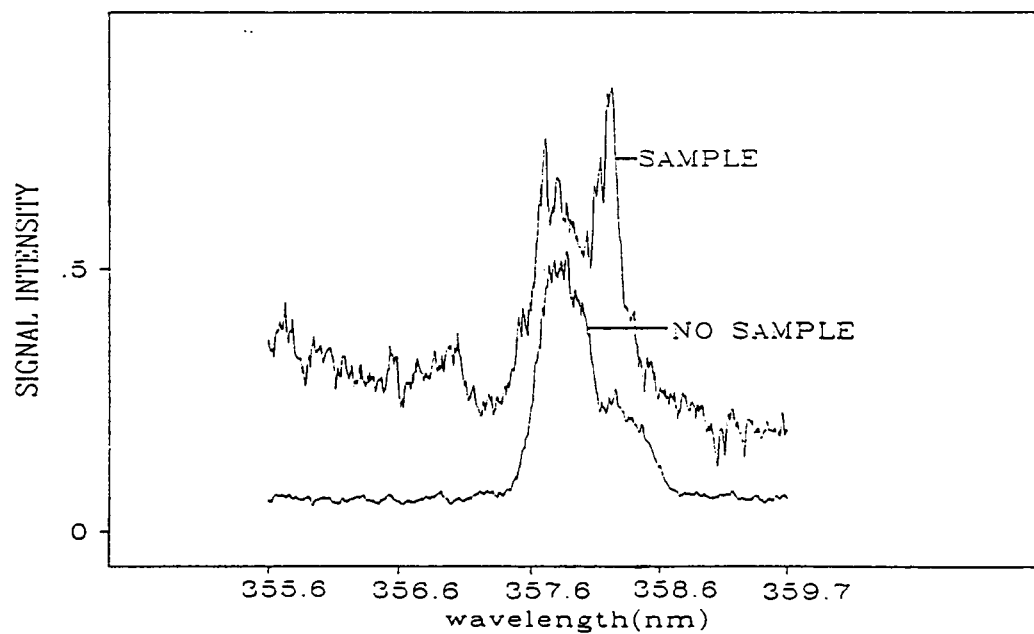


Figure 3.24 LIF Excitation Spectrum of Fe from Fe(hfa)₃

Iron Hexafluoroacetylacetonate ; LIF Spectra
193 nm Photolysis/ 358.1 nm Probe

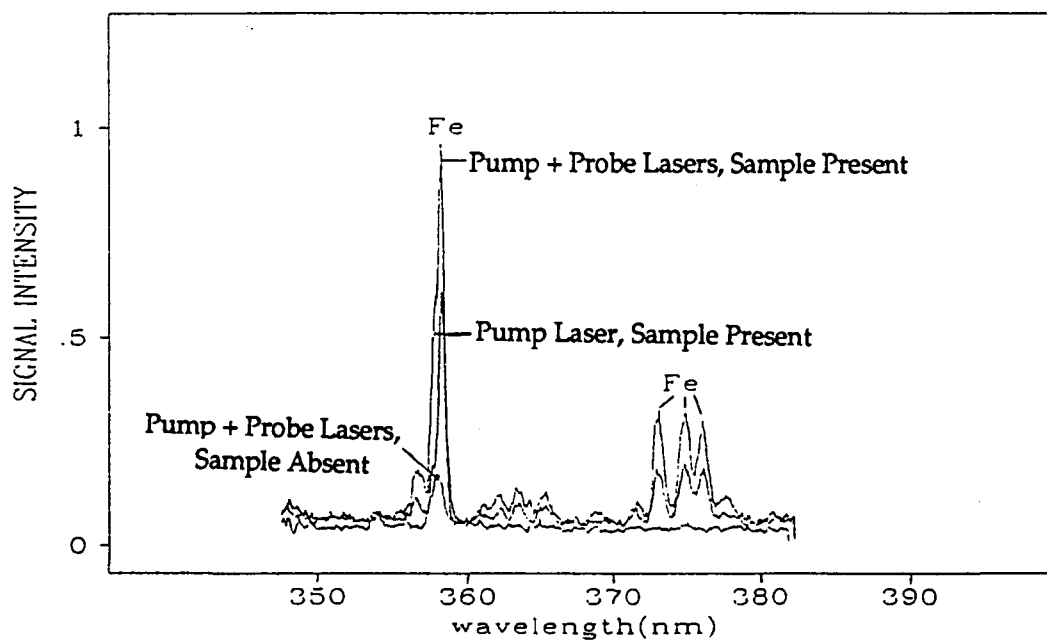


Figure 3.25 LIF Emission Spectrum of Fe from the 193 nm Laser Photolysis of $\text{Fe}(\text{hfa})_3$

in the absence of sample. In the presence of sample, a peak was observed, in addition to that due to the probe laser scattered radiation. This peak was small in magnitude, but presumed to be due to the LIF of Fe. Emission spectra were recorded over the range of 367 - 381 nm, but in this case, the extent of signal improvement as a result of using a probe laser is so minimal that it is of no practical interest; no further experiments involving Fe atomic fluorescence at 373.5 nm were performed.

i. Dependence of Fe LIF Signal from Fe(hfa)_3 on Sample Pressure

Laser-induced fluorescence spectra of Fe (at 358.1 nm) from Fe(hfa)_3 were recorded at five different sample pressures, from a range of 8×10^{-6} to 3×10^{-4} torr. Three separate spectral scans were recorded as the monochromator was scanned over the Fe fluorescence signal at 358.1 nm: (a) pump + probe beams, sample present; (b) pump beam only, sample present; and (c) pump + probe beams, sample absent. Just as described for the analogous Ga(hfa)_3 study, an estimate of the signal due to LIF by the probe laser at each pressure sampled was obtained. The factor of enhancement was also calculated as described on p.112.

In Figure 3.26 [p.123], two sets of data points are shown. The lower set represents the linear dependence of the fluorescence signal (only the photolysis laser) on sample pressure. The best fit linear regression line is drawn through the data points (slope = 1.0). The data presented in this curve agree well with those which were reported for the one-laser linear dynamic range study in Figure 3.5. The top set represents the dependence of the LIF signal on sample pressure, the shape of which is similar to that observed with the other metal chelates studied.

In Figure 3.27 [p.124], the apparent factor of enhancement of the LIF of Fe at 358.1 nm is plotted vs. the sample pressure. At the lowest pressure sampled (8×10^{-6} torr), the extent of enhancement was the largest (150). As the sample pressure increased, the apparent factor of enhancement decreased. The general observations and shape of this plot were observed for

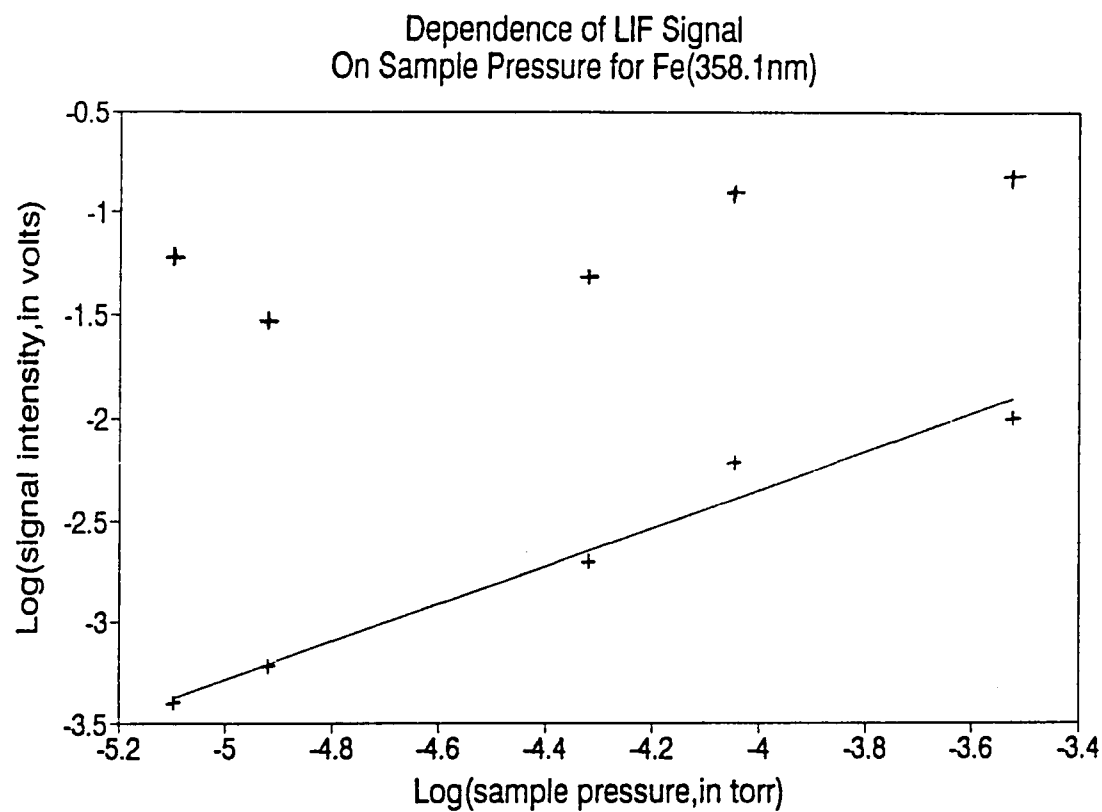


Figure 3.26 Dependence of Fe LIF on Sample Pressure for Fe(hfa)_3
bottom: pump laser only; top: both pump and probe lasers

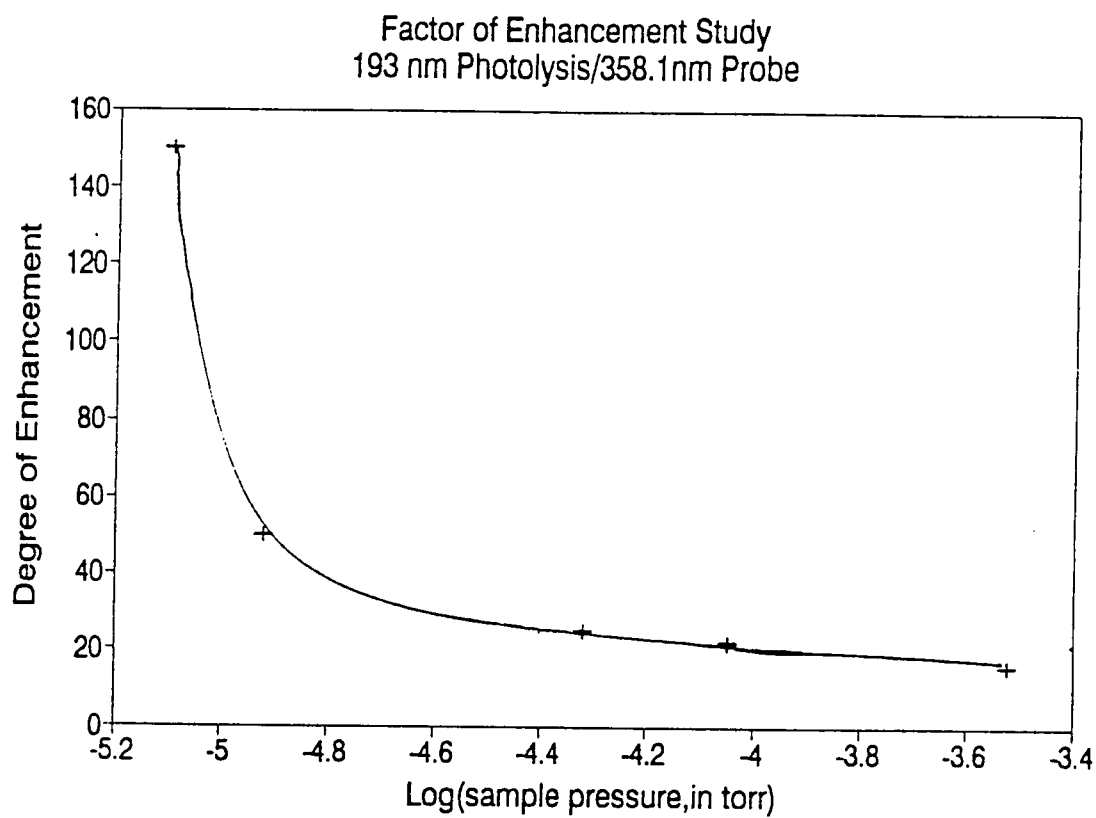


Figure 3.27 Factor of Enhancement Study for Fe(hfa)_3

Ga(hfa)_3 and Cu(hfa)_2 . It can be concluded from this study that the addition of a second laser would likely improve the sensitivity of the LP-AFS technique, if the metal ion under study was Fe^{3+} , but only at sample pressures of 10^{-5} torr or smaller.

ii. Dependence of Fe LIF Signal from Fe(hfa)_3 on Photolysis Laser Pulse Energy

The dependence of the iron fluorescence signal at 358.1 nm in a two-laser experiment was studied at a sample pressure of 1.5×10^{-4} torr ($T = 49^\circ\text{C}$). Five different photolysis laser pulse energies within the range 12.5 - 82.5 mJ/pulse (laser fluence = 4.67×10^{17} - 3.08×10^{18} photons/cm²) were recorded. For each laser pulse energy sampled, three spectra were recorded: (a) pump + probe laser beams, sample present; (b) pump beam, sample present and (c) pump + probe laser beams, sample absent. The magnitude of the LIF signal was measured in each case by subtracting the peak due to the scattering signal (b) from the peak for the spectrum in which the sample was present. Since the dependence of signal on photolysis energy (one-laser study) reported earlier (p.84) was for the atomic Fe line at 373.5 nm, it was necessary here to determine the power dependence for the atomic Fe fluorescence at 358.1 nm for an accurate comparison between the one and two laser power dependence studies. Therefore, the spectral scans for case (b) were recorded at a higher amplification boxcar setting than that for cases (a) and (c).

The results for the dependence of the LIF signal on the photolysis laser pulse energy are displayed in Figure 3.28 [p.126]. The best fit linear regression line is drawn through the data points, the slope of which was calculated to be 1.11 ± 0.08 for the two-laser experiment. The dependence of the signal on the photolysis laser pulse energy in the one-laser experiment was calculated to be 1.52 ± 0.13 . That the dependence of the Fe atomic fluorescence signal in a two-laser experiment on the photolysis laser pulse energy is smaller than that in the one-laser experiment is consistent with the results reported earlier for Cu(hfa)_2 (64).

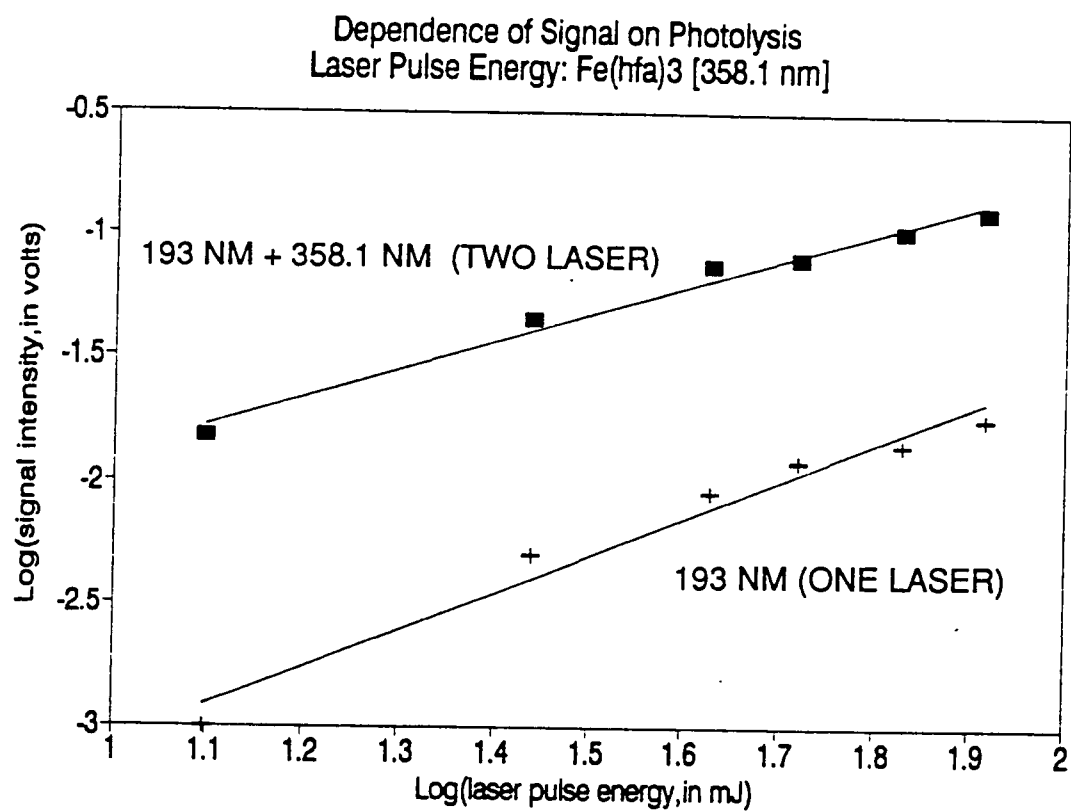


Figure 3.28 Dependence of Fe Signal at 358.1 nm on Photolysis Laser Pulse Energy
top: 2-laser signal dependence; bottom: 1-laser signal dependence

iii. Precision of Fe LIF Signal

Fifteen consecutive fluorescence decay scans were obtained for iron resonance fluorescence at 358.1 nm in a two-laser experiment from the 193 nm photolysis of Fe(hfa)_3 in the continuous-flow vacuum chamber. The boxcar gate was scanned from 0 - 125 ns, with the monochromator set to transmit radiation at 358.1 nm. Since the decay time of the Fe atomic fluorescence at 358.1 nm was appreciably greater than that of the scattering peak maximum due to the probe laser alone, the measurement of the LIF peak maximum was simplified. The experimental conditions employed during data collection were: sample pressure in the continuous-flow chamber = 9×10^{-5} torr; exit/entrance monochromator slits = $50\mu\text{m} / 115\mu\text{m}$; boxcar gate width = 10 ns; excimer laser photolysis energy = 97.5 mJ/pulse; XeCl excimer laser energy = 85 mJ/pulse; dye laser output at 358.1 nm = 0.95 mJ/pulse; and two-laser delay time = ~ 20 ns. The signal magnitude at a boxcar delay time of 36ns (LIF decay maximum) was obtained from each of the fifteen scans. The relative standard deviation in the signal magnitude was calculated to be 5.0%, a value which is essentially the same as that for the one-laser precision study. In this case, an improvement in precision did not result upon use of the second laser, as was the case for Cu(hfa)_2 (64). However, this result might be dependent on the technique that was used here to measure precision (e.g, fluorescence decay scans rather than wavelength scans). It should also be noted that the pulse-to-pulse stability of the XeCl pumped dye laser used in the Fe LIF experiments is significantly worse than that for the Nd:YAG pumped dye laser used as the probe source for the Cu(hfa)_2 studies reported earlier.

d. LIF of Fe from the Laser Photolysis of Fe(CO)_5

A series of two-laser experiments was performed for Fe(CO)_5 using pulsed valve sample introduction. The objective was to determine if the limitations associated with the continuous-flow vacuum chamber (e.g. problems encountered due to the probe laser scattering off the glass-lined tubing and probe laser reflection from deposits on the chamber windows) limited the

attainment of maximum LIF enhancement for Fe(hfa)_3 studied, and additionally, as an experimental aid for identification of Fe atomic fluorescence lines.

