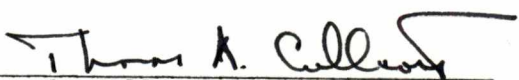


To the Graduate Council:

I am submitting herewith a dissertation written by Daniel W. Beekman entitled "Development of Time-of-Flight Mass Spectrometer with Laser Microprobe and Multiphoton Resonance Ionization." 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 Physics.


Thomas A. Callcott, Major Professor

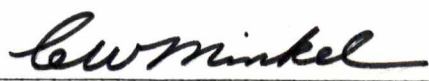
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The Graduate School

DEVELOPMENT OF TIME-OF-FLIGHT MASS SPECTROMETER WITH LASER
MICROPROBE AND MULTIPHOTON RESONANCE IONIZATION

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Daniel W. Beekman

December 1983

DEDICATION

I dedicate this volume to my parents, who assumed the existence of this document many years ago, and whose unending faith, encouragement, and support eventually made that a good assumption.

ACKNOWLEDGMENTS

I would like to express my sincere gratitude to Dr. Tom Callcott for his guidance and for the benefit of his wisdom and experience in solving innumerable experimental and theoretical problems; to Dr. Ed Arakawa for his assistance and support at Oak Ridge National Laboratory; to Dr. Jack Young for providing samples and sage advice; to a host of graduate student colleagues for fellowship and empathy throughout the years; to those in the carpool who endured accounts of my trials and tribulations on a daily basis; and especially to all those friends who supplied the human perspective which allowed the retention of some degree of normalcy.

The contributions of Elisabeth Farshing will be properly acknowledged elsewhere.

ABSTRACT

We have designed and assembled a Resonance Ionization Mass Spectrometry (RIMS) system which includes a Nd:YAG laser microprobe, laser-induced multiphoton resonance ionization, a time-of-flight (TOF) mass spectrometer, and a novel data acquisition system. The laser microprobe allows the analysis of any solid sample with a minimum of sample preparation, and requires only a small amount of material (~ 100 μg per pulse). The ionization technique is based on Resonance Ionization Spectroscopy (RIS). This method uses photons from a tuneable dye laser to resonantly excite atoms of a single element from the ground state to an intermediate state. The excited atoms are then ionized by other photons from the same dye laser pulse. Using RIS, one can selectively ionize atoms of one element in the presence of many other elements. The chemical selectivity of RIS coupled with mass analysis provides an effective technique for isotopic analysis without interference from other elements having isotopes of the same mass. The TOF mass spectrometer allows the measurement of each isotope for every pulse of the ionizing laser system. The data acquisition system digitizes each mass peak individually for computer analysis.

Here we have described the RIMS system in detail and have reviewed the theory of laser vaporization, RIS, TOF mass spectrometry, and also isotope shifts, since these were found to be important. Using the RIMS system, we have measured the relative population of

ground levels and the velocity distribution for Sm atoms vaporized by the laser microprobe to determine the excitation and kinetic temperatures, respectively. The excitation temperature was slightly greater, and this is explained by reference to a theoretical model. The selectivity of the RIMS system is demonstrated by experiments with Cr in steel and with a Nd-Sm alloy. The importance of isotope shifts in isotope ratio measurements is shown for Nd and Sm.

Finally, we have discussed conclusions based on this work and have suggested future investigations and possible modifications to the current RIMS system.

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LIST OF SYMBOLS

<u>Symbol</u>	<u>Definition</u>	<u>Numerical Value</u>	<u>First Used</u>
a	nuclear radius		p. 31
a_0	Bohr radius	5.3×10^{-9} cm	p. 94
c	speed of light	3×10^{10} cm/s	
$-e$	charge of electron	1.602×10^{-19} C	
$f(v)$	Maxwell speed distribution function		Eq. (2-2), p. 9
$f'(V)$			Eq. (2-4), p. 10
$g(t)$			Eq. (2-3), p. 10
$g'(t,u)$			Eq. (2-5), p. 11
g	statistical weight or or degeneracy	$2J+1$	p. 14
g'	effective degeneracy		p. 16
h	Planck's constant	6.625×10^{-27} erg-s	p. 9
$\hbar$	$h/2\pi$		
$\hbar\omega$	energy of photon		
k	Boltzmann constant	8.6164×10^{-5} eV/K	p. 9
λ_0	distance for speed distribution function	s	p. 10
$\Delta\lambda$	radius of ionization region		p. 10
m	mass		
m_J	magnetic quantum number		p. 16
n	refractive index of air		p. 89

<u>Symbol</u>	<u>Definition</u>	<u>Numerical Value</u>	<u>First Used</u>
$\vec{p}_i$	momentum of ith electron		p. 29
q	charge		
$\langle r^2 \rangle$	mean square radius of nucleus		p. 31
s	TOFMS dimension		Fig. 2-4, p. 22
s_0	TOFMS dimension		p. 25
t	time		
u	hydrodynamic velocity		p. 10
v	thermal velocity		p. 9
A_i	mass number of isotope i		p. 31
A,B,D	TOFMS dimensions		Fig. 2-4, p. 22; Fig. 3-3, p. 42
E	energy		
E_I	ionization energy		Fig. 1-1, p. 2
F	flux (photons $\cdot$ cm ⁻² s ⁻¹)		p. 14
I	laser intensity (W/cm ²)		p. 17
J	total angular momentum quantum number		
L	TOFMS dimension		Fig. 2-4, p. 22; Fig. 3-3, p. 42
M	nuclear mass		p. 29
N_i	relative population of electronic state i		Eq. 2-1, p. 9

<u>Symbol</u>	<u>Definition</u>	<u>Numerical Value</u>	<u>First Used</u>
N_i'	effective relative population of state i		Eq. 4-1, p. 74
R	ratio of electric fields in TOFMS		p. 24
R_0		$1.2 \times 10^{-15} \text{ m}$	p. 94
S	TOFMS dimension		Fig. 2-4, p. 22; Fig. 3-3, p. 42
T_{exc}	excitation temperature		p. 9
T_k	kinetic temperature		p. 9
U	energy		p. 23
V	total velocity	$u+v$	p. 10
V_i	voltage in TOFMS region i		p. 26
$V(r)$	electrostatic potential		p. 31
Z	atomic number		
β	rate at which excited state decays to a state other than the ground state		p. 14
ϵ	isotope shift		p. 97
ϵ_0	capacitivity of vacuum	$8.854 \times 10^{-12} \text{ V/m}$	p. 94
λ	photon wavelength		
μ	reduced mass of electron		p. 29
$\tilde{\nu}$	wavenumber	E/hc	Eq. 2-1, p. 9
ρ	electronic charge density at nucleus	$e \psi(0) ^2$	p. 93
σ	cross section		p. 14

<u>Symbol</u>	<u>Definition</u>	<u>Numerical Value</u>	<u>First Used</u>
τ	laser pulse duration		p. 17
τ_i	contribution to time speed of mass peaks due to source i		p. 25
ϕ	fluence (photons/cm ²)		p. 14
$\phi\sigma$	transition probability		p. 72
$\psi(r)$	radial wavefunction of electron		p. 31
ω	photon frequency		

CHAPTER I

INTRODUCTION

A. PREVIOUS WORK

Resonance Ionization Spectroscopy (RIS) is a method of selectively ionizing atoms of a single element which are initially in a particular energy level. Such atoms are resonantly excited by photons from a pulsed laser which is tuned to a transition from the particular initial level to an intermediate level. Atoms excited to the intermediate level are then ionized by photons from the same laser pulse. This is shown schematically in Figure 1-1.

Hurst and his colleagues were the first to use saturated resonance ionization ($\sim 100\%$ ionization probability) to determine the absolute population of a selected energy level [1.1] and also the first to detect a single atom surrounded by large numbers of other types of atoms [1.2]. RIS has been reviewed by Hurst et al. [1.3].

Early work using unsaturated resonance ionization was done by Ambartsumyan et al. [1.4], Stebbings et al. [1.5], and others [1.6-8]. Bibliographies concerning resonance ionization applied to isotope separation were published by Farrar and Smith [1.9] and by Smith [1.10].

Soon after the development of RIS, investigators recognized the advantages of combining the elemental selectivity of RIS with mass spectrometry. The first such experiment was done by Tuccio et

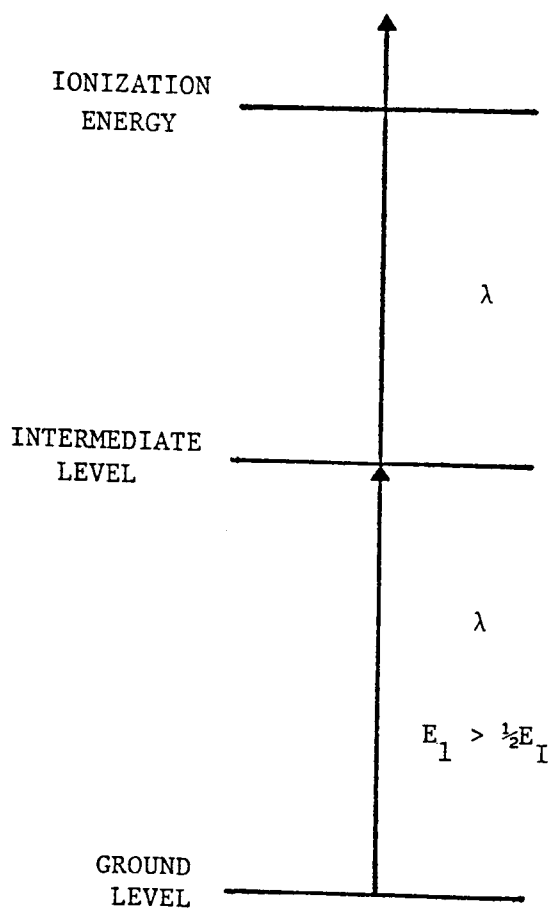


Figure 1-1. Schematic of the RIS Process. Here λ is the Wavelength of the Laser Photons, E is the Photon Energy, and E_I is the Ionization Energy.

al. [1.11] to monitor the laser isotope separation of uranium. Much of the subsequent work has been done with molecules.