The pulsed valve interface and vacuum chamber were not designed for the atomic fluorescence work; rather, they were employed for molecular fragment fluorescence research, concurrently under investigation in our laboratory. However, this method of sample introduction offered several interesting advantages over continuous-flow sample introduction. The absence of glass-lined tubing that exists inside the continuous-flow vacuum chamber (see discussion on p.28) resulted in the possibility of reducing the probe laser scattering to a more manageable level. Due to the effectively larger volume and more highly directed sample flow in the pulsed valve chamber (see Figure 2.6 [p.35]), a reduction in product build-up on the vacuum chamber windows would likely result. In addition, the possibility of using a buffer gas to force a sample of low volatility into the vacuum chamber might be an asset. Molecular fragment fluorescence (observed in 193 nm fragmentation-fluorescence spectra of many metal acetylacetonate chelates) is more highly resolved with pulsed valve sample introduction, which may be beneficial in distinguishing between molecular and atomic fluorescence signals.

The timing and spatial overlap were set up as described on p.50. A mixture of 19.5 torr of Fe(CO)_5 and 117 torr of argon was introduced into the sample introduction line. The experimental conditions were as follows: ArF excimer laser pulse energy = 45 mJ/pulse; XeCl excimer laser pulse energy = 75 mJ/pulse; boxcar gate width = 10 ns; current output on the power supply = 3 kA; and two-laser delay time = 35 ns. The dye laser was pumped by the XeCl laser and contained DMQ laser dye dissolved in p-dioxane. DMQ delivered the following dye laser outputs over the tuning curve range of interest: 357.1 nm: 2 mJ/pulse; 358.1 nm: 2 mJ/pulse; 368 nm: 2.7 mJ/pulse and 373.5 nm: 0.9 mJ/pulse. In all cases, the photodiode which detected the probe laser radiation triggered the boxcar.

Several excitation and fluorescence spectra were obtained under these conditions, the results of which are summarized in Table 3.1 [p.129]. For the excitation spectra, the dye laser

TABLE 3.1

EXPERIMENTAL RESULTS: LIF OF FE FROM THE 193 NM LASER PHOTOLYSIS OF IRON PENTACARBONYL

Type of Spectrum	Monochromator Wavelength (nm)	Wavelength Scan (nm) ^a	Probe Laser Wavelength (nm)	LIF Enhancement ^b Resonance	Non-Resonance
EXCITATION	373.5	372.5 - 377.5 (L)	n/a	n/a	n/a
FLUORESCENCE	n/a	350 - 388 (M)	373.5	373.5(6)	n/a
EXCITATION	358.1	356.6 - 359.1 (L)	n/a	n/a	n/a
FLUORESCENCE	n/a	350 - 388 (M)	358.1	358.1(10)	n/a
EXCITATION	357.1	356.0 - 358.4 (L)	n/a	n/a	n/a
FLUORESCENCE	n/a	350 - 388 (M)	357.1	357.1(12)	358.1(2)
EXCITATION	373.5	365.9 - 370.9 (L)	n/a	n/a	n/a
FLUORESCENCE	n/a	350 - 388 (M)	368.0	n/a	373.5(3)

^a L, probe laser wavelength was scanned; M, monochromator wavelength was scanned.^b observed enhancement factors are in parentheses.

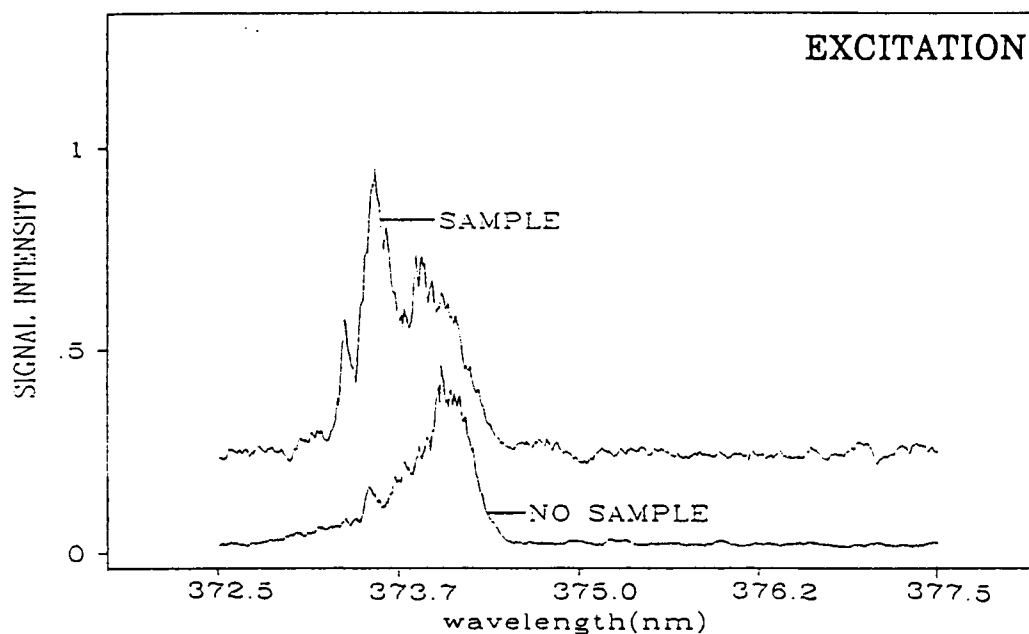
was scanned while the monochromator was tuned to transmit the particular iron fluorescent line being studied. For the fluorescence spectra, the dye laser wavelength was set to that which produced the maximum fluorescence signal, as inferred from the corresponding excitation spectrum. Resonance laser-induced iron fluorescence at 373.5 nm from 193 nm laser photolysis was observed when probed with 373.5 nm dye laser radiation, as observed in Figure 3.29 [p.131]. When the probe laser wavelength was changed to 368 nm, non-resonance laser-induced iron fluorescence was observed at 373.5 nm, as depicted in Figure 3.30 [p.132]. In Figure 3.31 [p.133], probing at 358.1 nm resulted in resonance LIF of Fe at 358.1 nm. In Figure 3.32 [p.134], probing at 357.1 nm resulted in resonance LIF of Fe at 357.1 nm as well as non-resonance LIF of Fe at 358.1 nm.

It can be concluded from these results that the use of a probe laser is highly likely to improve the sensitivity of the technique for $\text{Fe}(\text{CO})_5$. To test this assumption, a series of two-laser experiments was performed for the LIF of Fe at 358.1 nm. Pulsed valve sample introduction was used in each case in order to achieve a longer operating time between chamber window replacements. Metallic iron, generated from the 193 nm photolysis of $\text{Fe}(\text{CO})_5$, had a tendency to build up rapidly on the surface of the chamber windows in the continuous-flow vacuum chamber, which led to a corresponding decrease in the photon flux actually reaching the sample vapor as it emerged from the sample introduction line inside the vacuum chamber.

i. Dependence of Fe LIF Signal from $\text{Fe}(\text{CO})_5$ on Sample Pressure

Laser-induced fluorescence spectra of Fe from $\text{Fe}(\text{CO})_5$ were recorded at six different sample pressures, from a range of 1.5×10^{-6} to 1.5×10^{-4} torr. The sample was introduced into the continuous-flow vacuum chamber in this experiment. The ArF pump laser was operating at an energy of 65 mJ/pulse, whereas the XeCl-pumped dye laser (at 358.1 nm) was operating at 1.4 mJ/pulse. Three separate spectral scans were recorded as the monochromator was

Iron Pentacarbonyl (PSV Sample Intro.) : Excitation Spectra
193 nm Photolysis / 373.5 nm Probe



LIF Spectra of Fe(373.5 nm) from 193 nm Laser Photolysis

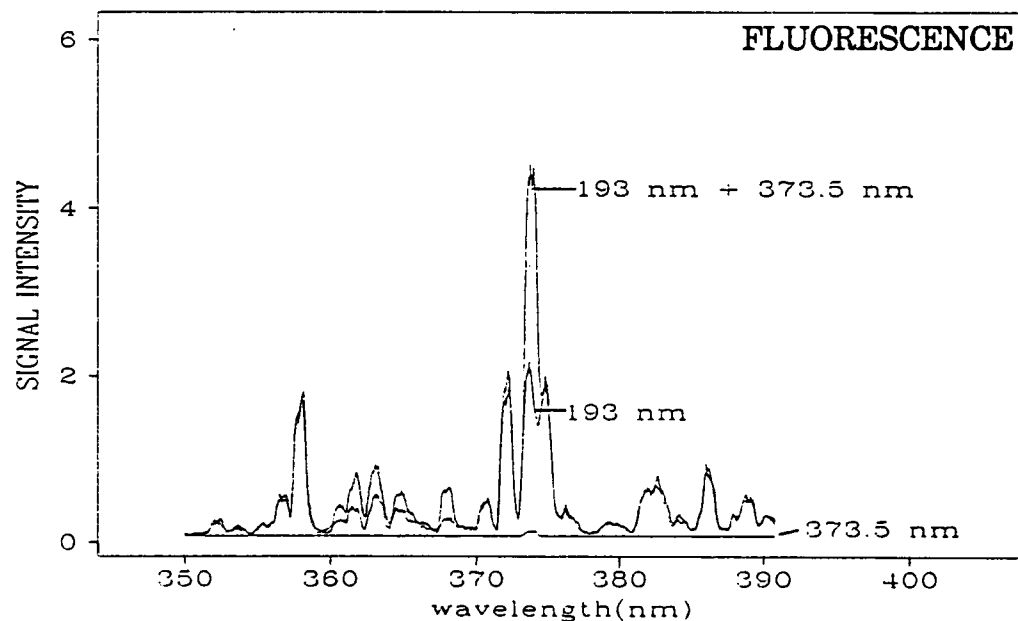
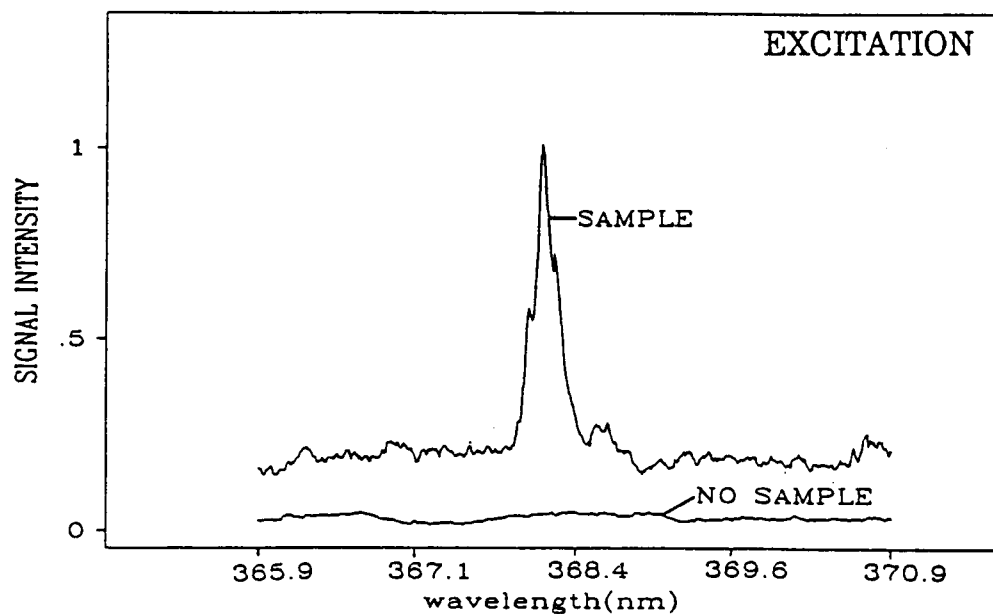


Figure 3.29 Excitation (top) and Fluorescence (bottom) Spectra for $\text{Fe}(\text{CO})_5$:
193 nm Photolysis/ 373.5 nm Probe/ 373.5 nm Fluorescence

Iron Pentacarbonyl (PSV Sample Intro.) : Excitation Spectra
193 nm Photolysis / 368 nm Probe



Iron Pentacarbonyl (PSV Sample Intro.) : LIF Spectra
193 nm Photolysis / 368 nm Probe

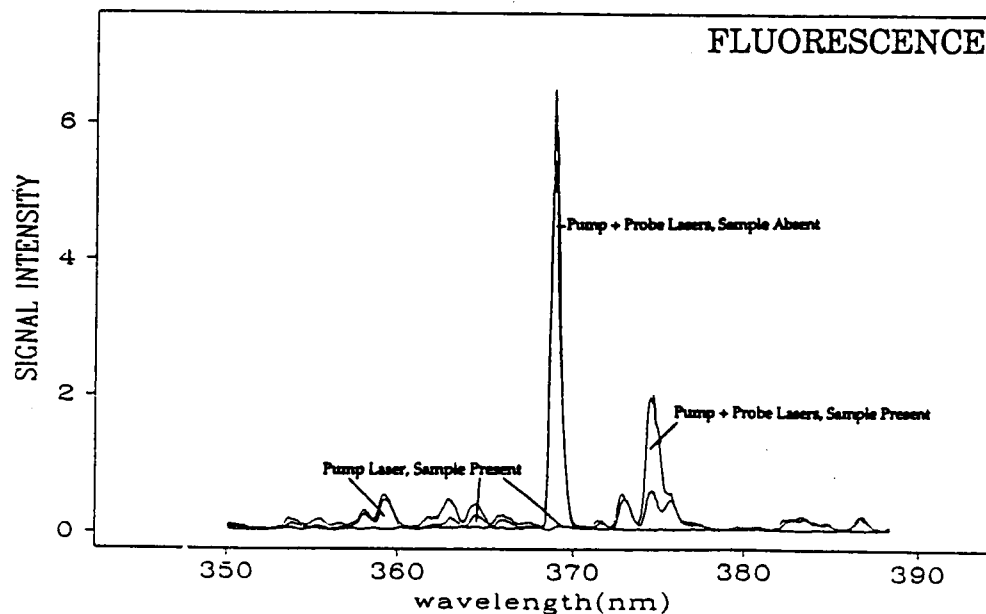
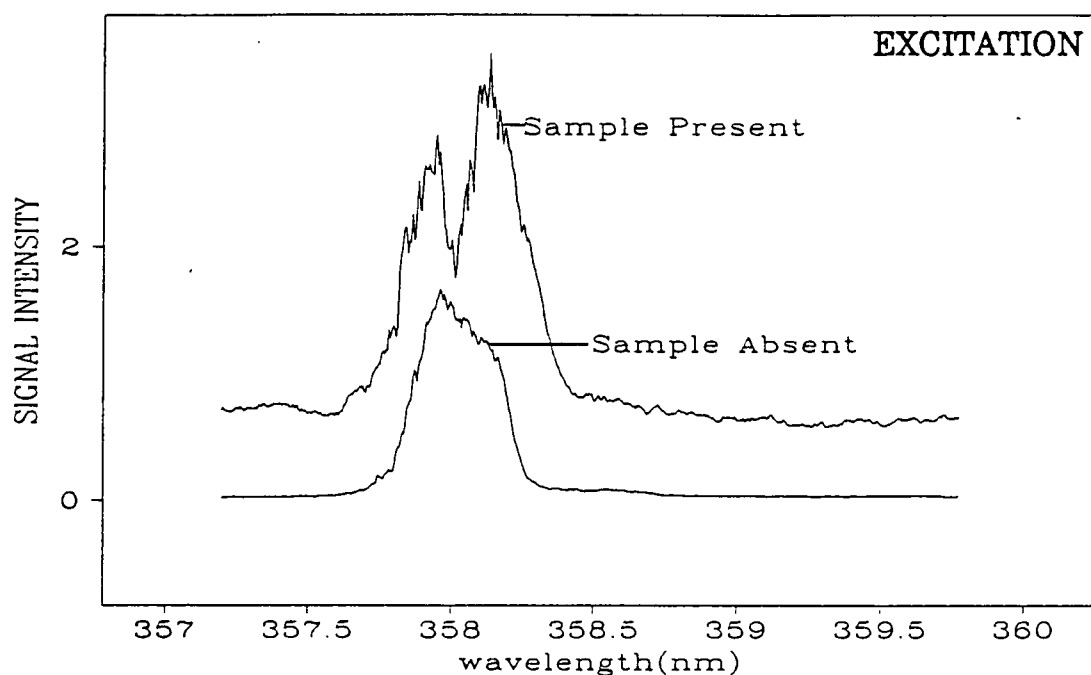


Figure 3.30 Excitation (top) and Fluorescence (bottom) Spectra for $\text{Fe}(\text{CO})_5$
193 nm Photolysis / 368 nm Probe / 373.5 nm Fluorescence

Iron Pentacarbonyl:Excitation Spectra



LIF Spectra of Fe(358.1 nm) from 193 nm Laser Photolysis

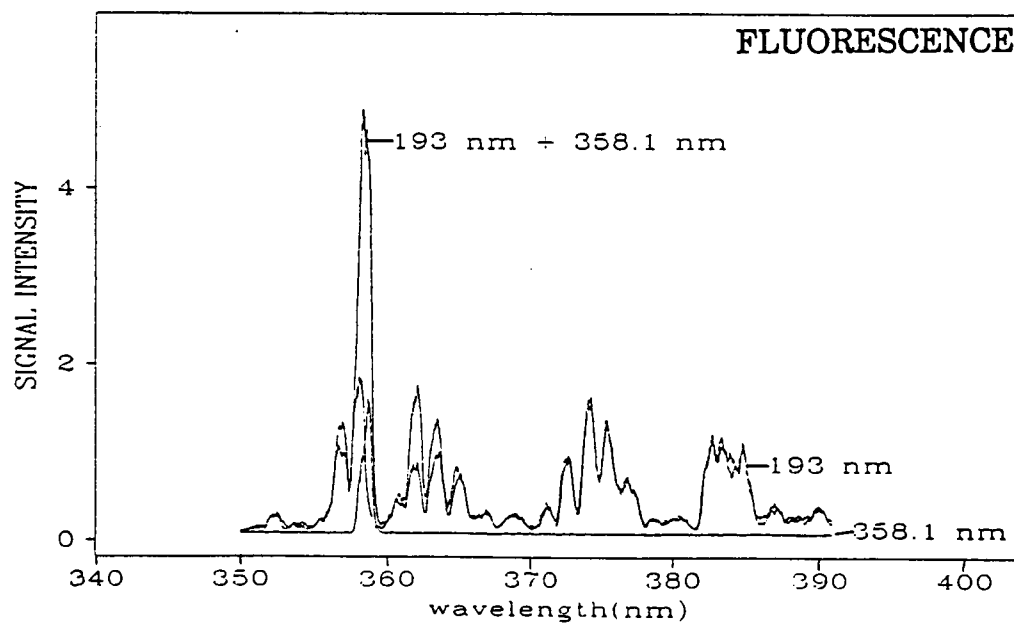


Figure 3.31 Excitation (top) and Fluorescence (bottom) Spectra for $\text{Fe}(\text{CO})_5$,
193 nm Photolysis/ 358.1 nm Probe/ 358.1 nm Fluorescence

Iron Pentacarbonyl (PSV Sample Intro.) ; Excitation Spectra
193 nm Photolysis / 357.1 nm Probe