Recently, several groups have used Resonance Ionization Mass Spectrometry (RIMS) for the analysis of elemental species [1.12,13]. The lanthanide and actinide series of elements present an analytical problem for which RIMS is especially appropriate, since these elements are difficult to separate by standard chemical processes, and there are several instances of isobaric interference (isotopes of the same mass for two different elements). Thus standard mass spectrometry, using nonselective ionization, produces ambiguous results for the isotopic analysis of samples containing these elements. Unambiguous isotopic analyses of lanthanides and actinides have recently been reported by Donohue and Young [1.15,16] and Miller et al. [1.17]. Previous work on atomic properties of lanthanides and actinides using RIMS has been reviewed by Worden and Conway [1.18].

Mass spectrometric analysis of solids requires that the sample be vaporized and ionized. Localized analysis of small portions of the sample can be accomplished by microprobe techniques such as bombardment by focussed beams of ions, electrons, or radiation. In each case, the ions to be analyzed can be those produced in the vaporization process or those produced by auxiliary ionization of vaporized neutral atoms.

The first use of a laser microprobe for mass analysis of solids was by Honig and Woolston [1.19] in 1963. For a review of laser microprobe mass spectrometry, see Ref. [1.20]. The fundamental

mechanisms of laser beam interactions with solids are reviewed in Ref. [1.21].

B. SCOPE OF THIS WORK

This work describes the construction of an RIMS system for the analysis of solid samples and the investigation of some basic physical processes involved in the operation of the instrument. The goal is to evaluate the current design and to suggest modifications and improvements based on the information obtained with this system. The eventual applications of RIMS systems will be the analysis of trace elements in environmental samples and the measurement of isotope ratios for samples containing isobars, such as the lanthanide and actinide elements. Another interesting application is radioisotope dating, which is accomplished by measuring the abundance of a radioactive isotope relative to that of a stable isotope of the same element, using, e.g., ^{10}Be , ^{14}C , ^{26}Al , ^{36}Cl , or ^{129}I . Thus in a carbon-14 dating measurement the background due to ^{14}N would be eliminated by the RIS technique.

For this project we have assembled the system shown in Figure 1-2. The vaporizing laser pulse is used to vaporize a small portion of the solid sample; then atoms of a single element are selectively ionized by the RIS technique. The resulting ions are analyzed by the time-of-flight mass spectrometer, and the signal is digitized for computer processing.

In the following chapter we discuss the theory of the laser vaporization process, RIS, time-of-flight mass spectrometry, and

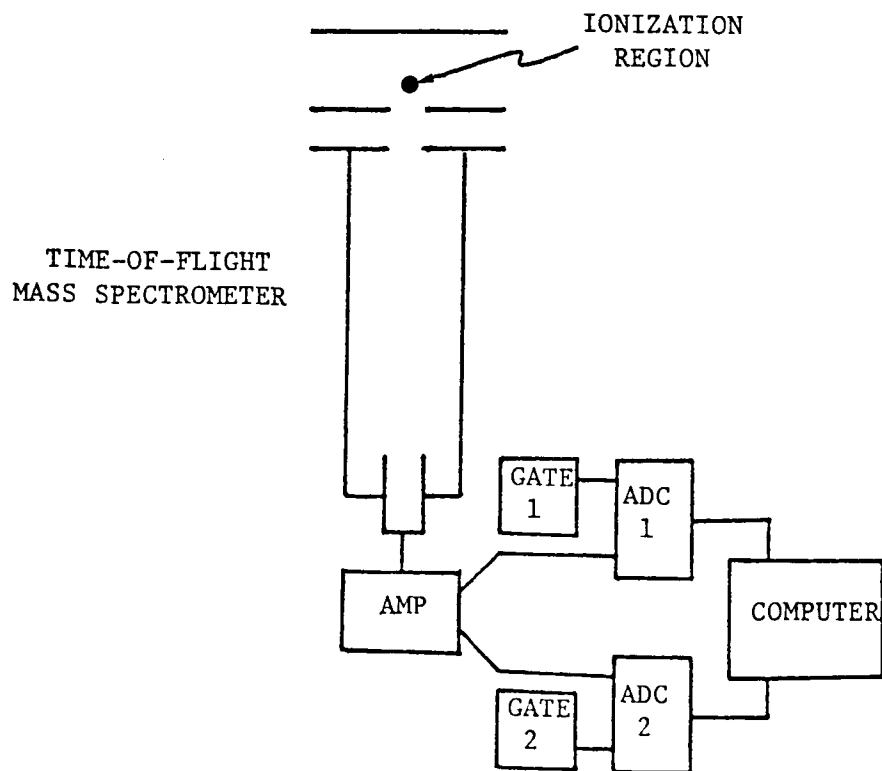
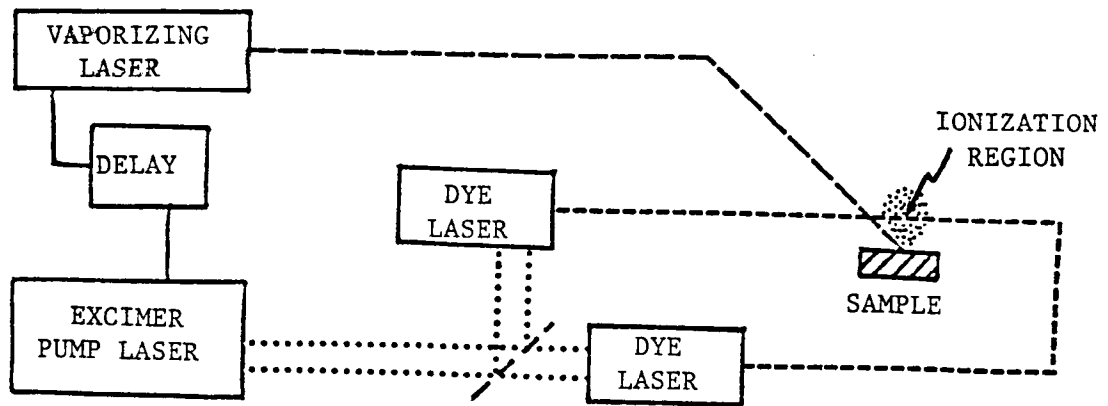


Figure 1-2. Simplified Schematic of the RIMS System. a) Laser Layout; b) TOFMS and Data Acquisition Electronics.

also isotope shifts of atomic transitions, since these shifts have been found to affect the results of our experiments.

The RIMS system is described in detail in Chapter III, which includes the specifications of components, the parameters used during experiments, and a general procedure for operating the system.

In Chapter IV we describe the experiments we performed using the RIMS system. To obtain information on the laser vaporization process, we measured the temperature of the vapor cloud by two different methods. As a demonstration of the selectivity possible with the RIS technique, we obtained the mass spectrum of Cr from a sample of steel, and we used a 1:1 alloy of Nd and Sm to obtain the mass spectrum of each element separately. Finally, we investigated isotope shifts in Nd and Sm transitions and determined the effect of these shifts on isotope ratio measurements.

The last chapter summarizes the results of the experiments and discusses the implications for the design and operation of the RIMS system. Some suggestions for future investigations are also given.

CHAPTER II

THEORY

A. INTRODUCTION

In this chapter, we discuss separately the four topics fundamental to this project—laser vaporization, resonance ionization spectroscopy (RIS), time-of-flight mass spectroscopy (TOFMS), and isotope shifts.

Section B considers the vaporization of solids by high-intensity laser pulses. Two basic mechanisms are possible, depending upon laser intensity and material properties. The temperature of the vapor cloud is given as the kinetic temperature, defined in terms of electron, ion, or neutral atom kinetic energies, or the excitation temperature, defined by the population distribution of atomic states.

The next section describes the general theory of RIS. Flux and fluence conditions necessary for saturation of the RIS process are discussed, along with the requirements these conditions place on the laser beam parameters.

Section D concerns TOFMS. Equations for the time-of-flight and mass resolutions are derived, and special considerations due to laser ionization are discussed.

The final section discusses the theory of isotope shifts in spectral lines and the implications for RIS.

B. LASER VAPORIZATION

As a laser beam strikes a solid surface, the energy is absorbed by conduction electrons and quickly transferred to the lattice. The specific processes involved in producing the vaporized species depend on the magnitude of the laser power density and the value of certain properties of the solid, including heat conductivity, heat capacity, heat of vaporization, and the temperature and pressure of the thermodynamic critical point [2.1,2].

For large laser power densities ($>10^9$ W/cm² [2.3]), the recoil of vaporized surface material creates a shock wave which propagates through the solid, melting and vaporizing the material as it passes. Above some threshold power density, the shock wave will increase the pressure and temperature of the sample material beyond the critical point, at which there is no longer a distinction between liquid and vapor. Vaporization then takes place as explosive expansion of the highly compressed, highly ionized plasma [2.1,2]. The plasma itself can absorb the laser radiation directly, producing multiply ionized atoms and net ionization up to 100%.

For lower power densities, the heated material forms a nearly transparent vapor. Net ionization is low since the thermal energy is much less than ionization energies, and the recombination rate is high at these temperatures [2.2].

The plasma temperature can be given as either the excitation temperature or various kinetic temperatures. The excitation temperature

T_{exc} is defined in terms of the population distribution of electronic states by

$$\frac{N_m}{N_n} = \frac{g_m}{g_n} \exp \left[- \frac{(E_m - E_n)}{kT_{\text{exc}}} \right]$$

or

$$\frac{N_m}{N_n} = \frac{g_m}{g_n} \exp \left[- \frac{hc}{k} \frac{(\tilde{\nu}_m - \tilde{\nu}_n)}{T_{\text{exc}}} \right] \quad (2-1)$$

where for energy level m , N_m is the number density, g_m is the degeneracy, E_m is the excitation energy, and $\tilde{\nu}_m = E_m/hc$; h is Planck's constant, c is the speed of light, k is the Boltzmann constant, and T_{exc} is the excitation temperature.

The kinetic temperatures T_k are defined in terms of the kinetic energy of the electrons, ions, or neutral atoms by the Maxwell speed distribution function:

$$f(v)dv = \left(\frac{m}{2\pi kT_k} \right)^{3/2} \exp \left[- \frac{mv^2}{2kT_k} \right] 4\pi v^2 dv$$

or

$$f(v)dv = \frac{4}{\sqrt{\pi}} \exp \left[- \frac{v^2}{v_0^2} \right] \frac{v^2 dv}{v_0^3} \quad (2-2)$$

where v_0 is the most probable speed, given by $v_0 = \left(\frac{2kT_k}{m} \right)^{1/2}$ and m is the mass of the appropriate particle.

Other forms of this equation are required for various experimental conditions [2.4,5]. For experiments in which the source

produces a constant flux of atoms, the distribution of velocities is proportional to $vf(v)$ [2.6]. Similarly, for experiments which measure the rate at which atoms arrive at a particular point in space, the response of the detector will require an additional factor of v .

The experiment described in Chapter IV, Section C, uses pulsed laser vaporization as the source of atoms. Thus the atoms are created in a time much less than the measured drift time for the distance ℓ_0 (7 ns vs. 20-200 μ s, respectively). The detector measures the relative number of atoms contained within the range ℓ_0 to $\ell_0 + \Delta\ell$. Thus we use Eq. (2-2) with no additional factors of v , then substitute $v = \ell/t$ and integrate to obtain

$$g(t) = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2kT_k} \right)^{3/2} \int_{\ell_0}^{\ell_0 + \Delta\ell} \exp \left[- \frac{m}{2kT_k} \frac{\ell^2}{t^2} \right] \frac{\ell^2 d\ell}{t^3}. \quad (2-3)$$

Peugnet has considered the expansion of compressed, vaporized material into a vacuum [2.4]. The hydrodynamic expansion velocity u is then superimposed upon the thermal velocity, but it is assumed that the system is not in equilibrium since the vapor expands radially and the atoms suffer few collisions. Then the expansion energy does not affect the exponential factor in the distribution function, which becomes

$$f'(V)dV = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2kT_k} \right)^{3/2} \exp \left[- \frac{m(V - u)^2}{2kT_k} \right] V^2 dV \quad (2-4)$$

where V is the total velocity and $V - u$ is the thermal velocity.

Using $V = \ell/t$ and integrating over ℓ , we obtain

$$g'(t, u) = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2kT_k} \right)^{3/2} \int_{\ell_0}^{\ell_0 + \Delta \ell} \exp \left[- \frac{m}{2kT_k} \left(\frac{\ell}{t} - u \right)^2 \right] \frac{\ell^2 d\ell}{t^3} . \quad (2-5)$$

The integrals of Eqs. (2-3) and (2-5) cannot be solved analytically.

Equation (2-5) will be numerically evaluated in Chapter IV for the experimental values of t , since it refers to the general case. If $u = 0$, Eq. (2-5) reduces to Eq. (2-3).

In the initial stages of the plasma, the density, electron temperature, and degree of ionization are all very high, so there are many collisions between the atoms, ions, and electrons. The characteristic time for transfer of energy from electrons to ions is short, and an equilibrium is quickly established among the various measures of temperature [2.7].

As the plasma expands and cools, the electron-ion recombination rate becomes larger than the excitation and ionization rates. For laser-produced plasmas, the main recombination process is three-body collision, in which an electron is captured into an upper atomic level and another electron absorbs the energy released [2.8]. De-excitation from the upper atomic levels occurs mainly through additional electron collisions, releasing more energy to the electron gas. This energy is distributed in collisions with atoms and ions. Transitions into the lower atomic levels occur by radiative de-excitation, and most of this energy is lost from the plasma.

If the recombination rate is high compared to the expansion rate of the plasma, most electrons and ions will recombine and the electron-ion energy transfer rate will be small. Then the subsequent recombination energy will be shared by the few remaining electrons and the electron temperature will fall more slowly than the ion and atom temperatures [2.9]. The excitation temperature is normally close to the electron temperature, since the electron energy is efficiently distributed in collisions between free electrons and bound electrons.

The relative values of the atom, ion, and excitation temperatures will depend on the excitation, ionization, recombination, and plasma excitation rates. Also, Numano [2.10,11] has calculated the dependence of the excitation temperature on the ratio of the characteristic times for impact ionization and electron density variation. If this ratio is near unity, the excitation temperature can be significantly different from the electron kinetic temperature.

C. RESONANCE IONIZATION SPECTROSCOPY

The RIS scheme discussed in Chapter I and shown in Figure 1-1 (page 2) is the simplest of several possible RIS schemes. In their review article, Hurst et al. [2.12] describe five basic types of RIS schemes, as shown in Figure 2-1. The schemes are numbered in order of increasing complexity, with the scheme required for each element determined by ionization energy, the energy of the first excited state, and the selection rules for transitions from the ground state to the appropriate excited state.

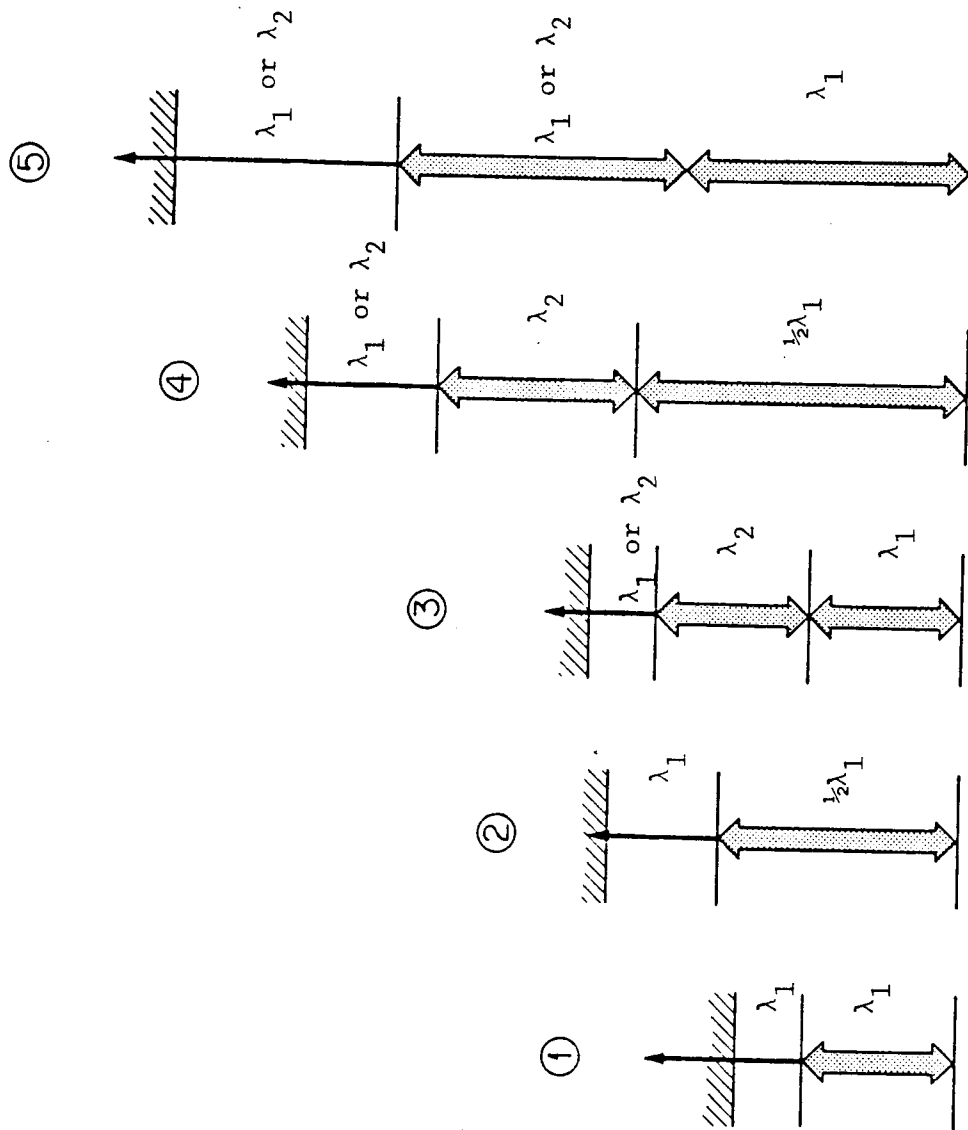


Figure 2-1. Classification of RIS Schemes. Here λ Refers to the Fundamental Wavelength of the Laser Photons, and $1/2 \lambda$ to the Frequency Doubled Wavelength. Figure Adapted from Ref. [2.12].

Using commercially available lasers, all elements except helium and neon may be ionized by the five RIS schemes of Figure 2-1.

Figure 2-2 gives a possible scheme for each element, showing chemical symbol, ionization energy, first excited state, and second excited state (when required), with the scheme designation circled in the center.