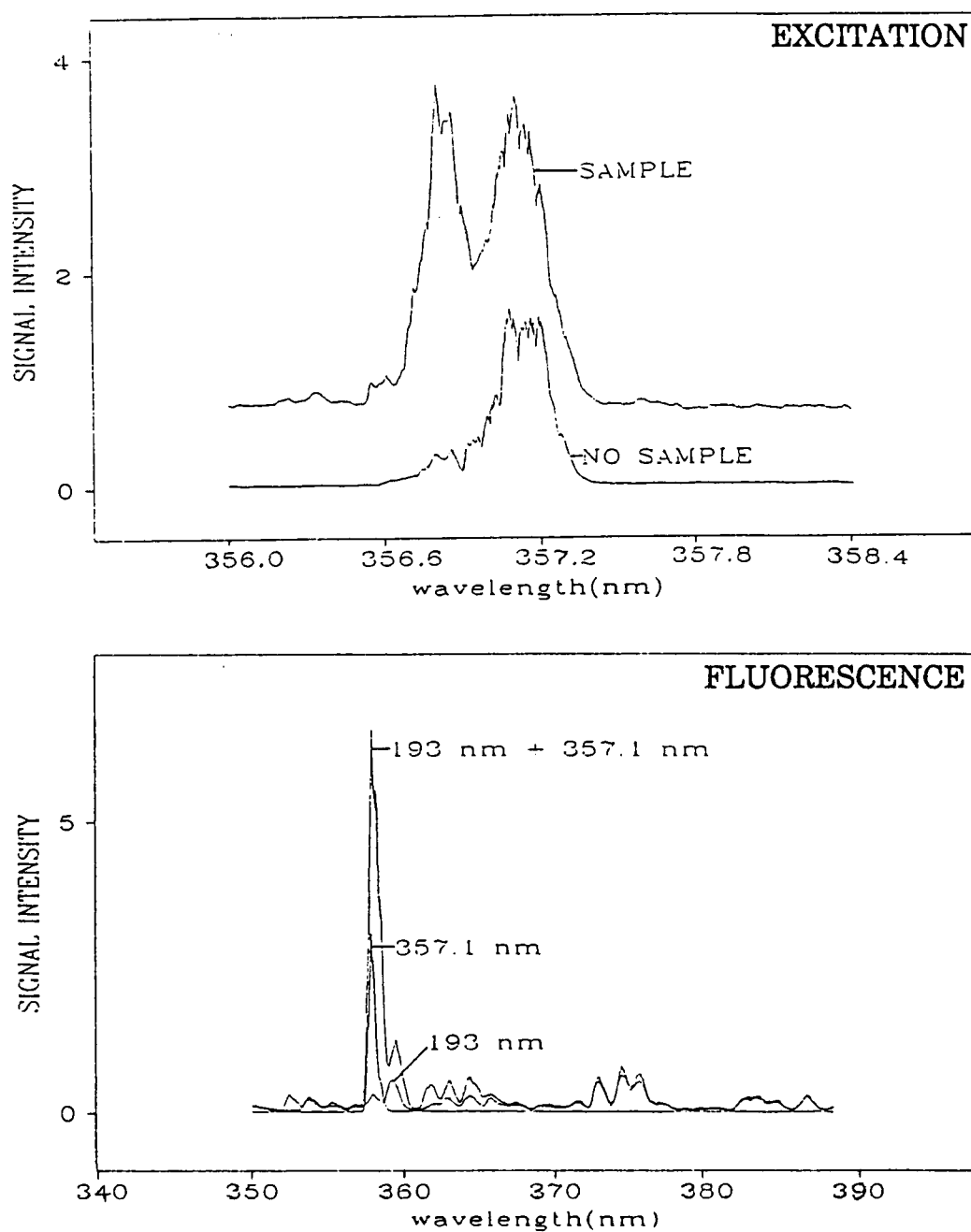


Figure 3.32 Excitation (top) and Fluorescence (bottom) Spectra for $\text{Fe}(\text{CO})_5$
193 nm Photolysis/ 357.1 nm Probe/ 357.1 nm Fluorescence

scanned over the Fe fluorescence signal at 358.1 nm: (a) pump + probe beams, sample present; (b) pump beam, sample present and (c) pump + probe beams, sample absent. An estimate of the signal due to LIF by the probe laser was obtained. In addition, the factor of enhancement at each pressure sampled was calculated (as described on p.112).

In Figure 3.33 [p.136], the dependence of the LIF signal on sample pressure is represented. A non-linear dependence is apparent, as was also observed with the acetylacetonate metal chelates which were studied. In Figure 3.34 [p.137], the apparent factor of enhancement of the LIF of Fe at 358.1 nm is plotted vs. the sample pressure. At the lowest pressure sampled (1.5×10^{-6} torr), the extent of enhancement was the "largest" (~ 10). As the sample pressure increased, the apparent factor of enhancement decreased.

ii. Dependence of Fe LIF Signal from $\text{Fe}(\text{CO})_5$ on Photolysis Laser Pulse Energy

This dependence was studied in the pulsed valve sample introduction chamber at a sample pressure of 9×10^{-5} torr [31 Torr $\text{Fe}(\text{CO})_5$ diluted in 415 Torr argon]. Nine different photolysis laser pulse energies within the range 12.5 - 92.5 mJ/pulse (laser fluence = 4.67×10^{17} - 3.46×10^{18} photons/cm²) were recorded. For each laser pulse energy sampled, two spectra were recorded: (a) pump + probe laser beams, sample present and (b) pump + probe laser beams, sample absent. The magnitude of the LIF signal was measured in each case by subtracting the peak due to the scattering signal (b) from the peak for the spectrum in which the sample was present. The results for the dependence of the LIF signal on the photolysis laser pulse energy are displayed in Figure 3.35 [p.138]. The best fit linear regression line is drawn through the data points, the slope of which was calculated to be 1.33 ± 0.05 . The corresponding value for the one-laser experiment was 0.37 ± 0.03 (p.89). The dependence of the Fe fluorescence signal at 358.1 nm is thus seen to be greater in the two-laser experiment than in the one-laser experiment, an unexpected result.

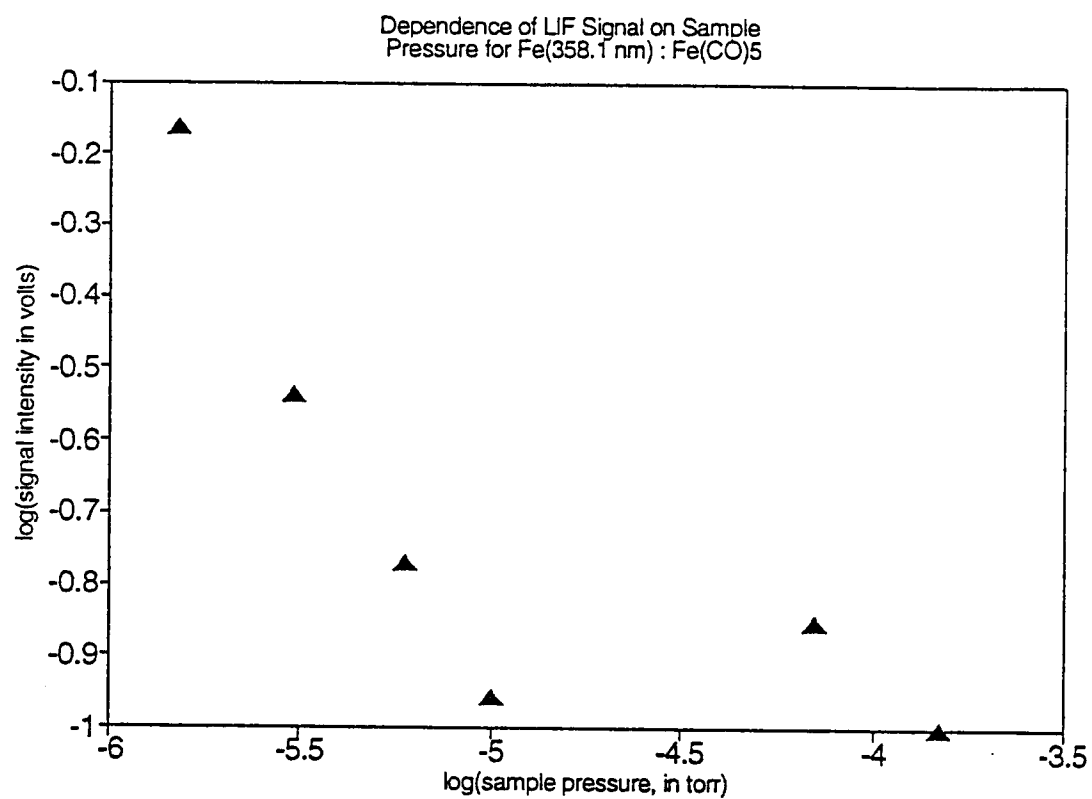


Figure 3.33 Dependence of LIF Signal on Sample Pressure for Fe(CO)₅

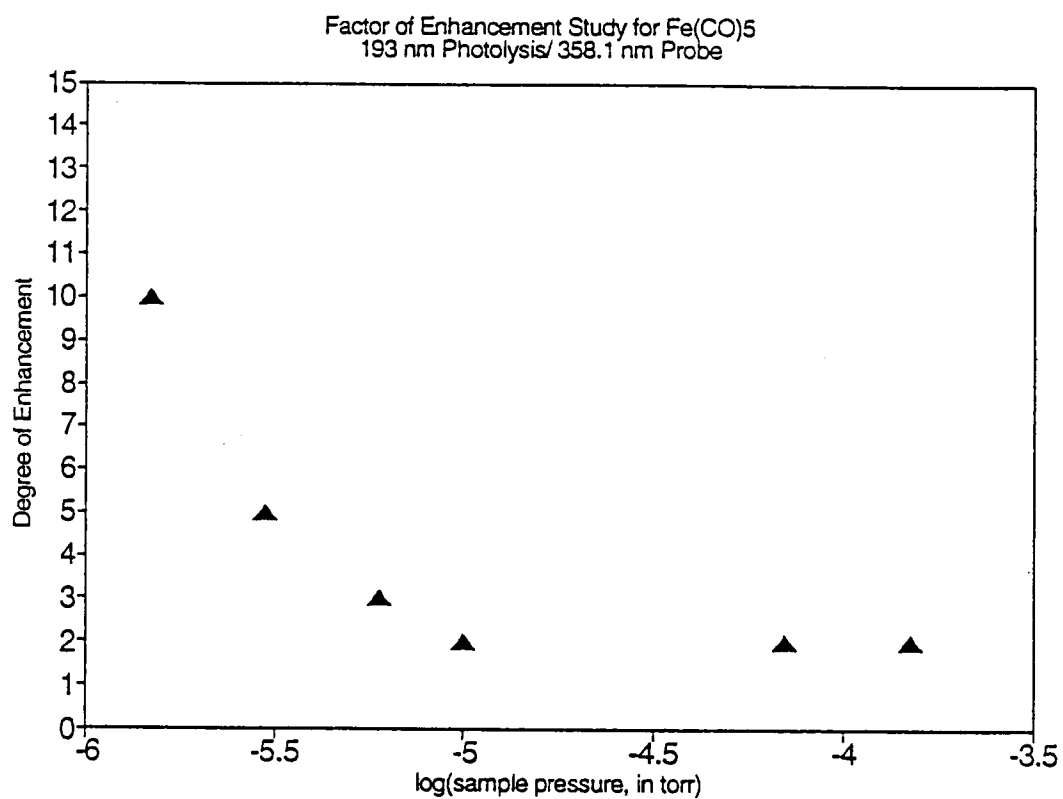


Figure 3.34 Factor of Enhancement Study for the LIF of Fe at 358.1 nm for $\text{Fe}(\text{CO})_5$

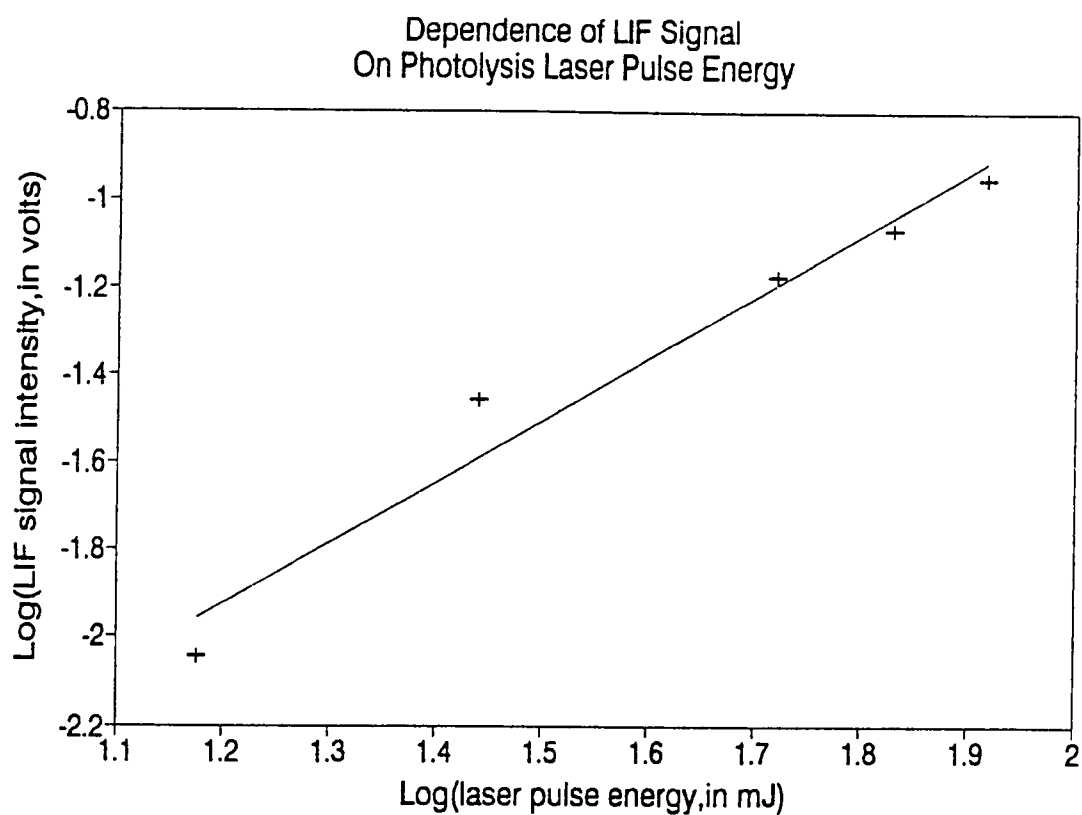


Figure 3.35 Dependence of Fe LIF Signal at 358.1 nm on Photolysis Laser Pulse Energy for $\text{Fe}(\text{CO})_5$

iii. Precision of Fe LIF Signal from $\text{Fe}(\text{CO})_5$

Fourteen consecutive fluorescence decay scans were obtained for the LIF of Fe at 358.1 nm from the 193 nm photolysis of $\text{Fe}(\text{CO})_5$. The boxcar gate was scanned from 0 - 125 ns, with the monochromator set to transmit radiation at 358.1 nm. The fluorescence decay time for Fe fluorescence (ca. 18 ns) was temporally longer than that for the scattering peak maximum due to the probe laser alone (10-12 ns), which simplified the measurement of the LIF peak maximum. The experimental conditions employed during data collection were: sample pressure in the continuous-flow chamber = 1.1×10^{-4} torr; exit/entrance monochromator slits = $40\mu\text{m}/100\mu\text{m}$; boxcar gate width = 10 ns; ArF excimer laser photolysis energy = 75 mJ/pulse; XeCl excimer laser energy = 70 mJ/pulse; dye laser output at 358.1 nm = 1.7 mJ/pulse; and two-laser delay time = ~ 25 ns. The signal magnitude at a boxcar delay time of 23 ns (LIF decay maximum) was obtained from each of the fifteen scans. The relative standard deviation in the signal magnitude was calculated to be 5.6%. In this case, a slight improvement in the precision resulted from the use of a probe laser, despite the use of the relatively noisy XeCl-pumped dye laser as the probe source.

e. LIF of Cr from the Laser Photolysis of $\text{Cr}(\text{hfa})_3$

A survey fluorescence spectrum from the 193 nm laser photolysis of $\text{Cr}(\text{hfa})_3$ at a sample pressure of 1×10^{-4} torr was collected, as shown in Figure 3.36 [p.140]. The existence of several intense atomic chromium fluorescence lines produced upon 193 nm laser photolysis made this beta-diketonate a good candidate for a resonance LIF experiment. To begin, it was decided that the most intense peak (425.4 nm) would be employed as the analytically significant line. The dye laser pumped by the XeCl excimer laser at 308 nm contained stilbene-420 laser dye dissolved in methanol, which delivered ~ 2 mJ/pulse at 425.4 nm. The ArF excimer produced 75 mJ/pulse and the XeCl excimer laser output was 50 mJ/pulse. The timing and spatial overlap between the photolysis and probe lasers was set up as described on p.47. The

LP-FFS of Chromium Hexafluoroacetylacetonate
193 nm Photolysis

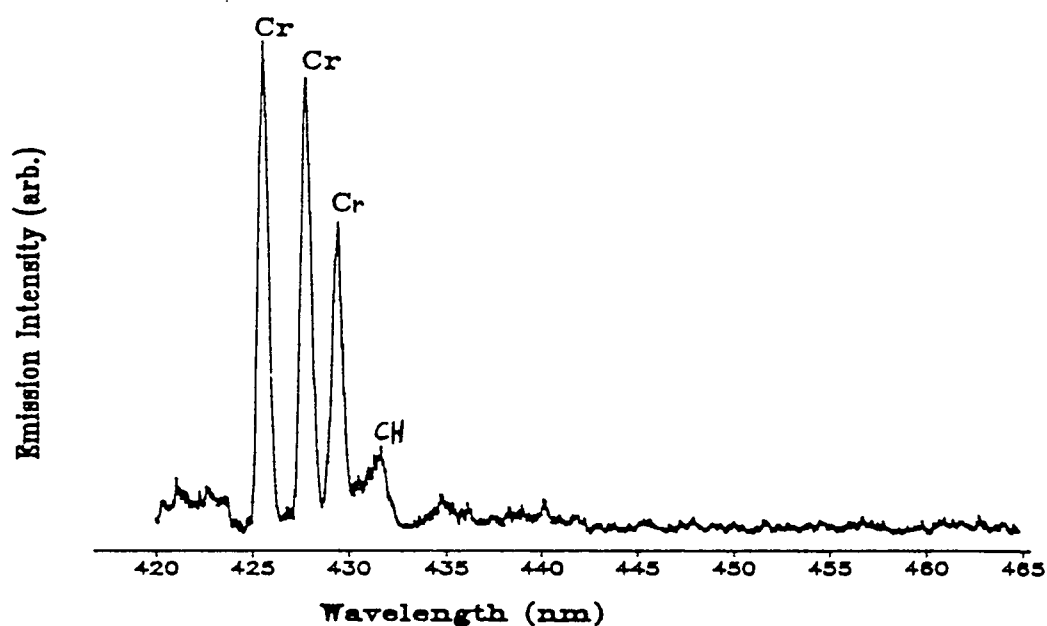


Figure 3.36 Fluorescence Survey Spectrum for the 193 nm Photolysis of $\text{Cr}(\text{hfa})_3$

experimental conditions: sample pressure in chamber = 1×10^{-4} torr; sample temperature = 75°C ; entrance/exit monochromator slits = $100\mu\text{m}/50\mu\text{m}$; boxcar gate width = 10 ns; boxcar delay time = 18.2 ns; excimer laser photolysis energy = 40 mJ/pulse at a repetition rate of 10 Hz

delay time between the two laser pulses was estimated to be ~ 30 ns as determined from an oscilloscope trace. The monochromator was tuned to transmit radiation at 425.4 nm. Cr(hfa)_3 vapor was introduced at a sample pressure of 8.5×10^{-5} torr, and the dye laser was scanned from 424.5 - 427.4 nm. The excitation scan was repeated in the absence of sample over the same wavelength range.