For analytical applications, it is often necessary to saturate the RIS process, i.e., to obtain all atoms of the selected type which are intercepted by the laser beam. Using rate equations, Hurst et al. [2.12] have derived a flux condition and a fluence condition that must be met for saturation to occur. Defining:

F = flux = number of photons $\text{cm}^{-2} \text{s}^{-1}$

σ_I = cross section for photoionization from the excited state

β = rate at which the excited state decays to a state other than the ground state

we have for the flux condition

$$\sigma_I F \gg \beta . \quad (2-6)$$

Defining:

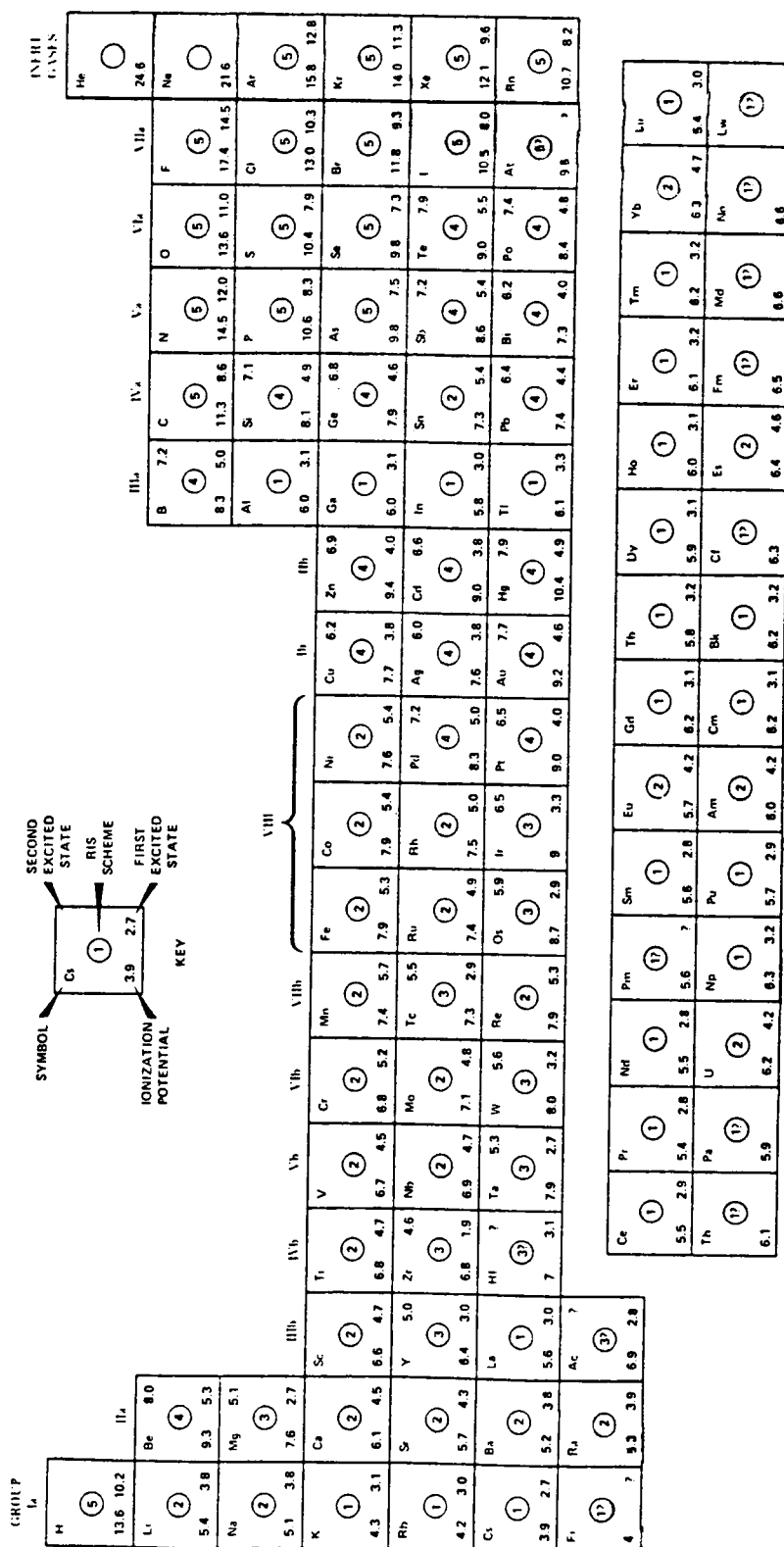
ϕ = fluence = number of photons cm^{-2}

g_i = statistical weight of state i

we have for the fluence condition

$$\left(\frac{g_2}{g_1 + g_2} \right) \phi \sigma_I \gg 1 \quad (2-7)$$

where g_1 refers to the ground state and g_2 to the excited state.



In practice, it is difficult to saturate the RIS process throughout the laser beam, since the intensity normally decreases smoothly at the beam edge. Then the ionization will be saturated in some region of the beam, while regions with lower intensity will have ionization probabilities less than unity. If the beam is focussed, the saturation region will also have limited longitudinal extent on either side of the focal point.

In the above equations, the statistical weight is generally equal to $2J+1$, which is the number of possible values of m_J . However, when a linearly polarized laser is used to induce a transition, the selection rule $\Delta m_J = 0$ applies. Thus transitions only occur between like values of m_J , and the effective statistical weights, g'_i , of the two levels involved are necessarily equal, i.e., $g'_1 = g'_2 =$ smaller of g_1 and g_2 . Therefore

$$\frac{g'_2}{g'_1 + g'_2} = \frac{1}{2}$$

and Eq. (2-7) becomes

$$\frac{1}{2} \phi \sigma_I \gg 1. \quad (2-8)$$

The effective statistical weights are also important for the measurement of relative populations of atomic states, as in Chapter IV, Section D.

To develop more practical flux and fluence equations in terms of laser parameters, we define

I = laser intensity = W/cm^2

$\hbar\omega$ = energy of each laser photon

τ = duration of a square laser pulse.

Then

$$I = \hbar\omega F = \frac{\hbar\omega}{\tau} \phi$$

and the fluence condition (2-8) becomes

$$\frac{1}{2} \frac{I\tau}{\hbar\omega} \sigma_I \gg 1 \quad \text{or} \quad I \gg \frac{2\hbar\omega}{\sigma_I \tau} \quad (2-9)$$

Using $F = \phi/\tau$ and Eq. (2-8), the flux condition (2-6) then becomes

$$\sigma_I \frac{\phi}{\tau} \gg \frac{2}{\tau} \gg \beta \quad \text{or} \quad \tau \ll \frac{2}{\beta}. \quad (2-10)$$

This condition is usually met by pulse widths < 10 ns.

It should be noted that excitation cross sections, σ_{exc} , for transitions between discrete levels are much greater than photo-ionization cross sections, σ_I . Typical values are:

$$\sigma_{exc} = 10^{-13} - 10^{-14} \text{ cm}^2$$

$$\sigma_I = 10^{-17} - 10^{-18} \text{ cm}^2.$$

Thus the excitation laser beam can have much less power than the ionizing laser beam while still achieving saturation of each transition.

The cross section for n -photon nonresonant ionization from the ground state of the atom is denoted σ_n and is estimated by [2.12]:

$$\sigma_n \sim \sigma_I I^{n-1} \left[\frac{3n \times 10^{-7}}{E_1} \right]^{2(n-1)}$$

where E_1 is the energy of the first excited state, in eV. The value of n is determined by the laser wavelength and the ionization potential of the atoms present. Thus the background due to nonresonant ionization is greatest when low ionization potential elements are present, and can be reduced by using long-wavelength laser beams for the ionization step, where high intensity is required.

Another important parameter for RIS is the spectral purity of the dye laser. A dye laser beam consists of high-intensity radiation within a specified linewidth (= signal) and low-intensity broadband radiation (= noise) outside the linewidth. The signal radiation typically has a linewidth of 0.1-0.01 nm, while the noise radiation is distributed over 20-40 nm, depending on the laser dye. Spectral purity has been defined [2.13] as the percentage of signal radiation in the total output while the laser is operating normally. This value is a function of wavelength and is greatest (~99%) at the center of the tuning curve of each dye.

The spectral purity determines the degree of excitation caused by the noise radiation, which can limit the selectivity of the RIS process. Although the intensity of the noise radiation at any wavelength is small, there are, in general, a large number of atomic

transitions located within the range of a laser dye. Thus atoms of any element are resonantly excited by the broadband noise radiation, and the total number of such excited atoms can be large. These excited atoms are then ionized by the high-intensity signal radiation if the sum of the photon energies is greater than the ionization energy of that element.

The background ions created in this manner can be from atoms of an element other than the element under investigation (see Chapter IV, Section E) or can be from atoms of the same element which begin in a different initial state (see Chapter IV, Section D) or proceed to ionization through a different intermediate state.

Another source of background ions could be molecules which are resonantly or nonresonantly dissociated. The result can be atomic ions or excited atoms which are then nonresonantly ionized.

To make most efficient use of the available laser power, the linewidth of the laser beam should be on the order of the width of the state to which the transition is proceeding. For laser isotope separation processes, the laser linewidth must be much less than the isotope shift to avoid excitation of more than one isotope. Conversely, for isotope ratio measurements, the linewidth should be large enough to include the isotope shift for all isotopes of the element under investigation.

In our work, we have used RIS scheme 1 and two modifications thereof, shown in Figure 2-3, which we have designated schemes 1A and 1B. For scheme 1A, we use a low power dye laser beam for the

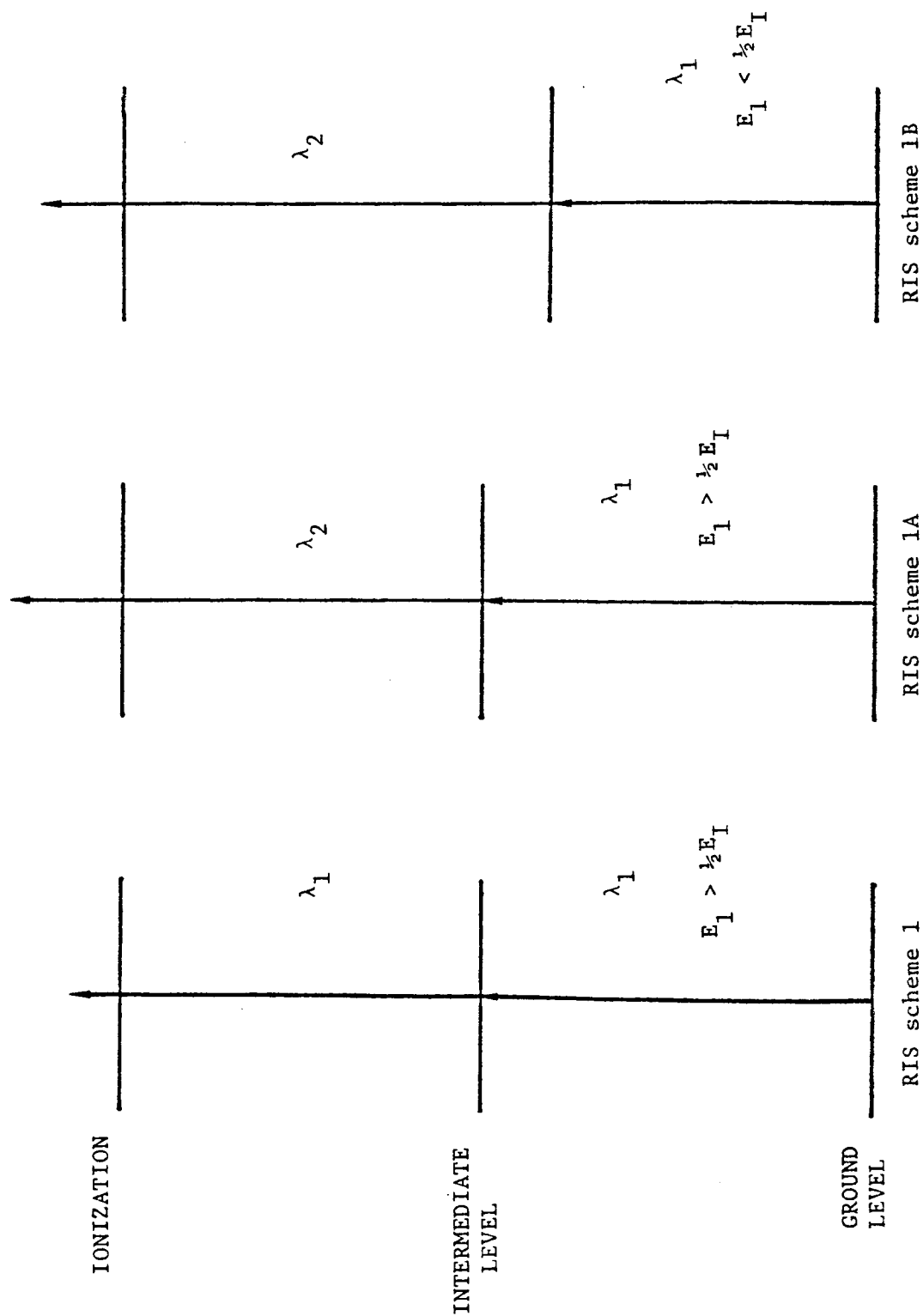


Figure 2-3. RIS Scheme 1 and Modifications Thereof, which we Designate Schemes 1A and 1B. Here λ Refers to the Wavelength of the Laser Photons, E_1 is the Energy of Photons from Laser 1, and E_I is the Ionization Energy.

excitation step and a high power dye laser beam for the ionization step. This allows independent tuning of the two wavelengths, and decreases the spectral purity requirement for the excitation laser. An experiment using RIS scheme 1A is described in Chapter IV, Section D. For scheme 1B, the first transition is to an energy level less than half of the ionization energy. Another laser provides photons of higher energy to ionize the atom from the excited state. The ionizing laser wavelength is chosen to not be resonant with any transition from the ground state. Thus each laser beam by itself is incapable of ionizing the atom, but both beams together will produce ions. This scheme can be used, for example, to measure the photoionization cross section of excited states as a function of frequency by scanning the ionizing laser wavelength while holding the excitation laser wavelength constant. Scheme 1B was used for the RIS of Cr, as described in Chapter IV, Section E.

D. TIME-OF-FLIGHT MASS SPECTROSCOPY

A schematic diagram of the time-of-flight mass spectrometer (TOFMS) is shown in Figure 2-4. The distances S , A , L , and D refer to the axial dimensions of the source, acceleration, drift, and detector regions, respectively. The ionization region is defined by the ionizing laser beam (or beams), and its center is located a distance s above the acceleration region. The depth of the first dynode of the detector is denoted ΔD , and E is the electric field, with a subscript corresponding to the appropriate region. Note that a conventional TOFMS uses a pulsed electric field in the source

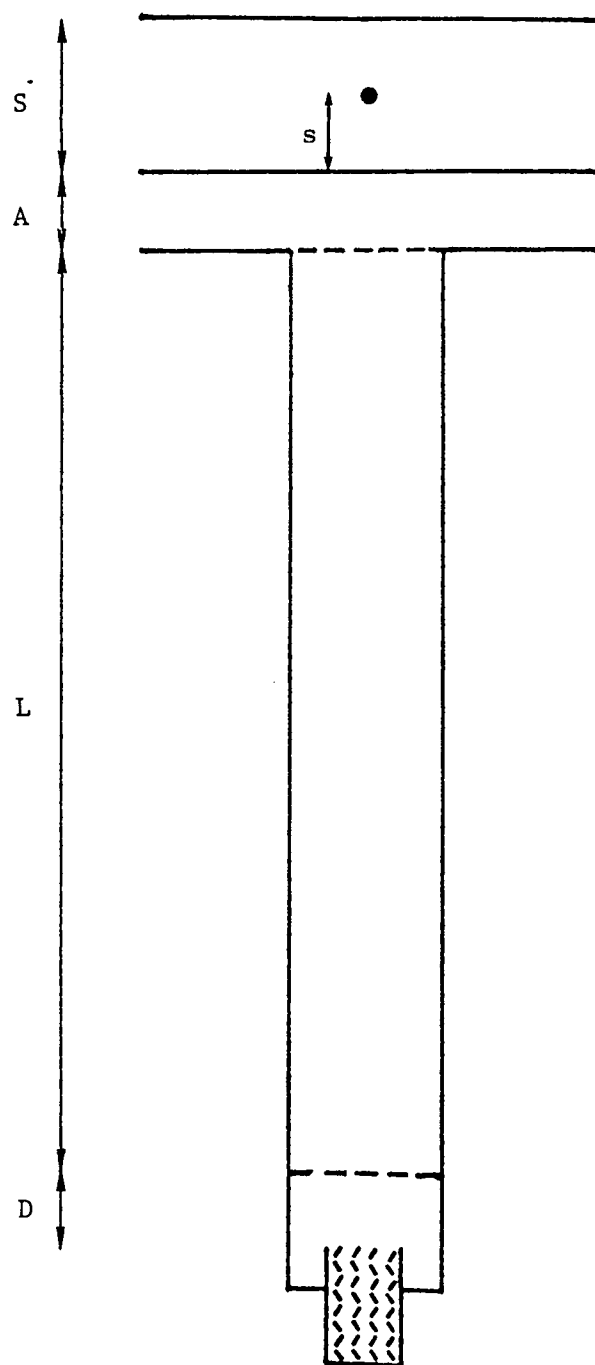


Figure 2-4. Schematic of the TOFMS.

region. In our instrument, the ions are all created during the 5 ns dye laser pulse, so the electric field E_S is held constant.

The two-stage ion acceleration system is based on the design of Wiley and McLaren [2.14]. The time-of-flight for ions of mass m and initial energy U_0 can be calculated from the equation for the motion of a body under uniform acceleration:

$$x = v_0 t + \frac{1}{2} a t^2$$

where x = distance, v_0 = initial velocity, a = acceleration, and t = time. Solving for t we get

$$t = \frac{1}{a} \left[(v_0^2 + 2xa)^{1/2} - v_0 \right] .$$

Using the notation of Figure 2-4, we have for the source region of the TOFMS:

$$x = s, \quad v_0 = \left(\frac{2U_0}{m} \right)^{1/2}, \quad a = \frac{qE_S}{m}$$

where E_S is the electric field in the source region. For the time-of-flight in the source region, we have

$$t_S = \frac{\sqrt{2m}}{qE_S} \left[U_S^{1/2} - U_0^{1/2} \right]$$

where $U_S = U_0 + sqE_S$. Similarly, for the acceleration region,

$$t_A = \frac{\sqrt{2m}}{qE_A} \left[U_A^{1/2} - U_S^{1/2} \right]$$

where $U_A = U_S + AqE_A$. In the field-free drift region,

$$t_L = \frac{x}{v_0} = L \left(\frac{2U_A}{m} \right)^{-1/2}.$$

In the final acceleration region just before the detector, we have

$$t_D = \frac{\sqrt{2m}}{qE_D} [U_D^{1/2} - U_A^{1/2}]$$

where $U_D = U_A + DqE_D$. The total time-of-flight is given by

$$t_T = t_S + t_A + t_L + t_D = \sqrt{2m} \left[\frac{1}{qE_S} (U_S^{1/2} - U_0^{1/2}) + \frac{1}{qE_A} (U_A^{1/2} - U_S^{1/2}) + \frac{L}{2} U_A^{-1/2} + \frac{1}{qE_D} (U_D^{1/2} - U_A^{1/2}) \right].$$

Setting $U_0 = 0$ and defining $R = E_A/E_S$, this becomes

$$t_T = \left(\frac{2m}{qE_S} \right)^{1/2} \left[s^{1/2} + \frac{1}{R} [(s + AR)^{1/2} - s^{1/2}] + \frac{L}{2} (s + AR)^{-1/2} + \frac{E_S}{E_D} \left[(s + AR + D \frac{E_D}{E_S})^{1/2} - (s + AR)^{1/2} \right] \right] \quad (2-11)$$

The time between mass peaks is

$$\Delta t_m = t_T(m_2) - t_T(m_1) = t_T(m_2) [1 - (m_1/m_2)^{1/2}]. \quad (2-12)$$

For large mass numbers, this is approximately

$$\frac{dt_T}{dm} = \frac{t_T}{2m}.$$

Several factors contribute to the calculated resolution of the TOFMS. The energy resolution is determined by the time spread in each mass peak caused by differences in initial energy of the ions, while spatial resolution is similarly determined by differences in initial position. Some time spread is also introduced by the geometry of the detector.