Both excitation spectra are depicted in Figure 3.37 [p.142]. In this figure, no evidence of enhancement of Cr fluorescence at 425.4 nm by the dye laser can be seen. Experimental conditions (e.g. delay between the two laser pulses, boxcar delay time, beam overlap) were carefully re-optimized in order to achieve enhancement, but a significant difference in the two excitation spectra was not achieved. These results are analogous to those reported previously for Al(hfa)_3 (64), in which no evidence of LIF resonance enhancement of aluminum at 394.4 nm was observed. Although no enhancement could be detected for Cr at 425.4 nm, this does not necessarily imply that no enhancement occurs (e.g., it might be so small as to be imperceptible over the probe laser scatter background). It is also possible that relatively few ground state chromium atoms (as compared with the number of excited-state chromium atoms) were generated upon 193 nm laser photolysis. In any case, it does not appear feasible to lower the limit of detection by the use of a probe laser for Cr(hfa)_3 under these experimental conditions.

Chromium Hexafluoroacetylacetonate ; Excitation Spectra
193 nm Photolysis / 425,4 nm Probe

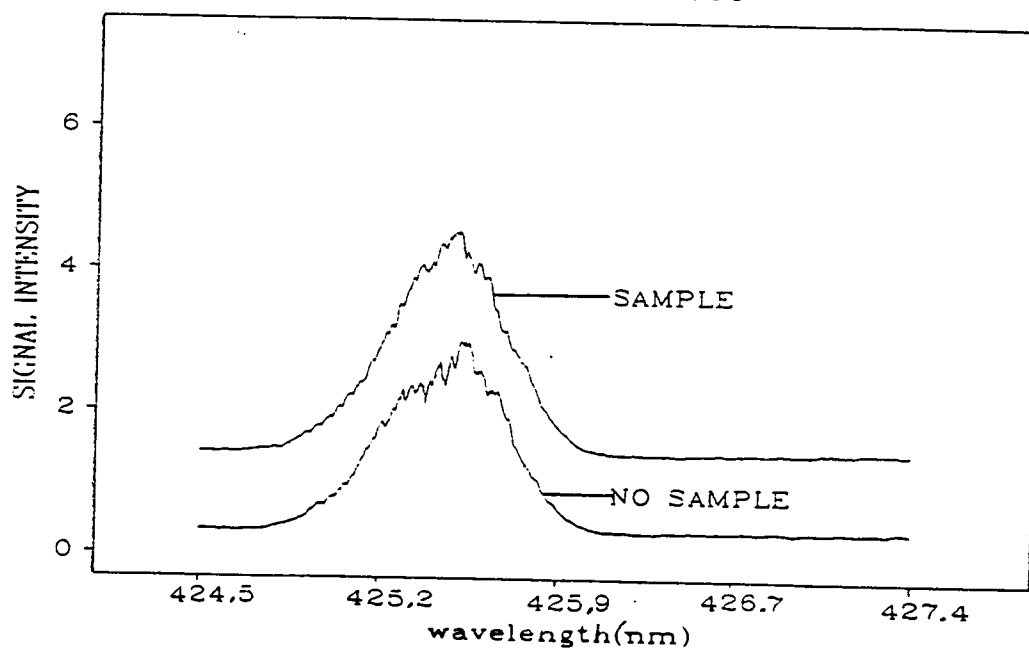


Figure 3.37 Excitation Spectra of Cr (425.4 nm) from the 193 nm Photolysis of $\text{Cr}(\text{hfa})_3$

3. Conclusions

The major conclusions derived from the results described in this chapter are:

- (a) One-laser (193 nm) figures of merit for the metal chelates and carbonyls studied indicate that laser photofragmentation of volatile metal chelates as an efficient atomization reservoir and its potential application as an ultra-trace method of metals analysis is impressive. Low limits of detection, respectable precision and a wide linear dynamic range were observed for the metal chelates and carbonyls studied.
- (b) Background interference due to photolytically generated ligand fluorescence was found to be present, but minimal, and in no case was the atomic fluorescence of interest obscured as a result of this background.
- (c) The usefulness of a probe laser to improve the sensitivity of this method of analysis is dependent on the metal ion under study, at least under the experimental conditions employed in this work. Two-color (pump and probe) results for Cu^{2+} and Fe^{3+} indicate that, for these metal ions, LIF is practical. Pump and probe results for Ga^{3+} and Cr^{3+} indicate that LIF is minimally useful and not worth the extra difficulty (or expense) associated with the use of the second laser.
- (d) The improvement in precision in a two-laser experiment over that of a one-laser experiment is found to be dependent on the characteristics of the probe source (especially the pulse energy reproducibility).
- (e) Two-laser experiments are not invariably superior to one-laser experiments, particularly if a resonance fluorescence transition is being monitored, due to difficulties diminishing the effects of probe laser scattered radiation. Unfortunately, there does seem to be a limitation to resonance atomic fluorescence transitions, even though in some cases weak non-resonance atomic fluorescence was observed.

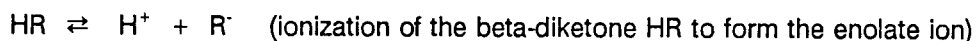
CHAPTER 4

LP-AFS OF METAL-CONTAINING SOLID AND SOLUTION SAMPLES

Two divisions exist in this chapter. In the first division, the method development involved in the application of the LP-AFS method to metal-containing liquid solutions (in particular those containing Fe^{3+} , Cu^{2+} , and Cr^{3+}) is discussed. The experimental objective was to investigate the utility of the LP-AFS technique for the detection of metal ions in "real" analytical samples in solution form. In the second division, evaluation of the LP-AFS method of analysis of selected solid metal-containing standard reference materials and inorganic salts is discussed.

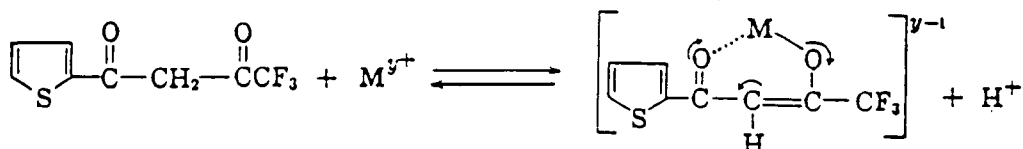
1. Metal-containing Liquid Solutions

Unless otherwise stated, the continuous-flow vacuum chamber and the sample introduction line diagrammed in Figure 2.5 [p.33] were used exclusively in the work described here. Complexation reactions were carried out in a 25 mL volume o-ring sealed glass sample bulb. A general complexation reaction can be represented by the following equations



where M^{n+} is metal ion, HR is the beta-diketone ligand and MR_n is the metal chelate. Equilibrium constant values (formation or stability constants) for the second reaction have been reported for many different metal ions and beta-diketone ligands. For instance, Walker and Li have reported formation constants ($\log K_f$) for Cu^{2+} beta-diketonates: acac (18.2), tta- thenoyltrifluoroacetone (6.55), tfa (6.59) and hfa (2.70) (75). Taft and Cook reported $\log K_f$ values for several different

metal ions complexed with the beta-diketone ligand thenoyltrifluoroacetone (tta): Fe^{3+} (7.2), Cu^{2+} (5.9) and Mg^{2+} (2.4) (76). This complexation reaction can be represented as



The determination of $\log K_f$ values for the complexation reaction of Fe^{3+} and several beta-diketone ligands, in order of increasing ligand acidity, were reported as: acac (26.7), tfa (19.8) and hfa (9.8).

Optimal instrumental parameters for observing the atomic fluorescence of the metal under investigation were set up prior to the introduction of the volatilized solution sample; hence, they are not repeated in detail. The sample bulb (described on p. 31) and introduction line were both carefully wrapped with a layer of glass wool, heating tape, and, in some cases, aluminum foil, in an effort to insure complete transfer of the gas-phase sample into the chamber. Previous research with the pure metal beta-diketonates indicated that solutions containing the metal ions Fe^{3+} , Cu^{2+} and Cr^{3+} were potential candidates for success.

a. Aqueous Solutions- General Considerations

The general approach for LP-AFS analysis would ideally involve complexation of the metal analyte ion(s) in a solution sample, introduction of the resulting metal chelate in the gas phase into a vacuum chamber, excimer laser photolysis of the gas phase chelate to produce metal atoms, and laser-induced fluorescence detection of the photolytically-produced metal atoms. Although this sequence of steps is straightforward in principle, there were many experimental considerations to be addressed.

The first step was to decide how to efficiently complex the metal ion(s) in solution. Of all the complexing agents known, which one would be most suitable to convert the metal ion(s) in solution to a volatile metal complex? Can high complexation efficiency be assured? Does the complexation process proceed in a timely fashion? Does the complexation process require

heat, and if so, would heating in a temperature-controlled oven or simply heating the sample vessel in a heating mantle be more successful? Would sonication aid in the complexation process, and if so, is there a limit to which it might improve complexation efficiency? What quantity of ligand is required for the complexation process? If an excess amount of ligand can be added, is there an upper limit to how much should be used? What total volume of solution would be needed for LP-AFS analysis? Can a direct approach be used for complexation of the metal ion(s) in aqueous solution or must one resort to applying a solvent extraction method? Using a direct approach to effect chelation involves directly reacting the neat ligand with the aqueous metal-containing solution - no solvent is involved. In contrast, in a solvent extraction method, chelation can be achieved by allowing the aqueous solution of the metal ion to react with an organic solvent containing the chelating agent, whereupon the metal chelate forms in the organic phase and thus, can be separated from the aqueous phase. Each of these questions had to be addressed to insure that the chemistry was optimized prior to coupling it with the spectroscopy.

Assuming that the metal ion(s) in the aqueous solution sample were efficiently complexed, the next step involved deciding upon the best way to convert the metal complex into the gas phase. Does the sample require external heating, and if so, to what degree? Will the presence of excess water cause problems when introducing the metal complex into the chamber? Will the sample require degassing with nitrogen?

Finally, parameters involved with the spectroscopy must be optimized. For instance, would it be better to collect fluorescence decay scans (wherein the monochromator is fixed at the atomic fluorescence wavelength of the metal being investigated), or spectral scans (whereby the monochromator is scanned over a wide range of wavelengths), the latter of which generally was the method of choice for the pure solid metal beta-diketonates and metal carbonyls studied? For samples containing more than one metal which may be complexed, will there be time to collect an entire spectral scan so that more than one metal may be quantified before the

vaporized sample leaves the spectral interrogation region? Presumably, instrumental parameters such as monochromator slit widths, excimer laser energy, delay time and fluorescence collection optics will have already been optimized, prior to the introduction of a "real" sample.

b. Aqueous Solutions- Experimental Section

A systematic investigation was undertaken, in which initial experiments involved a series of simple complexations using concentrated aqueous solutions of various metal nitrate salts and one of the two ligands chosen for study (tfa or hfa), to determine conditions under which efficient complexation could apparently be achieved. A 250 μL volume of hfa or tfa was added to a 250 μL volume of the metal ion solution in a 5 mL sample vial. The qualitative observations of the complexation process are shown in Table 4.1 [p.148]. These results suggest that directly chelating these metals from an aqueous matrix without prior sample preparation steps (e.g., acid digestion) might be feasible for LP-AFS, which would limit the number of steps involved in the analysis. The reaction rate was observed to be most rapid for Fe^{3+} and Cu^{2+} , so these metal ions were chosen for initial study. Even though the reaction rate was slow for Cr^{3+} , it was additionally chosen for further investigation because of its clean atomic fluorescence spectrum generated by 193 nm laser photolysis (see Figure 3.36 [p.140]). Since metal hexafluoroacetylacetonates are more volatile than metal trifluoroacetylacetonates, hfa was initially chosen as the complexing agent of choice.

The first of many experiments involved complexing 10 mL of a 0.15M $\text{Fe}(\text{NO}_3)_3$ aqueous solution with 1 mL of excess hfa; an excess amount of ligand was added due to a significant body of literature in which this was done (56, 61, 63). An immediate reaction occurred at the interface between the aqueous solution containing the metal ion and the ligand; a blood-red liquid "sphere" appeared which deepened in color upon gentle swirling of the contents in the sample bulb. After approximately five minutes, the complexation process appeared to be complete. The sample was degassed via a freeze-thaw cycle, installed on-line (directly attached

TABLE 4.1

QUALITATIVE CHELATION OBSERVATIONS BETWEEN SELECTED METAL NITRATE SOLUTIONS WITH HFA AND TFA

METAL ION (0.05 M)	COLOR OF SOLUTION AFTER ADDITION OF COMPLEXING AGENT		RELATIVE REACTION RATE	HEAT REQUIRED?
	HFA	TFA		
Cu ²⁺	green	green	immediate	no
Fe ³⁺	blood-red	cherry-red	immediate	no
Cr ³⁺	green	purple-brown	slow (complete in several hours)	yes
Pb ²⁺	no change	no change	no evidence	-
Co ²⁺	yellow-brown	dark brown	moderate (complete < 1 hr)	yes
Ni ²⁺	pale green	green	moderate (complete < 1 hr)	yes

to the sample introduction line), heated to 80°C, and introduced into the chamber without any significant problems associated with the water matrix (sample was volatilized out of solution without clogging the sample introduction line). Although the 193 nm excimer laser energy output was rather low (35 mJ/pulse due to a malfunction), a spectral scan was collected as shown in Figure 4.1 [p.150]. Other than the low excimer laser pulse energy, conditions similar to those used for the pure Fe(hfa)₃ chelate discussed previously (p.80) were used here. It is evident that the spectrum collected here is identical to the iron atomic fluorescence spectrum collected for Fe(hfa)₃, despite the fact that relatively wide monochromator slits (~250 μm) were used for this spectrum. The signal to noise ratio is significantly greater than 2, which suggested that looking at samples containing lower iron concentrations would be plausible.

Serial dilutions of an acidified 0.01M Fe(NO₃)₃ solution were analytically performed, which ranged in concentration from 1 × 10⁻³ to 1 × 10⁻⁸M. Each solution thus prepared was stored in a refrigerator in a nalgene container until the analysis for that particular solution could be performed. Just prior to analysis, a 5 mL quantity was withdrawn from the solution under investigation and allowed to react with 1 mL of the complexing agent (hfa). It was experimentally determined that using an aqueous solution volume of ≤5 mL minimized interferences from the aqueous matrix upon volatilization of the sample. In each of the cases to be discussed, the complexation reaction was accelerated by placing the sample in an oven held at 100°C for ca. one hour. It was found that sonication did not significantly aid the complexation process (that is, no visual evidence of further chelate formation was observed). In each of the cases discussed here, experimental conditions were kept as nearly constant as possible. The gas-phase samples were introduced into the chamber at a pressure of ~1-2 × 10⁻⁴ torr.

Visual evidence of immediate complexation between hfa and the 0.01 and 0.001M Fe³⁺ solutions appeared in the form of a red "sphere" at the interface between the ligand and the aqueous phase. A representative one-laser fluorescence spectrum was collected for the 193 nm

LP-FFS of an aqueous $\text{Fe}(\text{NO}_3)_3$
solution + excess hexafluoroacetylacetone

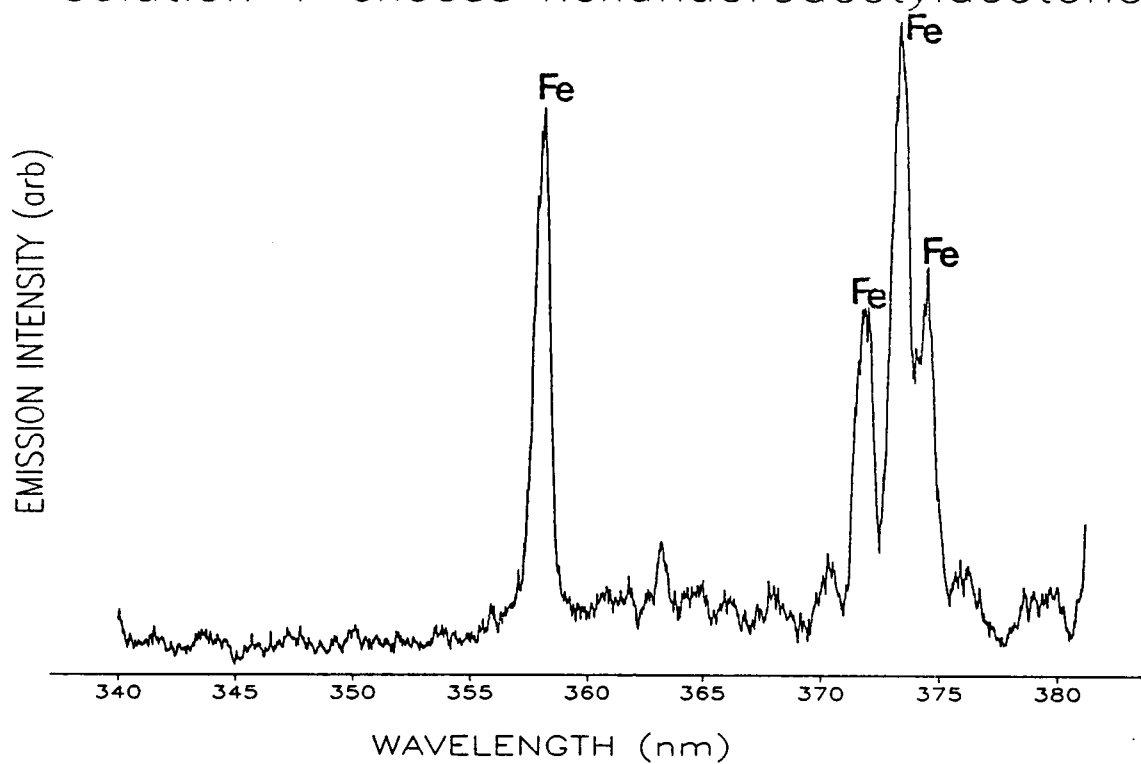


Figure 4.1 Emission Spectrum from the 193 nm Photolysis of 0.15M Fe^{3+} after Complexation with hfa

photolysis of the complexed 0.001M Fe^{3+} solution at an excimer-laser energy of 50 mJ/pulse, as shown in Figure 4.2 [p.152]. Complexation between hfa and 0.0001M Fe^{3+} as well as with 0.0005M Fe^{3+} resulted in the formation of a very pale red precipitate in each case. One-laser spectra at 193 nm at an excimer-laser energy of 75 mJ/pulse of both of these samples are depicted in Figure 4.3 [p.153]. In these cases, the monochromator was scanned over the 358.1 nm iron line only. A comparison between Figures 4.1, 4.2 and 4.3 indicates that, as the metal ion concentration decreases, the signal to noise ratio for the atomic fluorescence signal deteriorates rather dramatically, which is not overly surprising. In the case of the complexed 0.00001M Fe^{3+} solution, no visual evidence of chelation was noted. Under the assumption that complexation did indeed occur, the sample was photolyzed; the observed spectrum consisted of background molecular fragment fluorescence and very weak atomic fluorescence. No visual evidence of metal chelate formation at metal concentrations lower than 0.00001M Fe^{3+} was observed, and similar one-laser spectra (i.e., absence of atomic fluorescence) were recorded. Thus, using these procedures, limits of detection lower than 10^{-4} M for Fe(III) could not be achieved.

At this point, it was necessary to determine if this was just an anomaly associated with Fe^{3+} or whether the problem lay potentially in the design of the sample introduction system (e.g., in the delivery of the gas-phase sample into the chamber). Thus, it was decided to use another metal ion, Cr^{3+} . A concentrated chromium nitrate solution (0.001M) was prepared from which a 5 mL aliquot portion was withdrawn and allowed to react with excess hfa. This complexation process was, as indicated previously, rather slow and required heating of the solution in an oven at 120°C for ca. four hours, after which visual evidence of chelation was observed as a color change from the original purple solution to a green "sphere" at the interface between the ligand and the ligand solution. The solution was allowed to come to room temperature, degassed with liquid nitrogen, and heated to 100°C on-line and analyzed. The resulting one-laser spectrum upon laser photolysis at 65 mJ/pulse is depicted in Figure 4.4 [p.154]. The signal to noise ratios for the Cr atomic lines at 425.4 and 427 nm are noteworthy. Thus, the metal ion

LP-AFS of a 0.001 M Iron nitrate solution plus excess hfa
193 nm Photolysis

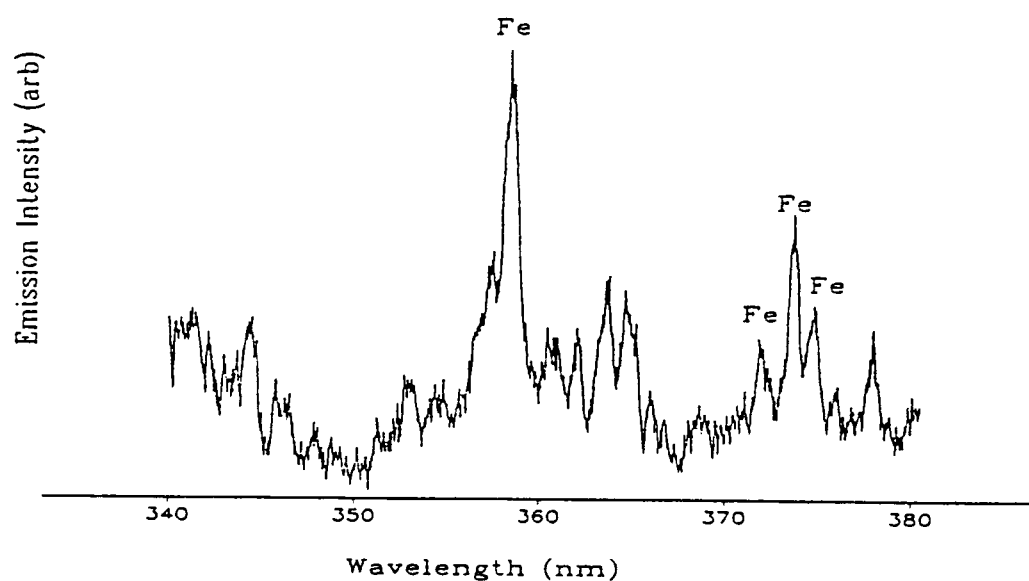


Figure 4.2 One-laser Emission Spectrum from the 193 nm Photolysis of 0.001M aqueous Fe^{3+} after Complexation with hfa

LP-AFS of an IRON NITRATE SOLUTION PLUS EXCESS HFA
193 nm Photolysis

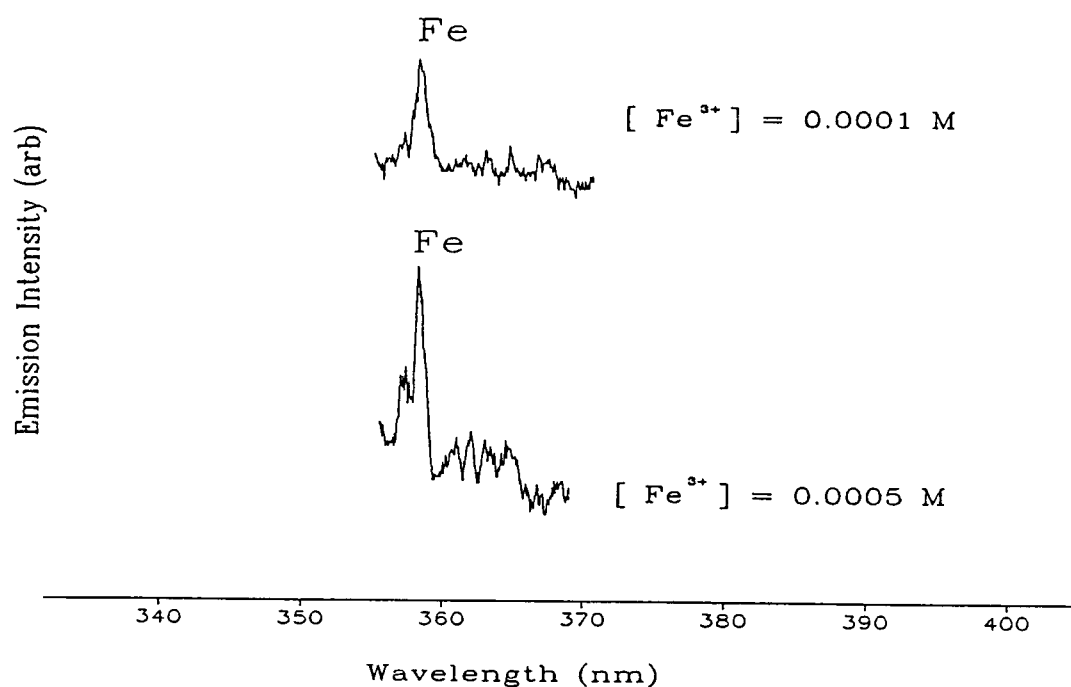


Figure 4.3 One-laser Emission Spectra from the 193 nm Photolysis of 0.0005M and 0.0001M aqueous Fe³⁺ after Complexation with hfa

LP-AFS of a 0.001 M CHROMIUM NITRATE SOLUTION + EXCESS HFA
193 nm Photolysis

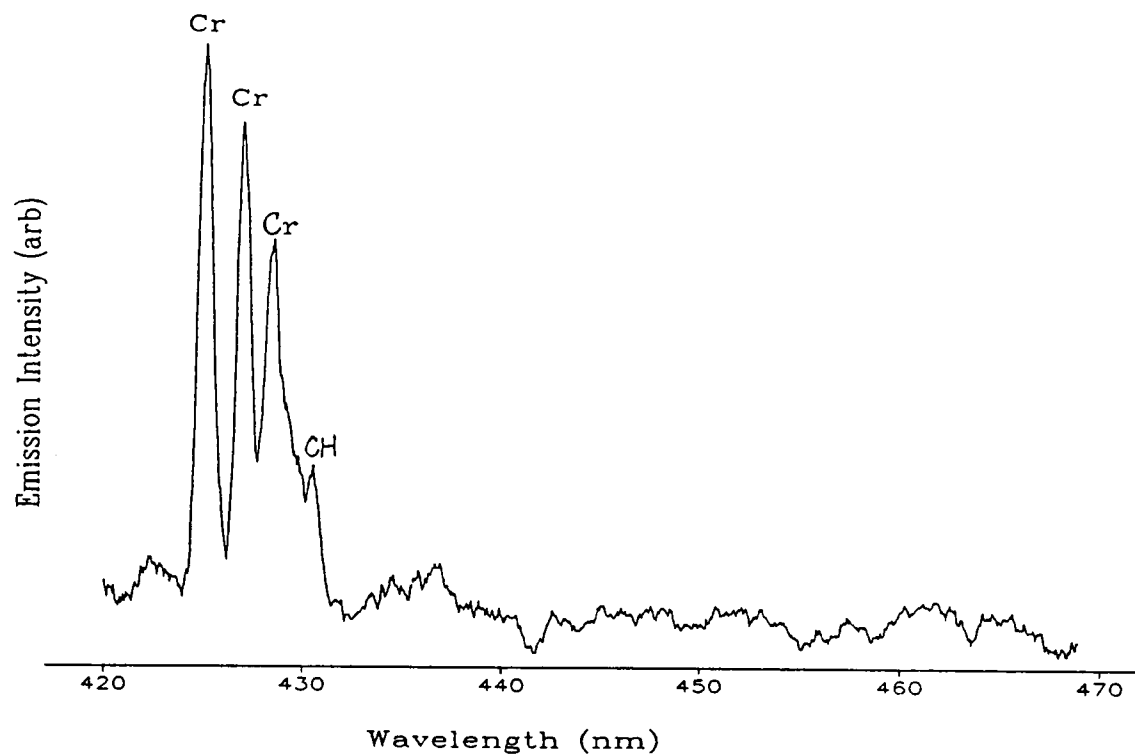


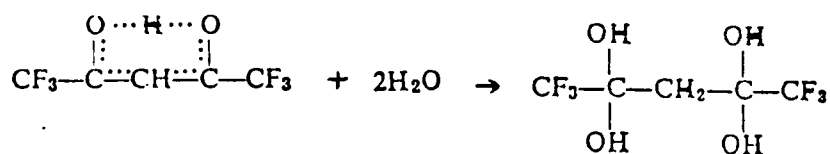
Figure 4.4 One-laser Emission Spectrum from the 193 nm Photolysis of 0.001M aqueous Cr^{3+} after Complexation with hfa

concentration was decreased even further.

A 5 mL aliquot of a 0.0001M Cr^{3+} solution was allowed to react with 1 mL of hfa, which required heating overnight in an oven held at 100°C . Slight visual evidence of the green chromium chelate was present. However, when photolyzed, only molecular fragments were observed in the spectrum, as was observed for the Fe^{3+} /hfa complexations at the same concentration (0.0001M). Again, as with Fe^{3+} , the limit of detection appears to be undesirably high.

Complexation of a 5 mL aliquot of a 0.001M aqueous $\text{Cu}(\text{NO}_3)_2$ with hfa was accelerated by sonication for ca. 15 min., resulting in the apparent formation of the characteristic green metal chelate $[\text{Cu}(\text{hfa})_2]$. Prior to degassing the sample, the green color faded rapidly (within minutes) and, upon laser photolysis, only molecular fragments were observed. In this case, it appeared that the complex was present and then decomposed minutes after chelate formation.

During the course of this investigation, with each of the three metal ions discussed, it was observed that, as the metal ion concentration was decreased, a thick mass of colorless needle-shaped crystals precipitated in the aqueous layer of the solution in the sample bulb. As time elapsed, the crystal growth became more extensive and the color indicating the presence of the chelate faded. This observation suggests that the direction of the equilibrium forming the metal chelate was being shifted. A very minimal amount of crystal growth was observed even with the aqueous solutions containing high concentrations of metal ion (e.g., 0.001M or greater). Upon further investigation in the literature, it was concluded that these crystals were 1,1,1,5,5,5-hexafluoro-2,2,4,4-tetrahydroxypentane, which is a product that is formed when hfa comes into contact with water (44,45):



1,1,1,5,5,5-hexafluoro-2,4-pentanedione

1,1,1,5,5,5-hexafluoro-2,2,4,4-tetrahydroxypentane

Experimentally, this presents a problem because the tetrahydroxy derivative is a much poorer coordinating ligand than the anhydrous enol, so the complexation efficiency is dramatically reduced. Since hfa is such a volatile complexing agent and therefore highly desirable for LP-AFS, measures were taken to remedy this situation.

It should theoretically be possible to dissolve the hfa ligand in an organic solvent and then add the aqueous solution containing the metal ion to it. The ideal solvent of choice to solubilize the ligand should possess a higher vapor pressure than that of the metal chelate of interest, and should not produce molecular photofragments which would interfere with the atomic fluorescence of interest. A wide range of solvents was chosen, as indicated in Table 4.2 [p.157]. In each case, 5 drops of the organic solvent, 5 drops of hfa and 5 drops of the indicated aqueous Fe^{3+} solution were added to a sample vial for visual observation. Of the solvents studied, carbon tetrachloride was the only one that satisfied all of the aforementioned criteria. Photolysis of carbon tetrachloride would yield CCl and Cl photofragments, which would not contribute to the background because these fragments fluoresce in the deep UV outside the spectral response range for the photomultiplier tube used in this work.

When a 0.0001M Fe^{3+} aqueous solution that had been reacted with excess hfa solubilized in carbon tetrachloride was introduced into the vacuum chamber and the resulting vapor photolyzed at 193 nm, photofragment fluorescence from hfa (CH , C_2) was observed, but Fe atomic fluorescence was not detectable.

Since this approach did not appear fruitful, another procedure was attempted. A 1 mL volume of aqueous 0.0001M Fe^{3+} solution was vacuum evaporated to dryness in the bottom of a 50 mL o-ring sealed round-bottomed sample flask. Afterwards, 0.5 mL of the ligand was added into the sample flask to effect the complexation. The characteristic orange-red color of the iron chelate was immediately observed, so this complex was sealed in a sample bulb and allowed to sit overnight. On the following day, it was observed that the hfa derivative had not formed (due to the absence of water) and, more important, the chelate appeared to be present. It was

TABLE 4.2

QUALITATIVE CHELATION OBSERVATIONS BETWEEN AQUEOUS Fe^{3+} SOLUTIONS, SELECTED ORGANIC SOLVENTS AND HFA

SOLVENT	CONCENTRATION OF Fe^{3+}	CHELATION ?	COMMENTS
glycerol	0.0001M	yes-pale orange	hfa and solvent immiscible
1-butanol	0.0001M	no	hfa and solvent immiscible
2-propanol	0.0001M	no	hfa and solvent immiscible
<i>tert</i> -amyl alcohol	0.0001M	no	hfa and solvent immiscible
<i>p</i> -dioxane	0.001M	yes-pale orange	chelate appeared to decompose after a few minutes
<i>p</i> -dioxane	0.0001M	no	thick mass of colorless crystals after 3 minutes
no solvent: hfa made basic with NaOH to pH = 8	0.0001M	yes-very pale orange	slight chelate formation and evidence of colorless basic crystals
cyclohexane	0.0001M	yes-pale orange	evidence of chelate formation
cyclohexane	0.00001M	yes-very pale orange	chelate appeared to decompose rapidly
glycerol/ <i>p</i> -dioxane	0.00001M	no	hfa and solvent immiscible
carbon tetrachloride	0.0001M	yes-pale orange	faint color, but still visible after 10 minutes
carbon tetrachloride	0.00001M	yes-very pale orange	very faint color, but still visible after 10 minutes

introduced into the chamber and photolyzed, which resulted in detectable iron fluorescence. It was then decided to repeat this experiment under similar conditions, except to decrease the metal ion concentration. A 0.00001M Fe^{3+} solution was prepared and treated with hfa, but upon photolysis, atomic fluorescence due to iron was not detectable.

For the aforementioned reasons, it was decided to switch to the tfa ligand to avoid interference of the tetrahydroxypentane derivative which contributed to experimental difficulties in the hfa solution work. The complexation of 5 mL of a 0.1M Fe^{3+} aqueous solution and 1 mL of hfa was initiated by heating the components in an oven for ~ 30 minutes at 120°C. The chelate thus formed was cherry-red in color. The sample was heated to 110°C and introduced into the vacuum chamber. Upon 193 nm illumination, a visibly bright fluorescent image was seen inside the chamber, which is a typical observation for organic molecules and metal carbonyls, but atypical for metal chelates. The excimer laser was operating at an output of 100 mJ/pulse; the collected spectrum in Figure 4.5 [p.159] indicates the presence of iron atomic fluorescence lines, similar to that of $\text{Fe}(\text{hfa})_3$, except for the relative signal magnitude of the three atomic lines at 372, 373.5 and 375 nm. These atomic lines are much less intense with respect to the 358.1 nm Fe line than is the case for $\text{Fe}(\text{hfa})_3$ (refer to Figure 3.4 [p.81]).

A similar experiment was performed in which 1 mL of tfa was complexed with 5 mL of a 0.01M Cr^{3+} solution. The sample contents were heated in an oven held at 120°C and remained overnight, because visual evidence of chelation was not noted after the first four hours. Chelate formation was observed as a color change from purple to a colorless solution with violet crystals on the bottom of the sample bulb. The spectrum produced upon 193 nm photolysis at 100 mJ/pulse is depicted in Figure 4.6 [p.160]. Complexation of a 0.001M Cr^{3+} and tfa was performed as described directly above, and atomic fluorescence due to chromium was observed, but the signals were barely detectable. The requirement of higher operating temperatures coupled with the observation of weaker atomic fluorescence signals renders tfa undesirable as a complexing agent when compared to hfa or other chelating agents which may

0.1M Iron Nitrate Aq. Soln. + excess Trifluoroacetylacetone
193 NM PHOTOLYSIS

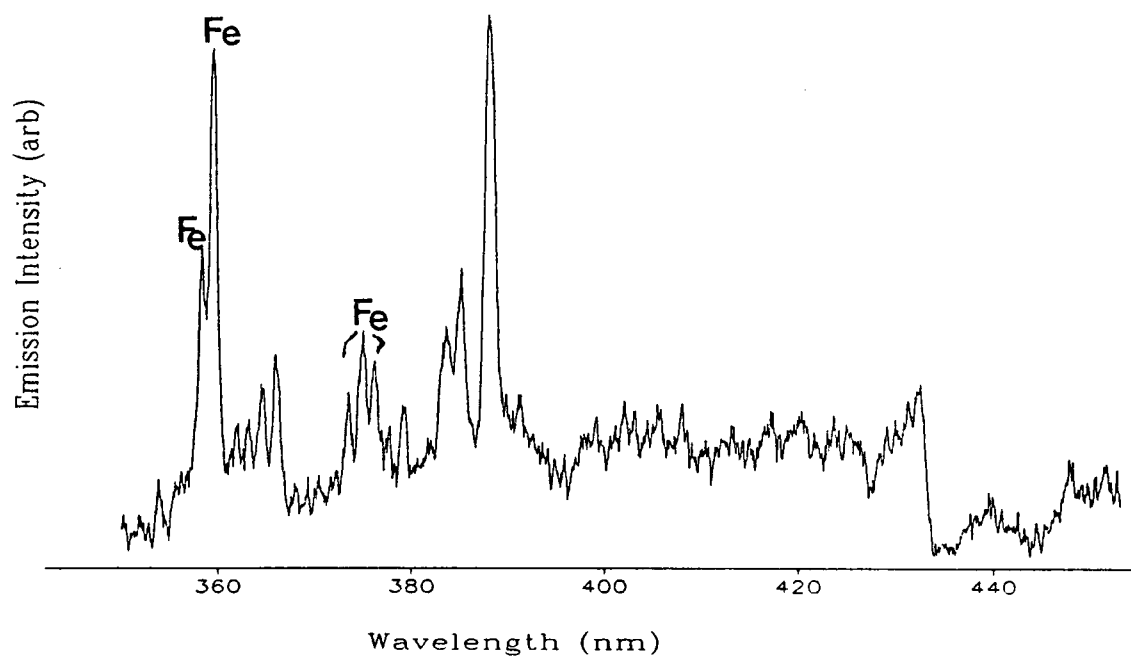


Figure 4.5 One-laser Emission Spectrum from the 193 nm Photolysis of 0.1M aqueous Fe^{3+} after Complexation with tfa

0.01M Chromium Nitrate (aq.) + excess trifluoroacetylacetone
193 NM PHOTOLYSIS

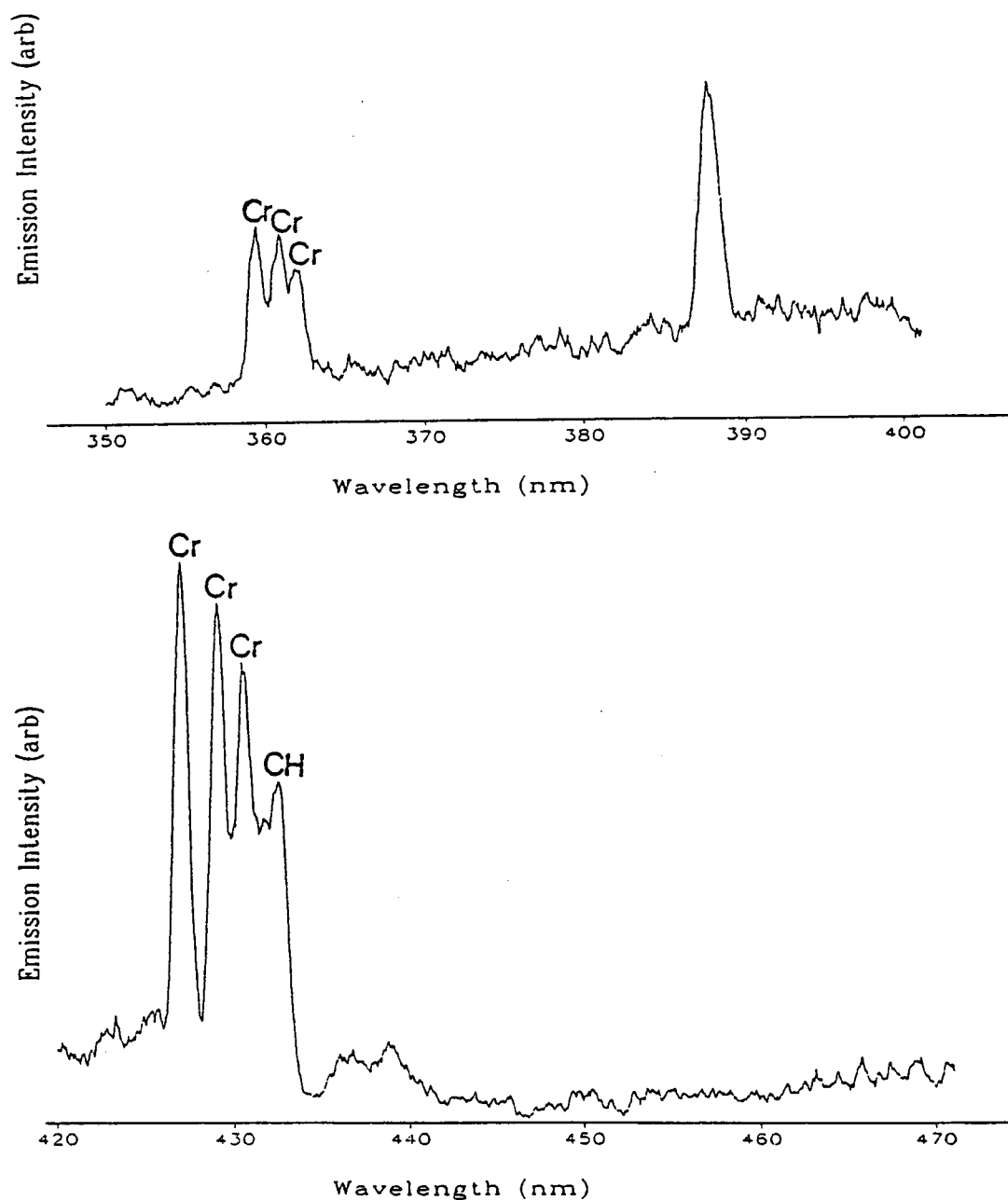


Figure 4.6 One-Laser Emission Spectrum from the 193 nm Photolysis of 0.01M aqueous Cr^{3+} after Complexation with tfa

be used.