The time spread introduced by differences in initial energy can be calculated by considering two ions created at the same axial position with oppositely directed axial velocities. These two ions will arrive at the detector with a time difference, τ_U , equal to the turnaround time for the ion initially headed away from the detector. This time is equal to

$$\tau_U = \frac{2mv_0}{qE_S} = \frac{2\sqrt{2mU_0}}{qE_S}. \quad (2-13)$$

Thus we should have large E_S for good energy resolution.

Two ions with no initial axial velocity which are created at $s - \delta$ and $s + \delta$ will arrive at the detector with a time difference given by Eq. (2-11) with s replaced by $s - \delta$ and $s + \delta$. This time difference can be minimized by setting $\left(\frac{dt_T}{ds}\right)_{s_0} = 0$. Using Eq. (2-11), we have

$$\begin{aligned}
 \left(\frac{dt_T}{ds} \right)_{s_0} = & \left(\frac{m}{2qE_S} \right)^{1/2} \left[s_0^{-1/2} + \frac{1}{R} \left((s_0 + AR)^{-1/2} - s_0^{-1/2} \right) \right. \\
 & - \frac{L}{2} (s_0 + AR)^{-3/2} + \frac{E_S}{E_D} \left((s_0 + AR + D \frac{E_D}{E_S})^{-1/2} \right. \\
 & \left. \left. - (s_0 + AR)^{-1/2} \right) \right] = 0 .
 \end{aligned} \tag{2-14}$$

The above equation will be solved numerically for R in Chapter IV for particular values of s_0 , with A , L , and D given by the dimensions of the instrument, and with E_S and E_D as additional parameters. From the definition of R we have

$$R = \frac{E_A}{E_S} = \frac{V_A}{A} \frac{S}{V_S} \quad \text{or} \quad \frac{V_A}{V_S} = R \frac{A}{S} .$$

Thus for any value of s_0 we can calculate the values of R and V_A/V_S and adjust the voltages to obtain $\left(\frac{dt_T}{ds} \right)_{s_0} = 0$. However, τ_s , the contribution to the width of each mass peak, will be nonzero for an ionization region of finite size. Optimum spatial resolution is obtained by properly adjusting the voltage ratio and minimizing the axial dimension of the ionization region.

Another contribution to the width of each mass peak is due to the geometry of the venetian-blind type electron multiplier. A screen held at ground potential is located about 1 cm in front of the detector, while the front end of the detector is operated at negative high voltage, V_D . When the ions strike the first dynode, they have gained additional energy equal to qV_D . The final velocity of the ions

as they strike the detector is $v_f = (2U_D/m)^{1/2}$, and the time spread introduced by the dynode geometry is $\tau_D = \Delta D/v_f$, where ΔD is the effective depth of the first dynode of the detector.

The calculated total width of each mass peak is a convolution of τ_U , τ_S , and τ_D , but is less than or equal to the sum of the three.

The overall resolution of the instrument is given as the maximum mass for which $\tau_T < \Delta t_{\Delta m}$ where $\Delta t_{\Delta m}$ is the time between adjacent mass peaks, as given in Eq. (2-12) with $m_2 = m_1 + 1$.

The resolution can be improved by the addition of a mass reflectron [2.15,16], as shown in Figure 2-5. This device provides second-order focussing of the ions with respect to their initial energy. Two additional regions are located at the end of the field-free drift region L_1 : a deceleration (braking) region B, and a reflection region R. As the ions enter the mass reflectron, they are slowed down, then reflected at a small angle to their original flight path. Ions with initial energy slightly higher than average will travel further into the reflection region and take longer to traverse that distance. The electric fields E_B and E_R can be adjusted to re-focus the ions onto the detector at the end of a second field-free drift region L_2 .

E. ISOTOPE SHIFTS

The isotope shift of a spectral line is defined as the change in wavelength (or wavenumber) of the electronic transition for different isotopes of an element. Isotope shifts are large for the lightest elements and for the heaviest elements, but even then they are often

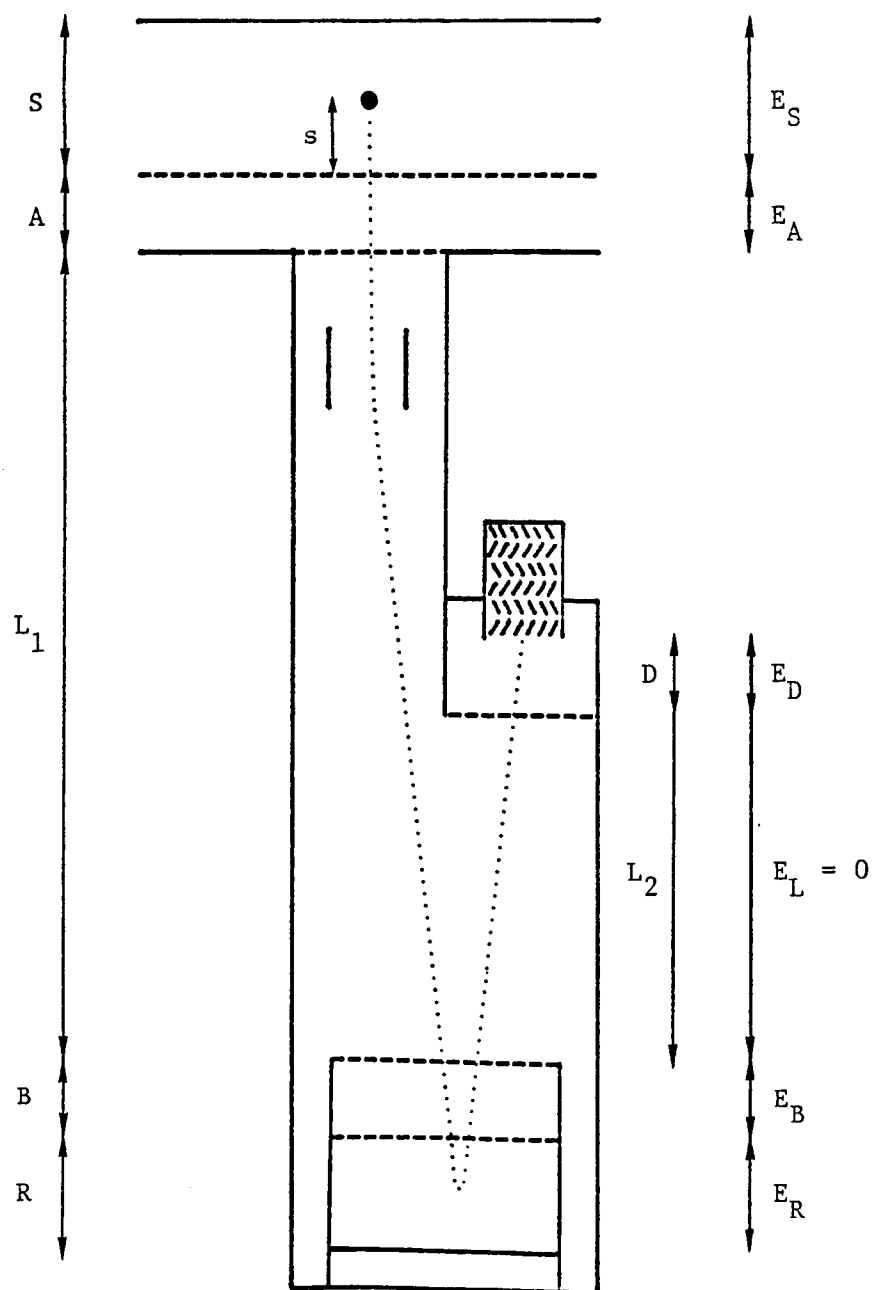


Figure 2-5. Schematic of the TOF Mass Reflectron.

masked by the width of the spectral line. The RIS process can detect the effects of isotope shifts that are larger than the combination of Doppler broadening, collision broadening, and the linewidth of the excitation laser. Chapter IV, Section E, discusses the implications of isotope shifts on isotope ratio measurements. Isotope shifts have been reviewed by Kopfermann [2.17], Stacey [2.18], and Kuhn [2.19].

We take as our reference model an atom with Z electrons moving above a point nucleus with infinite mass and charge Z_e . To allow for a nucleus of finite mass, we place the reference energy levels E_i by

$$E'_i = E_i - \frac{1}{2M} \left(\sum_i \vec{p}_i \right)^2$$

where M is the nuclear mass, $\vec{p}_i$ is the momentum of the i th electron, and the sum is over all electrons of the atom. The energy shift is due to the kinetic energy of the nucleus about the center of mass.

We can write the shift as

$$(E_i - E'_i) = \frac{1}{2M} \sum_i (p_i^2) + \frac{1}{M} \sum_{i < j} \vec{p}_i \cdot \vec{p}_j. \quad (2-15)$$

The first term is referred to as the normal mass shift, and is accounted for by replacing the electron mass m by the reduced mass $\mu = mM/(M + m)$.

An electronic transition between shifted energy levels E'_a and E'_b ($E'_a < E'_b$) for isotopes with masses M_1 and M_2 ($M_1 < M_2$) will show an isotope shift given by:

$$\begin{aligned}
 [\Delta E'_{ba}(M_2) - \Delta E'_{ba}(M_1)] &= (E_b - E_a) \left(\frac{M_2}{M_2 + m} \right) - (E_b - E_a) \left(\frac{M_1}{M_1 + m} \right) \\
 &= (E_b - E_a) \left[\frac{m(M_2 - M_1)}{(M_2 + m)(M_1 + m)} \right] \\
 &\doteq (E_b - E_a) \left[\frac{(M_2 - M_1)m}{M_2 M_1} \right] > 0 .
 \end{aligned} \tag{2-16}$$

This indicates the transition will have a slightly higher energy for the isotope of heavier mass, which is defined as a positive isotope shift. Eq. (2-16) above gives the value of the normal mass shift and indicates the mass dependence is approximately $m\Delta M/(M_1 M_2)$.

The second term of Eq. (2-15) is the specific mass shift, which is due to correlated motion of the electrons. In the classical model, if the electrons move around the nucleus in the same direction, the normal mass shift is increased. If the electrons tend to move in opposite directions, the normal mass shift is decreased. The magnitude of the specific mass shift for a transition depends on the details of the electron interactions in each level, and can be an order of magnitude larger than the corresponding normal mass shift. For many-electron atoms, however, the calculations become prohibitively complex.

For elements with $Z > 58$, both mass effects are small due to the factor $1/M$ in Eq. (2-15) and can be neglected in comparison with field shifts.

The field shift, or volume shift, is a result of the finite size of the nucleus, which reduces the electrostatic potential within the

nuclear volume in comparison with the potential due to a point nucleus. The resulting decrease in the potential energy of the electron is shown in Figure 2-6 for a uniformly charged sphere of radius a . This model will also be used for specific calculations in Chapter IV, Section F. The shift in an electronic energy level from the reference level is:

$$(E' - E)_{c,A} = \int_0^a (-e)|\psi(r)|^2 [V'_A(r) - V(r)] 4\pi r^2 dr \quad (2-17)$$

where E and E' are the reference and shifted energy levels, respectively, c denotes the valence electron configuration, A is the mass number, a is the nuclear radius, $(-e)|\psi(r)|^2$ is the electron charge density, $V(r)$ is the potential due to a point nucleus, and $V'_A(r)$ is the actual potential due to the radial charge distribution of an extended nucleus. For a given element, the energy shift depends on nuclear properties only through the mean square nuclear radius $\langle r^2 \rangle$, with heavier isotopes having larger values of $\langle r^2 \rangle$. The value of $\langle r^2 \rangle$ does not increase regularly with mass number A , but shows odd-even staggering effects, shell model effects, and effects due to nuclear deformation [2.19]. From Figure 2-6 we see that an increase in $\langle r^2 \rangle$ produces a larger difference in potential $[V'_A(r) - V(r)]$. Equation (2-16) then indicates that the heavier isotope has the larger increase in energy from the reference level.

The magnitude and sign of the field shift of a spectral line also depend on the relative electronic charge density inside the nucleus $(-e)|\psi(r)|^2$ for the two electronic levels. For small r , the number densities for s , p , and d electrons are given by [2.20,21]:

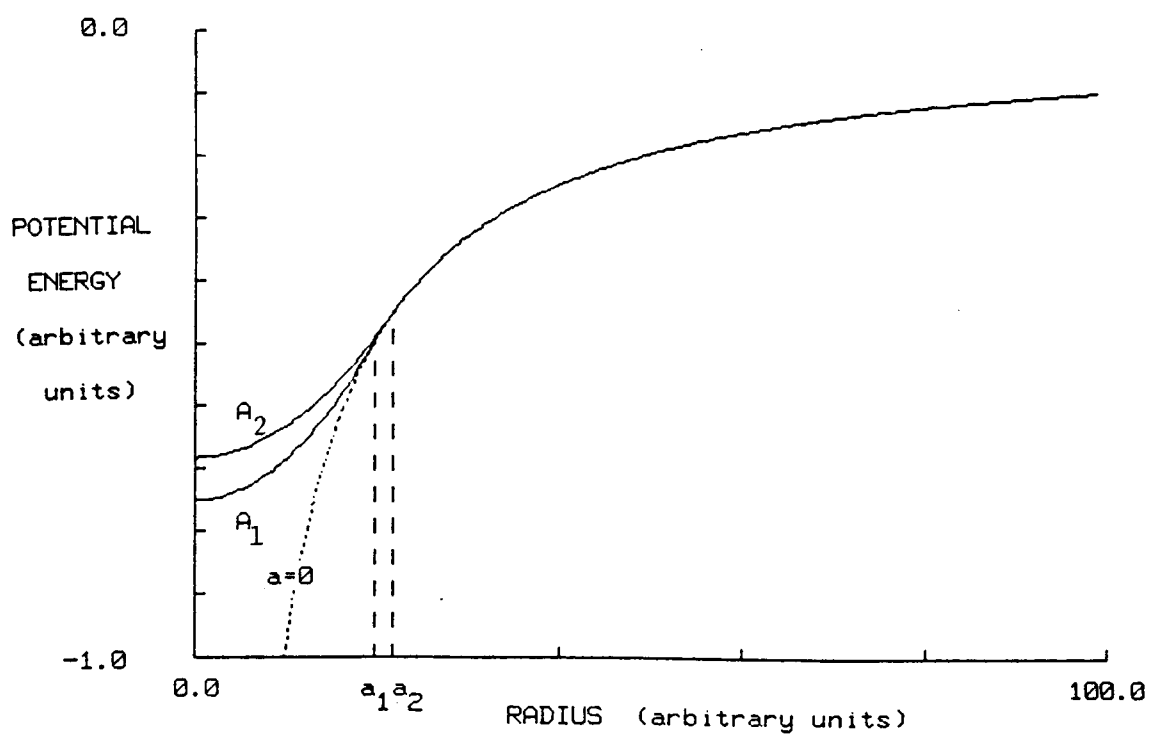


Figure 2-6. Potential Energy of an Electron as a Function of the Distance from the Center of the Nucleus. A is the Mass Number and a is the Nuclear Radius for Isotopes 1 and 2.

$$|\psi(r)|_s^2 \propto \left(1 - \frac{Zr}{a_0}\right)^2$$

$$|\psi(r)|_p^2 \propto \left(\frac{Zr}{a_0}\right)^2 \left(1 - \frac{Zr}{2a_0}\right)^2$$

$$|\psi(r)|_d^2 \propto \left(\frac{Zr}{a_0}\right)^4 \left(1 - \frac{Zr}{3a_0}\right)^2$$

where $a_0 = 0.053 \text{ nm} = \text{Bohr radius}$. As $r \rightarrow 0$, $|\psi(r)|_s^2$ remains finite while $|\psi(r)|_p^2 \rightarrow 0$ and $|\psi(r)|_d^2 \rightarrow 0$ strongly. For Nd and Sm, the nuclear radius is about $0.008 a_0/Z$. Thus only s-electrons have significant charge density within the nucleus, so the volume effect is evident mainly as changes in s-electron energy levels. Spectral lines with substantial field shifts result from s-electron transitions or from transitions which change the screening of the s-electrons. For example, an s-p transition decreases the electron density at the nucleus [2.22]. Using Eq. (2-16) with mass numbers $A_1 < A_2$ and corresponding nuclear radii $a_1 < a_2$, and assuming the electronic charge density is nearly constant inside the nucleus, we have:

$$(E'_{p,A_2} - E_p) = (-e) |\psi(\phi)|_p^2 \int_0^{a_2} [V'_{A_2}(r) - V(r)] 4\pi r^2 dr$$

where subscript p refers to the electronic state. Defining

$$\rho_p = (-e) |\psi(0)|_p^2$$

and

$$I_2 = \int_0^{a_2} [V'_{A_2}(r) - V(r)] 4\pi r^2 dr$$

the above equation becomes

$$(E'_{p,A_2} - E_p) = \rho_p I_2 .$$

Similarly,

$$(E'_{s,A_2} - E_s) = \rho_s I_2$$

$$(E'_{p,A_1} - E_p) = \rho_p I_1$$

$$(E'_{s,A_1} - E_s) = \rho_s I_1 .$$

Taking the above equations in pairs, we have

$$(E'_p - E'_s)_{A_2} = (E_p - E_s) + (\rho_p - \rho_s) I_2$$

$$(E'_p - E'_s)_{A_1} = (E_p - E_s) + (\rho_p - \rho_s) I_1 .$$

Subtracting these two equations gives

$$(\Delta E'_{p,s})_{A_2} - (\Delta E'_{p,s})_{A_1} = (\rho_p - \rho_s) (I_2 - I_1) .$$

The first factor on the right-hand side is positive, and for the second factor we have $a_2 > a_1$ and $[V'_{A_2} - V] < [V'_{A_1} - V] < 0$, so $(I_2 - I_1) < 0$. Then $(\Delta E'_{p,s})_{A_2} < (\Delta E'_{p,s})_{A_1}$ which is the definition of a negative isotope shift. By the same reasoning, we see that an increase in $(-e)|\psi(0)|^2$ produces a positive isotope shift.

CHAPTER III

EXPERIMENTAL APPARATUS

A. INTRODUCTION

A simplified diagram of the Resonance Ionization Time-of-Flight Mass Spectrometer system is shown in Figure 3-1. Each data cycle is initiated by the firing of the vaporizing laser. The beam is focussed onto a solid sample, creating a vapor cloud containing a large number of neutral atoms. After a variable delay, during which the vapor cloud expands, the excimer laser is triggered. The excimer laser pumps one or two dye lasers which provide photons of the appropriate wavelength to resonantly ionize atoms of a particular element in the vapor cloud, according to one of the RIS schemes described in Chapter II. The ions are created between the accelerating plates of a TOFMS. The time-of-flight of the ions from the point of creation to the detector is proportional to the square root of the mass of each ion. The resulting mass spectrum is displayed on an oscilloscope and is digitized by separately gated analog-to-digital converter (ADC) modules. The entire mass spectrum is sent to the input of each ADC, but the gate pulses allow only one mass peak to be digitized by each module. A microprocessor reads the ADC's and calculates the ratio of the digitized signals. The results are then displayed on the terminal and printer and stored on disks.