The combined results of these representative experiments suggest that (1) another appropriate complexing agent should be used, (2) a solvent extraction procedure will be required to extract the metal ions from the aqueous solution into an organic solvent, or (3) a major reconfiguration of the design of the apparatus for introducing the chelate vapors into the vacuum chamber must be undertaken. A quantitative chelation reaction in the liquid or solid phase is critical for LP-AFS to be a valid analytical method; hence, the suggestion of using a more appropriate complexing agent is made. Potential candidates include the fluorinated diethyldithiocarbamates, the only drawback being that they are commercially unavailable and would have to be synthesized. It has been reported that the trifluoroethyldithiocarbamate ligand (as the sodium salt) quantitatively reacts with a large number of metals including Zn, Cd, Cu, Ni, Co, Hg, Pb, Bi, Fe, Pt, Pd, Rh, Sb, Tl, In, Cr and Se (78). More importantly, the resulting chelates are reported to be volatile and thermally stable at nanogram levels (79).

To address the suggestion of reconfiguring the method of gas-phase sample introduction, argon gas was steadily blown over the sample vapor region via a gas delivery line installed on one side of the sample bulb containing the reaction mixture, in an effort to force the sample vapor into the vacuum chamber. Unfortunately, the dilution effect of the carrier gas far outweighed any advantages in sensitivity. This may mean that a two-laser experiment is essential to improve the sensitivity of the technique. It must be noted that, under conditions of low metal ion concentration (submicrogram), the gas-phase chelate is introduced into the chamber as a "plug", so analysis must proceed under inherent time constraints. The collection of 2-laser resonance fluorescence spectra requires three separate scans to distinguish the probe laser scattering background from the probe-laser induced signal and the one-laser signal, which is time-consuming. Now that the groundwork has been established in this area, further research is suggested to implement the two-laser experiments to attain better sensitivity.

To summarize, for the initial development of LP-AFS in this work, the following steps

were found overall to be the most appropriate way to effect complexation in aqueous metal-containing solution samples using a direct chelation approach, followed by atomic fluorescence detection of the resulting metal atoms:

- (1) Pipet 5 mL of the aqueous solution containing the metal ion of unknown concentration into a 25 mL sample bulb equipped with an o-ring sealed valve.
- (2) Pipet 0.5 mL of the neat ligand (hfa or tfa) into a sample bulb, and close the valve.
- (3) Allow the reaction to take place in a temperature-controlled oven (the appropriate temperature depends on the ligand used as the complexing agent and the metal ion) for a specified time.
- (4) Remove the sample bulb from the oven and allow it to cool to room temperature.
- (5) Degas the sample via a freeze-thaw cycle.
- (6) Wrap the sample bulb with glass wool and heat the sample bulb with a heating mantle.
- (7) Introduce the sample vapor into the vacuum chamber and photolyze.

c. Non-Aqueous Solutions - Method Development

In an effort to investigate the practicality of a solvent extraction method in which metal ions in aqueous solution could be extracted into an organic phase and to eliminate experimental difficulty associated with the hfa ligand when it contacts water, carrying out the complexation in a non-aqueous environment was attempted. Prior to directly reacting a non-aqueous metal-containing solution with hfa, a small amount of previously synthesized $\text{Fe}(\text{hfa})_3$ was dissolved in enough toluene to prepare a 0.5M solution. A 5 mL aliquot of this solution was withdrawn and placed in a sample bulb. The sample was installed on-line, heated and introduced in the gas phase into the chamber. Intense fragment fluorescence signals due to toluene and the ligand (CH , C_2) were observed after introduction of the gas-phase chelate into the chamber, but no iron atomic fluorescence lines were observed. It is believed that the vapor pressure due to the solvent far exceeded the partial pressure of the gas-phase chelate, which would explain why

atomic fluorescence was undetectable.

Nonetheless, several organic solvents were tried (acetone, dimethylformamide (DMF) and acetonitrile) to find a solvent miscible with hfa as well as with a metal nitrate salt. A 0.0001 M $\text{Fe}(\text{NO}_3)_3$ solution was prepared in each of the organic solvents listed. In DMF, the original pink solution turned wine-red after complexation with the hfa, indicative of successful complexation. In acetonitrile, the original yellow solution showed no evidence of change after complexation with hfa. In acetone, undissolved metal nitrate solid remained suspended in solution even after reaction with hfa. The former two solutions, when vaporized and photolyzed, produced only molecular fragment fluorescence from the ligand and solvent. It was concluded, on the basis of these results, that organic solvent extraction of the aqueous metal ions would not be very practical for LP-AFS. If a solvent extraction method is implemented to extract the metal ions out of aqueous solution into an organic solvent, the solvent should not contribute in a major way to the background fluorescence from the molecular fragments. Since most organic solvents contain carbon and hydrogen, the likelihood of forming C_2 and CH fragments is high, as the aforementioned experiments indicate. It can be inferred that a solvent extraction technique would be impractical for this method of analysis.

2. Solid Metal-Containing Samples

Generally, samples in the form of gels, suspensions or solids are typically prepared for spectroscopic trace metal analysis by a variety of procedures including wet ashing, acid digestion and/or fusion treatments (80). The resulting liquid solutions are directly aspirated into a plasma or flame atom reservoir, or inserted into a graphite furnace atomizer. The accuracy of such an analysis is highly dependent on the ability to prepare a solution that is representative of the original sample. A variety of experimental difficulties must be overcome to satisfy these criteria. Complete dissolution of the sample is essential; any volatile analytes must be prevented from escaping during the heating process; and care must be taken to avoid sample

contamination. Clearly, avoiding these costly (in terms of time and effort) sample preparation steps would be beneficial.

Many solid analysis techniques have been developed which address these concerns, with varying degrees of success. Of particular interest are those methods employing photons as the excitation source in laser solid sampling techniques. For instance, LS-ICPMS (laser solid sampling inductively coupled plasma mass spectrometry) and LAMMA (laser microprobe mass spectrometry) both exhibit high sensitivity primarily because ions are the measured species, but there are reproducibility problems associated with sample heterogeneity (80). In the LS-ICPMS method of analysis, a pulsed laser is used to vaporize material from a solid surface (laser sampling), after which a carrier gas sweeps the vaporized material into a plasma of an ICP. The resulting ions are detected by mass spectrometry. In LAMMA, laser sampling is employed followed by mass spectrometric detection. Precision is an important consideration in all of the solid sampling techniques because concentration gradients do exist in all "real" solid samples. In LP-AFS, this problem is not as apparent because the sample is converted to the gas phase, after which laser bombardment of the gaseous species produces the resulting metal atoms which are detected.

a. Metal-containing Solids: Method Development

The general approach for LP-AFS analysis of metal analyte(s) in solid samples was virtually identical to that described for the solution samples. However, in this case, the solid matrix was important and posed different experimental concerns than those for the solution samples. Perusal of the literature indicated that analysts typically ash or digest solid samples (e.g. organic matrix) prior to complexation with the ligand (79, 81); a few have implemented the direct chelation approach, whereby no sample preparation steps are involved prior to complexation. For instance, Black and Browner carried out direct chelation reactions with beta-diketone ligands and certain metals in various solid matrices (e.g. pure metals, metal salts) and

the resulting atomic emission from the metal(s) of interest was detected via ICP-AES (63). Black and Browner described two direct complexation procedures; one involved reacting a solid sample and ligand in a heated, closed vessel from which, upon opening, chelate vapor was flushed out (63). In the second procedure, a sample and ligand were sealed in an ampule, frozen with dry ice, and then heated. After cooling, the ampule was refrozen with dry ice, opened and placed in a on-line heated reaction vessel (63).

Ross and Sievers described an interesting direct chelation approach, in which two different solid ferrous alloys were allowed to react with tfa (82). The complexation reaction was accelerated by subjecting the sample/ligand to a microwave radiofrequency field. The resulting red solution was dissolved in benzene and analyzed by gas chromatography. It was accordingly considered appropriate to carry out a direct chelation reaction to analyze metals with LP-AFS.

For the first trial, a NIST bovine liver reference material, SRM 1577a, was chosen because the concentrations of the metals of interest were all in the $\mu\text{g/g}$ range: Fe ($194 \pm 20 \mu\text{g/g}$), Cu ($158 \pm 7 \mu\text{g/g}$) and Co ($0.21 \pm 0.05 \mu\text{g/g}$). As suggested by NIST, ca. 300 mg of the bovine liver sample was dried in a vacuum desiccator. Afterwards, ca. 250 mg of bovine liver was weighed into a 25 mL sample bulb. A 1 mL aliquot of neat hfa ligand was added to the bovine liver in the sample bulb. The formation of a slurry was observed, with no color change noted. The sample contents were sonicated for several hours with no visible chelate formation, which was not overly surprising. The sample was then placed in an oven at 120°C for several hours to accelerate the chelation process. Even though chelate formation was not evident, it could not be assumed that it did not occur, so the sample was introduced at a pressure of 3×10^{-4} torr into a vacuum chamber and photolyzed. No detectable iron fluorescence was observed (iron was the metal having the highest certified concentration in the sample). In Figure 4.7 [p.166] a representative spectrum reveals that photofragmentation is certainly taking place, because molecular fragment fluorescence from the ligand and/or volatile organic constituents of the sample is observable.

LP-FFS of NBS Bovine Liver (Hfa chelation)

193 nm Photolysis

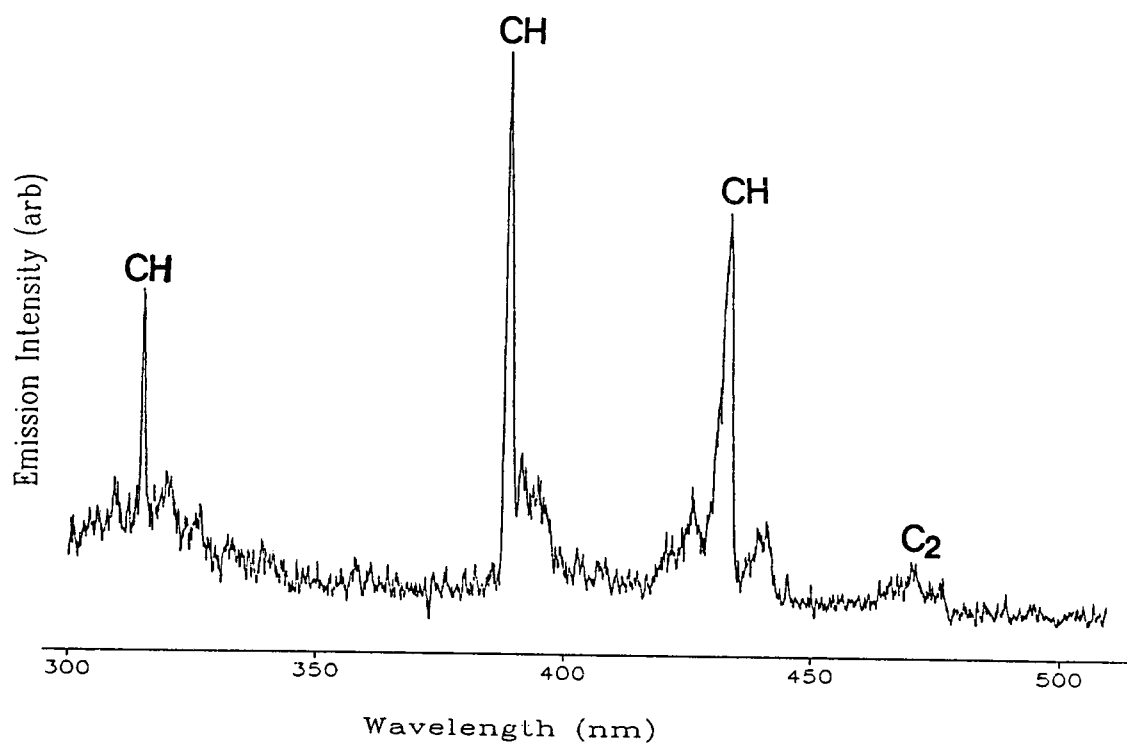


Figure 4.7 One-laser Spectrum from the 193 nm Photolysis of the Vapor Produced after Bovine Liver (NIST SRM 1577a) was Treated with hfa

Many different approaches were then implemented to induce chelation prior to the introduction of the sample into the chamber. These included varying the length of sonication and heating, in addition to varying the amounts of ligand and bovine liver sample. Since the concentrations of the metal ions of interest in this sample were moderately low, other solid samples containing higher concentrations of the metal ions of interest were also evaluated in an effort to systematically develop LP-AFS as a method of detection of metal ions in solid samples.

Proceeding from high to progressively lower metal ion concentrations, the following solid samples were examined:

- (1) copper oxide : 4.55% Cu by mass
- (2) iron (III) ammonium sulfate : 2.18% Fe by mass
- (3) silicon metal powder (NIST SRM 57a) : 0.5 % Fe by mass; 0.024% Cr by mass; 0.004% Cu by mass; 0.47% Al by mass
- (4) aluminum casting alloy millings (NIST SRM 855a) : 0.14% Fe by mass; 0.13% Cu by mass

These particular samples were chosen for study based on availability, documented certificates of analysis, and suitable sample form (i.e. powders). Since a direct chelation approach was desirable, samples in the form of metal disks or blocks were not chosen, because acid digestion would almost certainly be required prior to analysis.

To begin, a 0.250 g sample of copper oxide was placed in a 25 mL sample bulb and allowed to react with 1 mL neat hfa ligand. No immediate visible reaction was observed, but after placing the sample in an oven at 100°C, the sample turned a grass-green color after ca. five minutes. The sample was then removed from the oven, degassed, heated, and introduced into the vacuum chamber whereupon it was photolyzed by the ArF laser operating at 70 mJ/pulse. The resulting spectrum can be seen in Figure 4.8 [p.168]. In this spectrum, the two characteristic atomic Cu lines at 324 and 327 nm are the prominent features.

The next sample analyzed was iron (III) ammonium sulfate, a pale yellow powder. A 0.250 g sample chelated with 1 mL of hfa resulted in an immediate color change from pale

Copper Oxide – Lot #171 (4.55% Cu) chelated with Hfa
193 NM PHOTOLYSIS

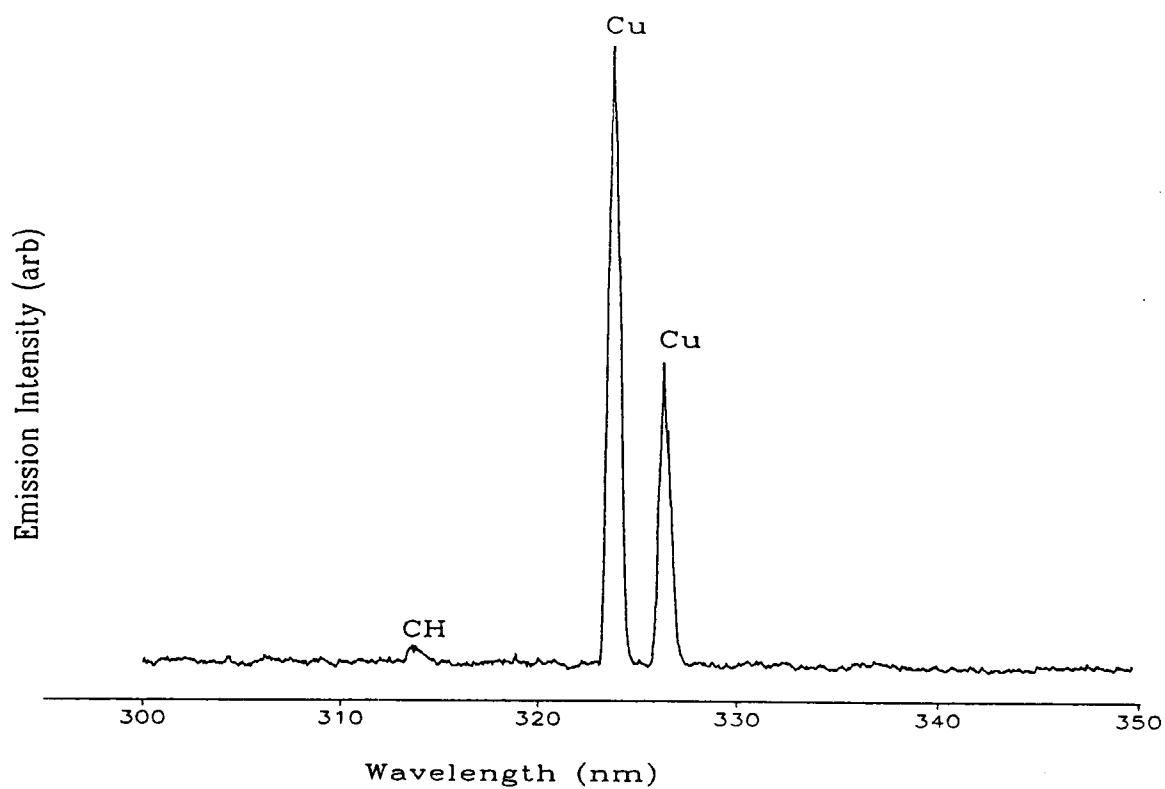


Figure 4.8 One-laser Emission Spectrum from the 193 nm Photolysis of the Vapor Produced after Copper Oxide was Treated with hfa

yellow to vibrant orange. After heating in an oven, the sample turned blood-red in color. Laser photolysis at 45 mJ/pulse resulted in a typical iron fluorescence spectrum, which is depicted in Figure 4.9 [p.170]. It is virtually identical to the survey spectrum depicted in Figure 3.4 for Fe(hfa)_3 .

The NIST silicon metal reference material, SRM57a, was in the form of a fine powder, similar to the copper oxide and iron (III) ammonium sulfate samples. A 0.5077 g sample of oven-dried SRM 57a was placed in a sample bulb, to which 1 mL of hfa was added. No immediate reaction appeared to occur, so the sample was sonicated for ca. one hour and then placed in a 110°C oven overnight to accelerate the reaction. After this time, inspection of the sample indicated the presence of mostly unreacted metal and a pale-orange liquid phase, which presumably contained the metal chelate(s). A survey spectrum was obtained for this sample over the range 350 - 406 nm, to determine if more than one metal could be detected. As seen in Figure 4.10 [p.171], iron and aluminum were present, as expected. It is clear that as the scan proceeded, the signal intensity became weaker and weaker as evidenced by the strong 358.1 nm Fe line and the considerably weaker 394.4 nm Al line. When dealing with transient samples (as in the case here), pulsed lasers having low duty factors (10^{-7}) do limit the efficacy of the technique. Nevertheless, this result does show that more than one metal in a sample can be detected simultaneously. Since the gradual disappearance of signal over time was observed, it may be best to scan the monochromator just over the particular line of interest if a conventional PMT detector is used. The availability of an array detector spectrograph, rather than a scanning spectrometer (as in the present work) clearly would tend to obviate this problem.

In an effort to determine how the atomic fluorescence signal varied with respect to metal ion concentration, varying amounts (ca. 1.0 - 0.1 g) of SRM57a were directly chelated with 1 mL hfa portions, each contained in a 25 mL sample bulb. Experimental conditions were held as nearly constant as possible for each of these runs. The ArF laser was operating at 100 mJ/pulse in each case, and the maximum amount of sample vapor possible was introduced (ca.

193 nm Laser Photolysis Survey Spectrum of
Iron (III) ammonium sulfate after treatment with hfa

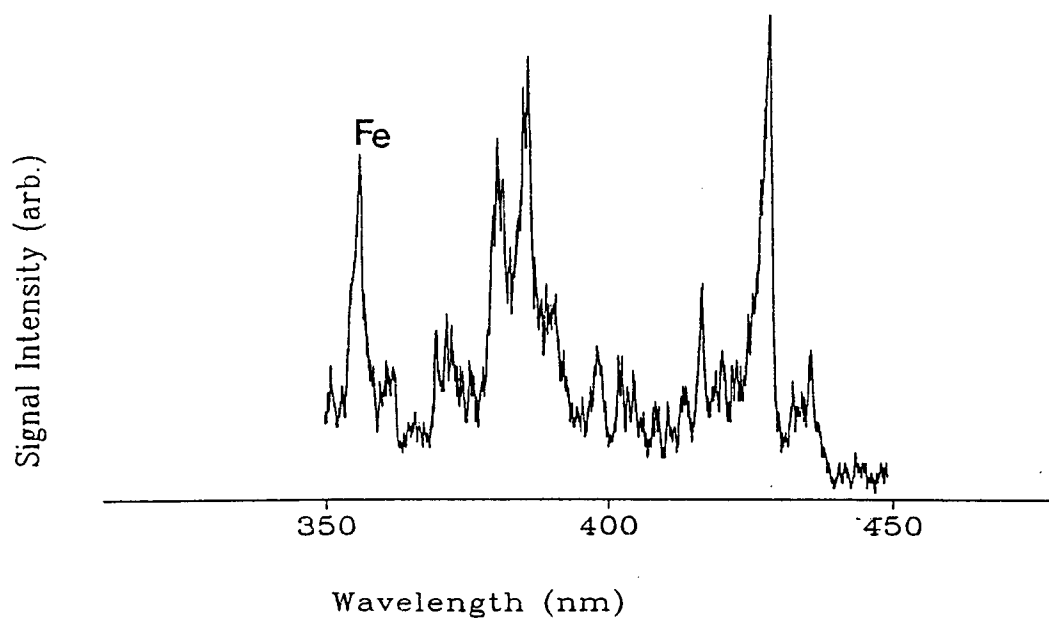


Figure 4.9 One-laser Emission Spectrum from the 193 nm Photolysis of the vapor produced after Iron (III) Ammonium Sulfate was Treated with hfa

SRM 57a / hexafluoroacetylacetone
193 NM PHOTOLYSIS

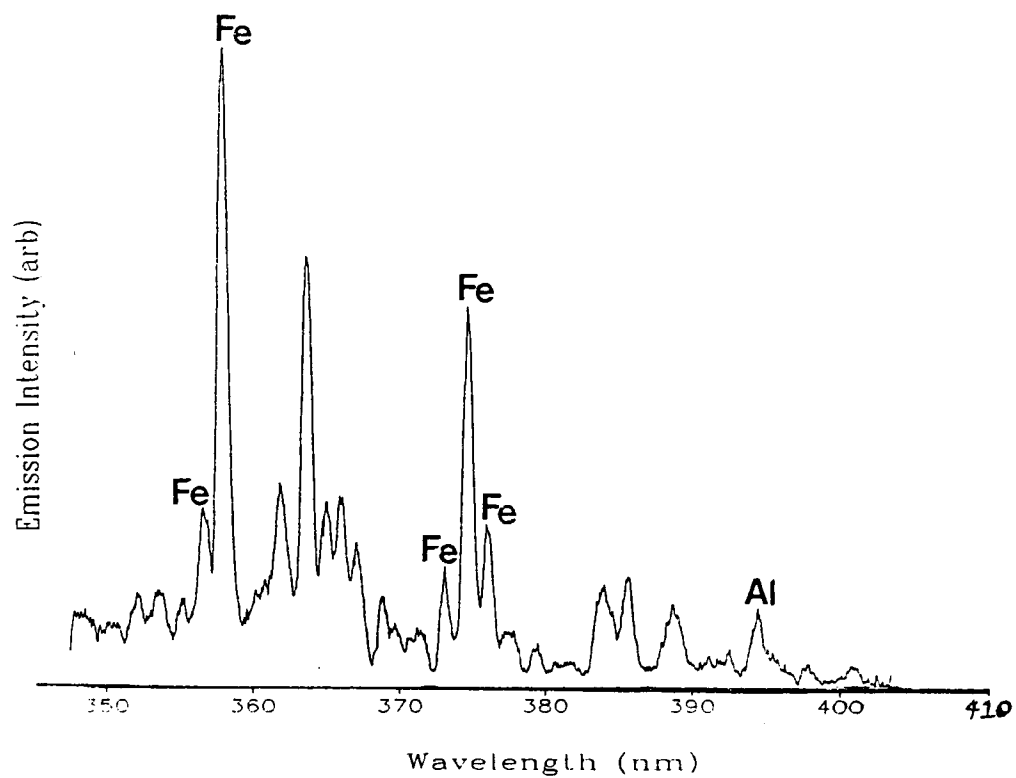


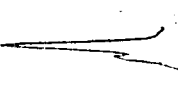
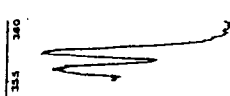
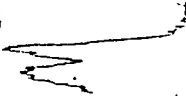
Figure 4.10 One-laser Emission Spectrum from the 193 nm Photolysis of NIST SRM 57a after Complexation with hfa

4×10^{-4} torr) into the chamber for analysis. The monochromator was scanned over the 358.1 nm line (Fe) and then over the 425.4 nm line (Cr). The results are depicted in Table 4.3 [p.173]. Absence of Cr data for some of the scans indicates a $S/N < 2$ (undetectable) under these conditions. For the 0.1045 g sample, if quantitative chelation is assumed, the detectable amount of iron is calculated to be 53 mg. This result is not necessarily totally discouraging; it may just imply that a 2-laser experiment is needed to improve sensitivity or the sample should be introduced at a higher sample pressure. The latter suggestion requires a major reconfiguration of the sampling chamber, so the former suggestion should be the first avenue of research.

The NIST aluminum casting alloy reference material, SRM855a, was in the form of shaved millings. A 0.5 g sample of SRM855a was placed in a sample bulb, to which 1 mL of hfa was added. No indication of chelate formation was present, so the sample was heated in an oven held at 110°C overnight. On the following morning, inspection of the sample showed mostly unreacted shaved millings and a pale-orange liquid phase, which was presumed to contain the chelate(s). A survey spectrum over the range 300 - 510 nm was obtained so that copper and iron signals could be monitored. This spectrum can be seen in Figure 4.11 [p.174]. Oddly enough, copper and aluminum signals were observed, but no signals due to iron fluorescence were observed. Additional survey spectra under similar experimental conditions yielded iron fluorescence when the monochromator was scanned, starting at 350 nm. A representative spectrum is depicted in Figure 4.12 [p.175]. As stated previously, this may imply that the monochromator should be scanned over just one atomic line at a time, in order to obtain the maximum signal, before the vapor leaves the interrogation region. Again, this is a consequence of inadequacies in the available instrumentation (i.e., use of a scanning spectrometer rather than an array-detector spectrograph), not an inherent failing of the technique itself. In Table 4.4 [p.176], the iron atomic fluorescence signals obtained by photolyzing varying amounts of SRM855a which were chelated with hfa are shown. In each case, the monochromator was scanned over the iron fluorescence line at 358.1 nm. The

TABLE 4.3

RESULTS OF LP-AFS ANALYSIS OF NIST SRM 57a^a

WEIGHED AMOUNT(g)	S/N at 358.1 nm (Fe) ^b	S/N at 425.4 nm (Cr) ^c	Signal Intensity 358.1 nm (in v)	Signal Intensity 425.4 nm (in v)	Atomic Fluorescence Spectra	
					Fe	Cr
1.0023	32	12.7	0.27	0.08		
0.4992	16	5.1	0.09	0.02		
0.2509	12.7	-	0.07	-		-
0.1045	2.3	-	0.01	-		-

^a Certified values for NIST standard: SRM 57a (Fe - 0.5% by wt.; Cr - 0.024% by wt.)^{b,c} Spectral scan over atomic line taken immediately after sample introduction

SRM855 chelated with hfa
193 NM PHOTOLYSIS

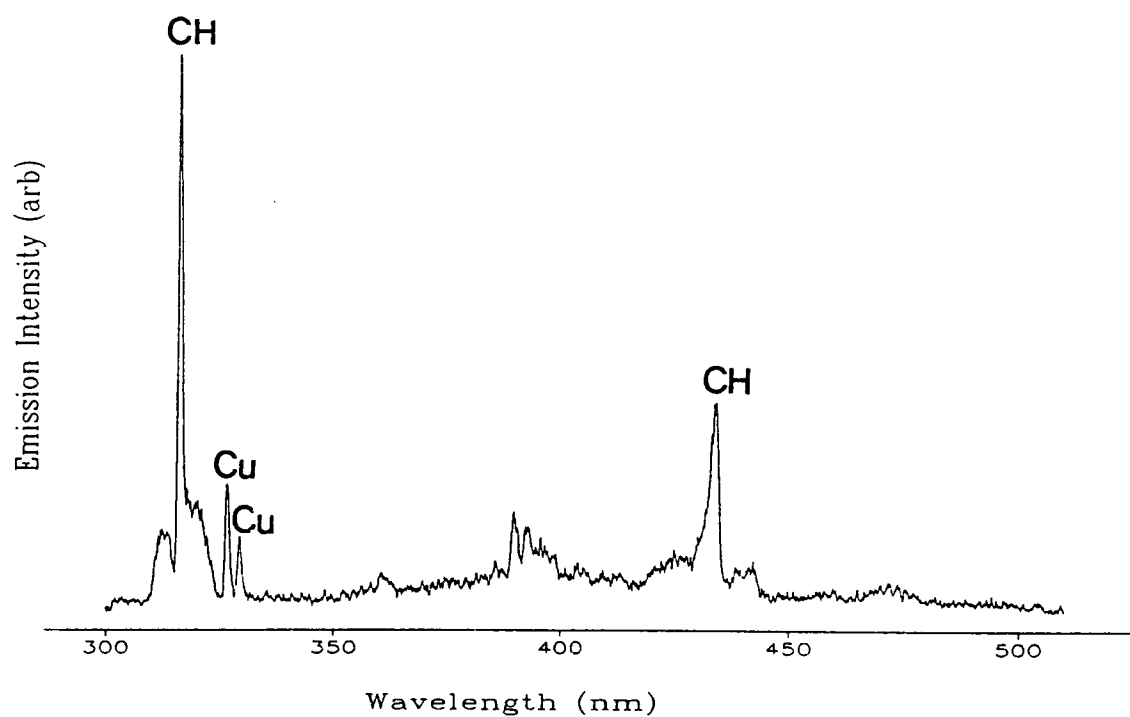


Figure 4.11 One-laser Emission Spectrum from the 193 nm Photolysis of NIST SRM 855a after Complexation with hfa

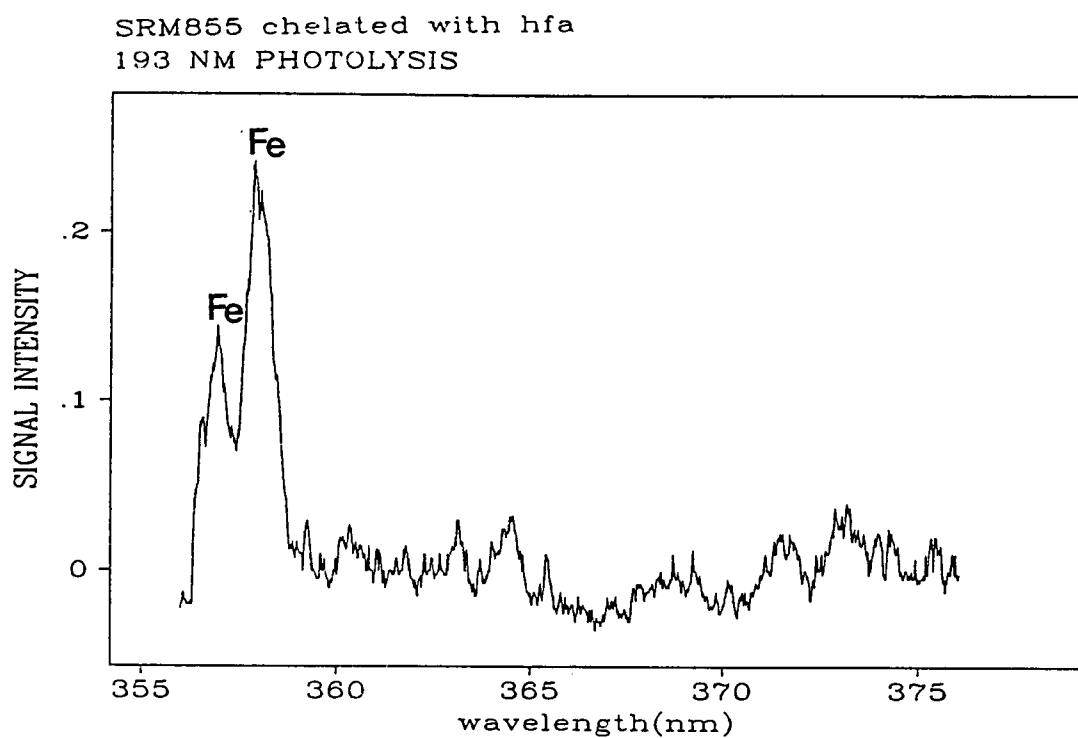


Figure 4.12 Survey Spectrum from the 193 nm Photolysis of NIST SRM 855a after Complexation with hfa

TABLE 4.4

RESULTS OF LP-AFS ANALYSIS OF NIST SRM 855a^a

WEIGHED AMOUNT(g)	S/N at 358.1 nm (Fe) ^b	Signal Intensity- 358.1 nm (in v)	Atomic Fluorescence Spectrum
1.006	26	0.12	
0.5057	9.2	0.02	

^a certified value for NIST standard: SRM 855a (Fe-0.14% by wt.)^b Spectral scan over atomic line taken immediately upon sample introduction

fluorescence signal dropped rather dramatically ($>$ factor of 2) when the weighed amount of the sample decreased by a factor of 2. Experimental conditions were held as nearly constant as possible, including the length of time the complexation was carried out in the oven. Since this sample was in the form of shaved millings, resulting in mostly unreacted material after complexation, prior acid digestion of the sample may be necessary. To investigate this idea, ca. 0.5 g of SRM855a was placed in a 25 mL sample bulb, to which a small amount of nitric acid was added. As expected, the sample partially dissolved, after which a small amount of hfa was added. The sample initially turned green and then brown upon heating, visually indicating the formation of the copper and the iron chelates. A one-laser spectrum was not collected for this sample because when it was heated, it began frothing and clogged the sample introduction line. As previously stated, prior sample preparation steps are clearly to be avoided, but may be necessary for solid samples in the form of millings.

3. Conclusions and Recommendations

The LP-AFS technique, as developed thus far, has not been demonstrated to be applicable to liquid solutions containing metal ion concentrations lower than ca. 10^{-5}M or solids containing trace metal concentrations (submicrogram). This situation can be attributed in part to the properties of the currently available ligands for forming highly volatile metal complexes (e.g., hfa), and in part to limitations in the sampling apparatus and laser system. For example, the use of a pulsed laser system that exhibits a very low duty factor (e.g., 10^{-7} for the lasers used in the present work) is not readily compatible with a sampling system in which the vaporized metal complex passes very rapidly through the spectroscopic interrogation region. For conventional pulsed lasers, this situation results in inefficient use of the analyte signal due to the limited irradiation time. Alternatively, a pulsed laser which exhibits a higher duty factor is a copper vapour- pumped dye laser, but is of limited use in this work because of the range of accessible wavelengths ($\lambda \geq 400\text{ nm}$) and low peak powers. Continuous-wave lasers exhibit long irradiation times but the limited wavelength range, low power for frequency doubling (allowing access to shorter wavelengths) and long-term power stability are current limitations. Thus, at the present time, the limitations associated with the use of pulsed lasers exhibiting low duty factors must be compensated for in other aspects of the analysis scheme.

To realistically decrease the limit of detection of metal atoms in "real" samples to acceptable levels (by ~ 3 orders of magnitude), modifications of the instrumental apparatus and the sampling procedure are recommended for LP-AFS. As described in the work presented in this dissertation, the limits of detection for the atomic fluorescence of analyte atoms generated by the 193 nm laser photolysis of pure solid metal chelates and carbonyls were impressive, yet when "real" samples containing trace metal ion concentrations were subjected to similar analysis, sensitivity suffered. Sample vapor generation and sample vapor introduction are two areas which need to be addressed to reverse this situation.

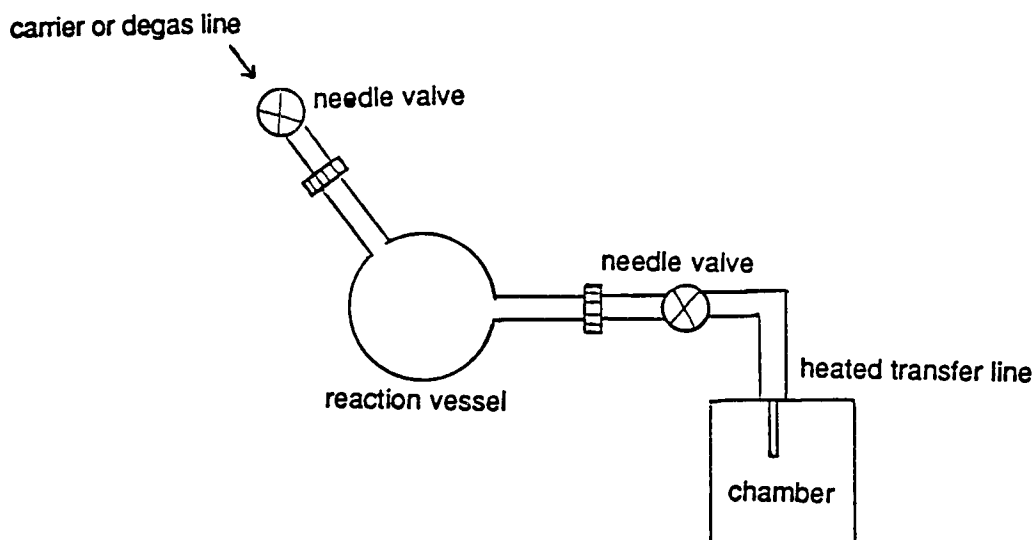
Although three established methods for sample vapor generation exist (hydride, carbonyl and volatile metal chelate), the latter was chosen for sample vapor generation for LP-AFS primarily due to the wide range of metal ions capable of being quantitatively chelated, a decision that is still strongly supported. However, as clearly demonstrated in this work, hfa is not the optimal ligand for LP-AFS of solution samples due to its tendency to react unfavorably with water. Since chelate volatility is currently a limiting factor in the choice of a suitable ligand, equipping the instrumental apparatus with high temperature (at least 250°C) components (e.g., o-rings, valves, ferrules and fittings) as appropriate would enable one to choose a ligand that would not be subject to the constraints of high volatility. Two recommended chelating agents that are not water-sensitive, relatively volatile and thermally stable are lithium or sodium bis(trifluoroethyl)dithiocarbamate and tfa (used to a limited extent in this work). The former has reportedly been used to chelate Bi, Co, Cu, Fe, Ni, U, Hg, Pd, Ag, Tl, Pb, Cd, Zn, In, Sb, Te, Mn, Pt, Rh, Cr and Se (78,79). Metal derivative formation involving tfa as the complexing ligand involves slow kinetics and necessitates higher operating temperatures as described in this dissertation. These limitations could potentially be overcome by accelerating complexation using microwave techniques and equipping the experimental apparatus with relatively high temperature components.

It is imperative that the metal chelate, once formed, be transported in the gas-phase as efficiently as possible into the spectroscopic interrogation region inside the chamber. The fact that liquid solutions containing metal ion concentrations lower than ca. 10^{-5}M are incapable of analysis may be a function of the ability of the sample introduction system to deliver the sample into the chamber and not the ability of the detection method to detect it. It is possible that the gas-phase chelate is being trapped in the interface (sample introduction line) before it ever reaches the chamber and/or is being introduced into the chamber as a "burst" of chelate vapor, thereby placing stringent time constraints on the detection system. This behavior was never considered during analysis involving the pure metal chelates, because chelate vapor was

continuously being replenished from the heated sample bulb over a long period of time as it passed through the sample introduction line. Reliance on a significant pressure difference between the heated metal complex in a static sample bulb and the vacuum chamber to introduce the chelate vapor (as used in the present work) is not as effective as required for the introduction of chelate vapor generated from "real" samples. For "real" samples, a carrier gas may be necessary to sweep the volatilized chelate into the spectroscopic interrogation region. Moreover, a buffer gas may serve to increase the residence time of atoms in the laser beam-chelate vapor interaction region, provided that the resulting dilution of the analyte vapor does not completely destroy sensitivity.

Devices for volatilizing metal chelates developed by Black and Browner (63), Rando and Heithmar (62), Castillo et. al (57) and Fujinaga et al. (58) are sufficient without modification if the chelate vapor is being introduced into an atomization reservoir operating at atmospheric pressure. However, it is a nontrivial matter when operating in a low pressure regime (inside of a vacuum chamber) because of the different pressure requirements. Gas-phase samples are typically introduced into a vacuum chamber by a pulsed valve, leak valve or from a gas chromatograph effluent (typically followed by a separator to attenuate the carrier gas), all three of which would be suitable for the introduction of volatile metal chelates. Although clearly highly speculative, the latter may potentially be of use for the introduction of chelate vapor generated from "real" samples. However, interfacing a gas chromatograph to the existing instrumentation would place certain requirements on the analysis scheme that would have to be carefully considered because this would be a costly endeavor. Namely, to improve the duty factor, the gc effluent should be pulsed into the chamber and synchronized with the laser pulse(s). The sample under investigation would have to be converted into a form amenable for gc analysis (e.g., solids would have to be digested, diluted, then chelated with an organic solvent/ligand solution and aqueous solutions would have to be chelated using a solvent extraction method). Chromatographic conditions would not be especially critical, since high resolution separation is

not the goal of the analysis. Rather, the primary function of the gas chromatograph would be to insure quantitative transfer of the sample into the chamber. Prior to implementing this type of instrumental overhaul, it is suggested that a modified version of the Black and Browner volatilization device be investigated, as shown below:



To take advantage of the potential capability of forming and detecting more than one chelate in a "real" sample, a single phase (direct) approach was taken in the generation of volatile metal chelates from both liquid solutions and solids, as described in this work. Since the pH dependence and distribution ratios involved in solvent extraction methods of metal chelate formation limit the number of metals that can be determined in the same analysis, this approach was not particularly desirable for LP-AFS. Although LP-AFS is technically a 2-laser, single element technique whereby a dye laser is used to induce fluorescence from generated metal atoms, in the present state of development, only one laser has been used (the photolysis laser). In this case, it is possible to detect more than one metal at a time. Using the modified volatilization device above, a direct approach may be suitable for solid and semisolid samples of clinical, biological or agricultural origin. However, samples of metallurgical or geological origin

will have to be digested prior to quantitative chelation. Liquid solutions can also be directly chelated (provided of course that hfa is not the ligand of choice). In all cases, whether the original sample is in a solid or liquid solution form, chelation should occur off-line, accelerated by microwave radiation. In addition, the reaction vessel should be preleached with ligand prior to chelation.

To make the transition from sample preparation to sample introduction time efficient, flow injection methodology should be eventually implemented. As suggested by Tyson, this methodology could be used to synthesize and then volatilize metal derivatives into a spectrometer (83).

Since the introduction of minute amounts of generated chelate vapor into a low pressure atomization cell poses an experimental challenge for LP-AFS, is it possible to operate this atomization cell under atmospheric or high pressure conditions? Laser-excited atomic fluorescence is traditionally performed in an atomization cell operating under conditions of atmospheric pressure. For example, Winefordner et al. successfully analyzed wheat flour, spinach and steel for Al, Mn and Cu using a graphite furnace atomization cell under conditions of atmospheric pressure (84). It should be noted that, in this report, the authors attempted to use a low pressure (25 torr) atmosphere without much success because the expected improvement in quantum efficiency was not realized due to the decreased residence time of the atoms in the spectroscopic interrogation region and the low duty factor of the pulsed laser used. However, it is speculated that a low-pressure atmosphere for LP-AFS is unavoidable. The advantages that accrue from using an ArF laser to photolyze the parent metal complex under conditions of low pressure currently far outweigh the disadvantages. An ArF laser as the photolysis source under conditions of atmospheric or high pressure could potentially result in spectral congestion and severe buildup of photolysis products on the vacuum chamber windows which would seriously limit the sensitivity of LP-AFS.

To improve sensitivity, use of an array detector spectrograph equipped with a highly

sensitive detector (e.g., a charge-coupled device (CCD)), rather than a scanning spectrometer, would be preferable. The use of such a rapid detection apparatus would permit multielement analysis, effectively deal with the transient nature of the sample being interrogated, and make it possible to perform two-laser pump and probe experiments in a reasonable time frame. The disadvantages of conventional PMT detectors include a low quantum efficiency (~20%), an inherent limitation of sequential signal monitoring, adverse sensitivity to ambient light (necessitating operating in complete darkness) and are limited by dark current shot noise. These limitations can potentially be overcome using CCD detectors.

Although measures were taken to significantly reduce the buildup of photolysis products on the vacuum chamber windows through which the laser beams passed, this is still an area of concern, particularly when dealing with volatile metal complexes (as opposed to pure organic samples). If a diode array spectrograph equipped with a CCD detector is implemented in instrumentation, this problem will be somewhat circumvented, a consequence of the reduced analysis time.

To conclude, there are two options for the further development of LP-AFS:

- (1) Continue to pursue LP-AFS as a trace metal analysis method, implementing some or all of the suggestions discussed above. The results of the work described in this dissertation suggest that confronting the surmountable limitations may result in LP-AFS becoming a recognizable acronym rather than a novel laboratory oddity.
- (2) Pursue LP-AFS (without the chelation step) as a diagnostic tool for the detection of metal atoms from minute amounts of hazardous or difficult-to-detect vapor phase organometallics in ambient air.

LIST OF REFERENCES

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- (1) V. Sychra, V. Svoboda and I. Rubeska, "Atomic Fluorescence Spectroscopy," Van Nostrand Reinhold, London, 1975.
- (2) J.D. Winefordner, J. Chem. Ed., 55, 72 (1978).
- (3) G.M. Hieftje, J. Chem. Ed., 59, 900 (1982).
- (4) C.B. Moore, ed., "Chemical and Biochemical Applications of Lasers," Academic Press, New York, vol.5, 1980.
- (5) J.C. Van Loon, Anal. Chem., 53, 332A (1981).
- (6) J.A. Holcombe and D.C. Hassell, Anal. Chem., 62, 169R (1990).
- (7) B.W. Smith, J.B. Womack, N. Omenetto and J.D. Winefordner, Appl. Spectrosc., 43, 873 (1989).
- (8) J.D. Winefordner, Appl. Spectrosc. Rev., 7, 147 (1973).
- (9) D.S. Gough and J.R. Meldrum, Anal. Chem., 52, 642 (1980).
- (10) N. Omenetto, B.W. Smith and J.D. Winefordner, Spectrochim. Acta., 43B, 1111 (1988).
- (11) E.L. Wehry, R. Hohmann, J.K. Gates, L.F. Guilbault, P.M. Johnson, J.S. Schendel and D.A. Radspinner, Appl. Opt., 26, 3559 (1987).
- (12) N. Mikami, R. Ohki and H. Kido, Chem. Phys., 141, 431 (1990).
- (13) J.A. Welch, K.S. Peters and V. Vaida, J. Phys. Chem., 86, 1941 (1982).
- (14) A. Gedanken, M.B. Robin and N.A. Kuebler, J. Phys. Chem., 86, 4096 (1982).
- (15) T.M. Mayer, G.J. Fisanick and T.S. Eichelberger, J. Appl. Phys., 53, 8462 (1982).

- (16) G.J. Fisanick, A. Gedanken, T.S. Eichelberger, N.A. Kuebler and M.B. Robin, J. Chem. Phys., 75, 5215 (1981).
- (17) J.B. Morris and M.V. Johnston, J. Phys. Chem., 89, 5399 (1985).
- (18) R.L. Whetten, K. Fu and E.R. Grant, J. Chem. Phys., 79, 4899 (1983).
- (19) G.W. Tyndall and R.L. Jackson, J. Am. Chem. Soc., 109, 582 (1987).
- (20) E. Weitz, J. Phys. Chem., 91, 3945 (1987).
- (21) I.M. Waller, H.F. Davis and J.W. Hapburn, J. Phys. Chem., 91, 506 (1987).
- (22) D.P. Gerrity, L.J. Rothberg and V. Vaida, Chem. Phys. Lett., 74, 1 (1980).
- (23) G.W. Tyndall and R.L. Jackson, J. Chem. Phys., 89, 1364 (1988).
- (24) G.W. Tyndall, C.E. Larson and R. L. Jackson, J. Phys. Chem., 93, 5508 (1989).
- (25) D.P. Gerrity, L.J. Rothberg and V. Vaida, J. Phys. Chem., 87, 2222 (1983).
- (26) B. Samoriski, J.M. Hossenlopp, D. Rooney and J. Chaiken, J. Chem. Phys., 85, 3326 (1986).
- (27) P.C. Engelking, Chem. Phys. Lett., 74, 207 (1980).
- (28) J.J. BelBruno, P.H. Kobsa, R.T. Carl and R.P. Hughes, J. Phys. Chem., 91, 6168 (1987).
- (29) Z. Karny, R. Naaman and R.N. Zare, Chem. Phys., 59, 33 (1978).
- (30) M.A. Duncan, T.G. Dietz and R.E. Smalley, Chem. Phys., 44, 415 (1979).
- (31) J.M. Hossenlopp, B. Samoriski, D. Rooney and J. Chaiken, J. Chem. Phys., 85, 3331 (1986).
- (32) J.J. BelBruno, Chem. Phys. Lett., 160, 267 (1989).

- (33) J.A. Welch, V. Vaida and G.L. Geoffroy, J. Phys. Chem., 87, 3635 (1983).
- (34) L.J. Rothberg, D.P. Gerrity and V. Vaida, J. Chem. Phys., 74, 2218 (1981).
- (35) Y. Nagano, Y. Achiba and K. Kimura, J. Chem. Phys., 84, 1963 (1986).
- (36) S. Leutwyler, U. Even and J. Jortner, Chem. Phys., 58, 409 (1981).
- (37) S. Leutwyler, U. Even and J. Jortner, J. Phys. Chem., 85, 3026 (1981).
- (38) H.T. Liou, Y. Ono, P.C. Engelking and J.T. Moseley, J. Phys. Chem., 90, 2888 (1986).
- (39) N. Mikami, R. Ohki and H. Kido, Chem. Phys., 127, 161 (1988).
- (40) E.E. Marinero and C.R. Jones, J. Chem. Phys., 82, 1608 (1985).
- (41) R.C. Oldenborg and S.L. Baughcum, Anal. Chem., 58, 1430 (1986).
- (42) R.C. Mehrotra, R. Bohra and D.P. Gaur, "Metal Beta-diketonates and Allied Derivatives," Academic Press, New York, 1978.
- (43) M.A.V. Ribeiro da Silva and M.L.C.C.H. Ferrao, Pure Appl. Chem., 60, 1225 (1988).
- (44) B.G. Schultz and E.M. Larsen, J. Am. Chem. Soc., 71, 3250 (1949).
- (45) R.L. Belford, A.E. Martell and M. Calvin, J. Inorg. Nucl. Chem., 2, 11 (1956).
- (46) R.W. Moshier and R.E. Sievers, "Gas Chromatography of Metal Chelates," Pergamon Press, London, 1965.
- (47) T. Gosink, Anal. Chem., 47, 165 (1975).
- (48) K. Utsunomiya, Bull. Chem. Soc. Jpn., 44, 2688 (1971).
- (49) K.W.M. Siu, M.E. Bednas and S.S. Berman, Anal. Chem., 55, 473 (1983).

- (50) J.C. Hansen, W.G. Scribner, W. Gilbert and R.E. Sievers, *Anal. Chem.*, 43, 249 (1971).
- (51) W.R. Wolf, M.L. Taylor, B.M. Hughes, T.O. Tiernan and R.E. Sievers, *Anal. Chem.*, 44, 616 (1972).
- (52) K.H. Hellmuth and H. Mirzai, *Fresenius' Z. Anal. Chem.*, 321, 49 (1985).
- (53) K.H. Hellmuth, *Fresenius' Z. Anal. Chem.*, 321, 131 (1985).
- (54) M.L. Taylor, E.L. Arnold and R.E. Sievers, *Anal. Lett.*, 1, 735 (1968).
- (55) P.C. Uden and D.C. Henderson, *Analyst*, 102, 889 (1977).
- (56) M.S. Black, M.B. Thomas and R.F. Browner, *Anal. Chem.*, 53, 2224 (1981).
- (57) J.R. Castillo, J.M. Mir and C. Bendicho, *Fresenius' Z. Anal. Chem.*, 328, 328 (1987).
- (58) T. Fujinaga, T. Kuwamoto, K. Isshiki and N. Matsubara, *Spectrochim. Acta.*, 38B, 1011 (1983).
- (59) F. Buhl and W. Galas, *Fresenius' Z. Anal. Chem.*, 332, 366 (1988).
- (60) C.I. Measures and J.M. Edmond, *Anal. Chem.*, 58, 2065 (1986).
- (61) J.R. Castillo, J.M. Mir, C. Bendicho and F. Laborda, *Fresenius' Z. Anal. Chem.*, 332, 37 (1988).
- (62) L.C. Rando and E.M. Heithmar, *Spectrosc. Lett.*, 16, 95 (1983).
- (63) M.S. Black and R.F. Browner, *Anal. Chem.*, 53, 249 (1981).
- (64) J.S. Schendel, Ph.D. Dissertation, University of Tennessee, 1987; J.S. Schendel and E.L. Wehry, *Anal. Chem.*, 60, 1759 (1988).
- (65) B.W. Smith, M.R. Glick, K.N. Spears and J.D. Winefordner, *Appl. Spectrosc.*, 43, 376 (1989).
- (66) C.E. Moore, "Atomic Energy Levels," National Bureau of Standards, Washington, D.C., 1952.

- (67) R.W.B. Pearse and A.G. Gaydon, "The Identification of Molecular Spectra," Wiley, New York, N.Y., 1963.
- (68) E.W. Berg and J.J. Truemper, J. Phys. Chem., 64, 487 (1960).
- (69) M.L. Morris, R.W. Moshier and R.E. Sievers, Inorg. Syn., 9, 28 (1967).
- (70) G.K. Schweitzer, B.P. Pullen and Y.H. Fang, Anal. Chim. Acta., 43, 331 (1968).
- (71) D. Zevgolts and P. Papagiannakopoulos, J. Phys. Chem., 92, 4654 (1988).
- (72) W.F. Meggers, C.H. Corliss and B.F. Scribner, "Tables of Spectral Line Intensities, Part I", National Bureau of Standards Monograph 32, U.S. Government Printing Office, Washington, D.C., 1961.
- (73) S.C. Lee, B.J. Stanton, B.A. Eldridge, and E.L. Wehry, Anal. Chem., 64, 268 (1992).
- (74) M.A. Bolshov, A.V. Zybin, L.A. Zybina, V.G. Koloshnikov and I.A. Majorov, Spectrochim. Acta., 31B, 493 (1976).
- (75) W.R. Walker and N.C. Li, J. Inorg. Nucl. Chem., 27, 2255 (1965).
- (76) R.W. Taft, Jr. and E.H. Cook, J. Am. Chem. Soc., 81, 46 (1959).
- (77) K. Inaba, N. Itoh, Y. Matsuno and T. Sekine, Bull. Chem. Soc. Jpn., 58, 2176 (1985).
- (78) G. Nickless, J. Chromatogr., 313, 129 (1985).
- (79) S.K. Aggarwal, M. Kinter, M.R. Wills, J. Savory and D.A. Herold, Anal. Chem., 61, 1099 (1989).
- (80) E.R. Denoyer, K.J. Fredeen and J.W. Hager, Anal. Chem., 63, 445A (1991).
- (81) J.R. Castillo, J.M. Mir and C. Bendicho, J. Anal. At. Spectrom., 4, 105 (1989).
- (82) W.D. Ross and R.E. Sievers, Anal. Chem., 41, 1109 (1969).

- (83) S.A. Darke, T.J. Gluodenis and J.F. Tyson, *Spectroscopy*, 7 (8), 28 (1992).
- (84) D. Goforth and J.D. Winefordner, *Anal. Chem.*, 58, 2598 (1986).

VITA

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