The following sections of this chapter describe in detail the lasers, time-of-flight mass spectrometer, and the detection electronics.

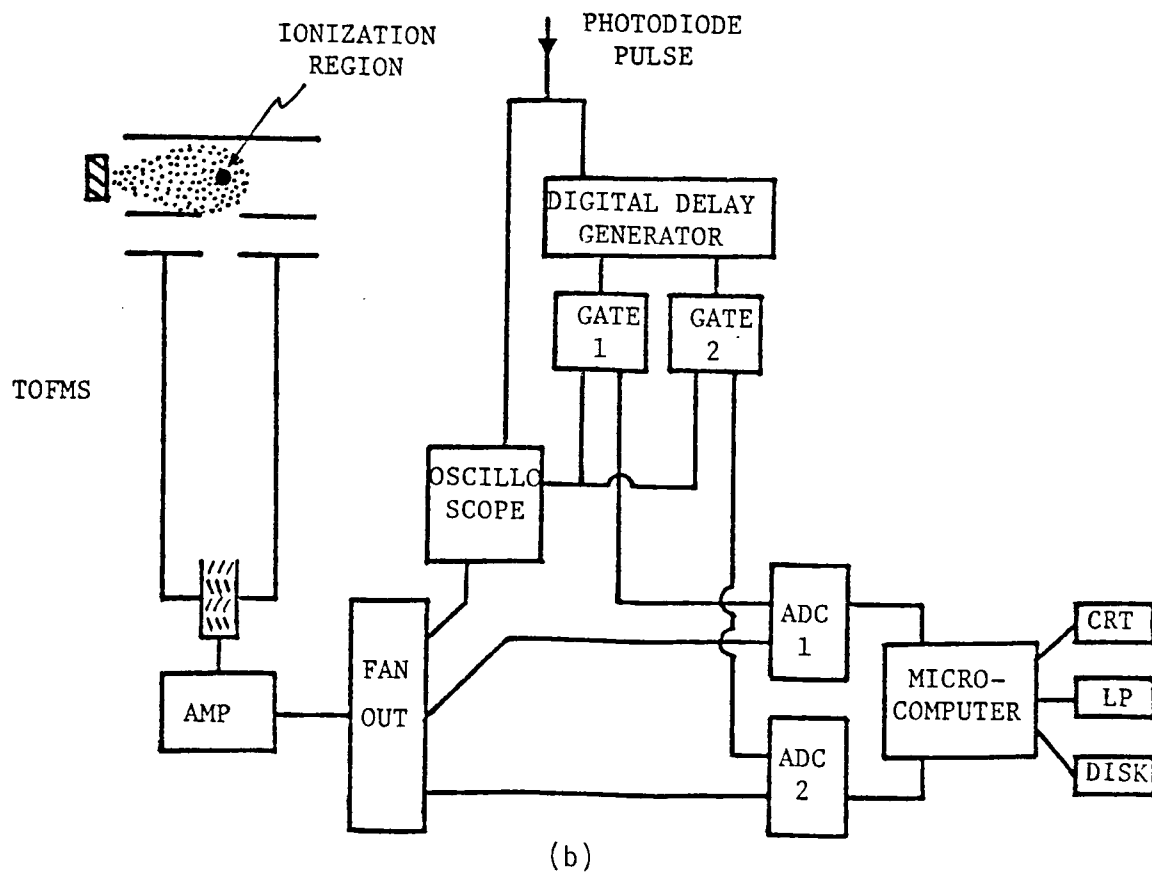
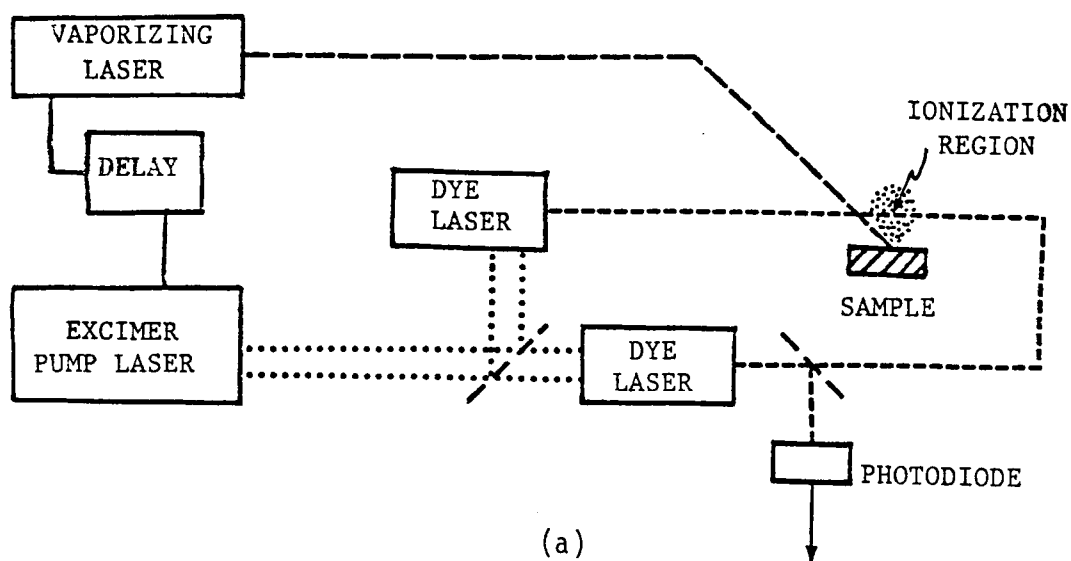


Figure 3-1. Schematic of the RIMS System. a) Laser Layout; b) TOFMS and Data Acquisition Electronics.

The last section is devoted to a detailed description of a general procedure, including the timing of the various events. The individual experiments, to be described in Chapter IV, will use this general procedure and vary one of the key parameters.

B. LASERS

The specifications for the lasers used in this system are given in Table 3-1. Table 3-2 gives the values of the energy pulse, spot size, and pulse power density for each laser beam at its respective interaction region, after attenuation (if any) and focussing.

For the Nd:YAG laser, the maximum pulse power and the spot size indicate a maximum pulse power density of $>10^{11}$ W/cm², with no attenuation. As stated in Chapter II, Section B, this is more than sufficient to create a vapor cloud which is representative of the solid sample. However, this power density also creates a large number of ions, which can short out the high voltages in the ion source and can saturate the detection electronics for times long enough to interfere with the mass spectrometer signal. Thus the Nd:YAG laser beam must be attenuated to an effective power density at the sample of 10^9 W/cm². This produces few ions and a vapor cloud whose composition depends strongly on the relative vapor pressures of the elements in the sample.

In Chapter II, Section C, we estimated that the RIS process could be saturated by providing 10^3 to 10^4 W/cm² for the excitation step and 10^7 to 10^8 W/cm² for the ionization step. Table 3-2 shows

TABLE 3-1
LASER SPECIFICATIONS

Specification	Vaporizing Laser	Pump Laser	Ionizing Laser #1	Ionizing Laser #2
Lasing material	Nd:YAG	XeCl	Flowing dye	Flowing dye
Manufacturer ^a	Quanta-Ray	Lumonics	National Research Group	Lambda-Physik
Model	DCR-1	TE861-S	DL-0.03	FL2001
Wavelength (nm)	1064	308	360-750	360-750
Maximum pulse energy (mJ)	250	80	0.4	8
Pulse width (ns)	9	7	5	5
Maximum pulse power (MW)	28	11	0.08	1.6
Average power at 15 Hz (W)	3.75	1.2	0.006	0.12

^aSee Refs. [3.1-4] for address information.

TABLE 3-2
LASER BEAM SPECIFICATIONS

Specification	Vaporizing Laser Beam	Pump Laser Beam	Ionizing Laser Beam #1	Ionizing Laser Beam #2
Interaction region	Sample surface	Dye cell	Vapor cloud	Vapor cloud
Pulse energy (mJ)	2.5	10 mJ to #1 70 mJ to #2	0.4	8
Spot size (cm ²)	0.0003	--	0.1	0.01
Pulse power density (W/cm ²)	1×10^9	--	8×10^5	1.6×10^8
Pulse energy density (J/cm ²)	8.3	--	0.004	0.8

that the excitation step is easily saturated by either dye laser, and that the high-power dye laser is marginally capable of providing sufficient power to saturate the ionization step. Since the power density is not uniform across the dye laser beam cross section, we assume the RIS process is saturated in a region near the middle of the dye laser beam, but not in the outer regions.

C. TIME-OF-FLIGHT MASS SPECTROMETER

The time-of-flight mass spectrometer (TOFMS) is composed of stainless steel components, with a clean 10^{-7} torr vacuum maintained by a CTI-Cryogenics [3.5] cryopump. A cutaway drawing of the TOFMS is shown in Figure 3-2, and a schematic of the system is shown in Figure 3-3. The source and acceleration regions are defined by three stainless steel plates [3.6], each 5 cm square. The middle and lower plate each have a 0.6 cm diameter hole at the center covered with 85% transparent nickel grid. This defines the entrance aperture to the TOFMS. The top plate is held at high positive voltage and the middle plate at a lower positive voltage, thus establishing a uniform electric field E_S in the source region. The bottom plate is grounded, setting up a uniform field E_A in the accelerating region. The sample is positioned adjacent to the source region, 2.9 cm from its center.

The Nd:YAG laser beam is focussed onto the sample at normal incidence and the vaporized material expands into the source region. The dye laser beam is directed through the vapor cloud above the entrance aperture and at right angles to both the TOFMS axis and the direction of motion of the vaporized atoms. The ions created by the

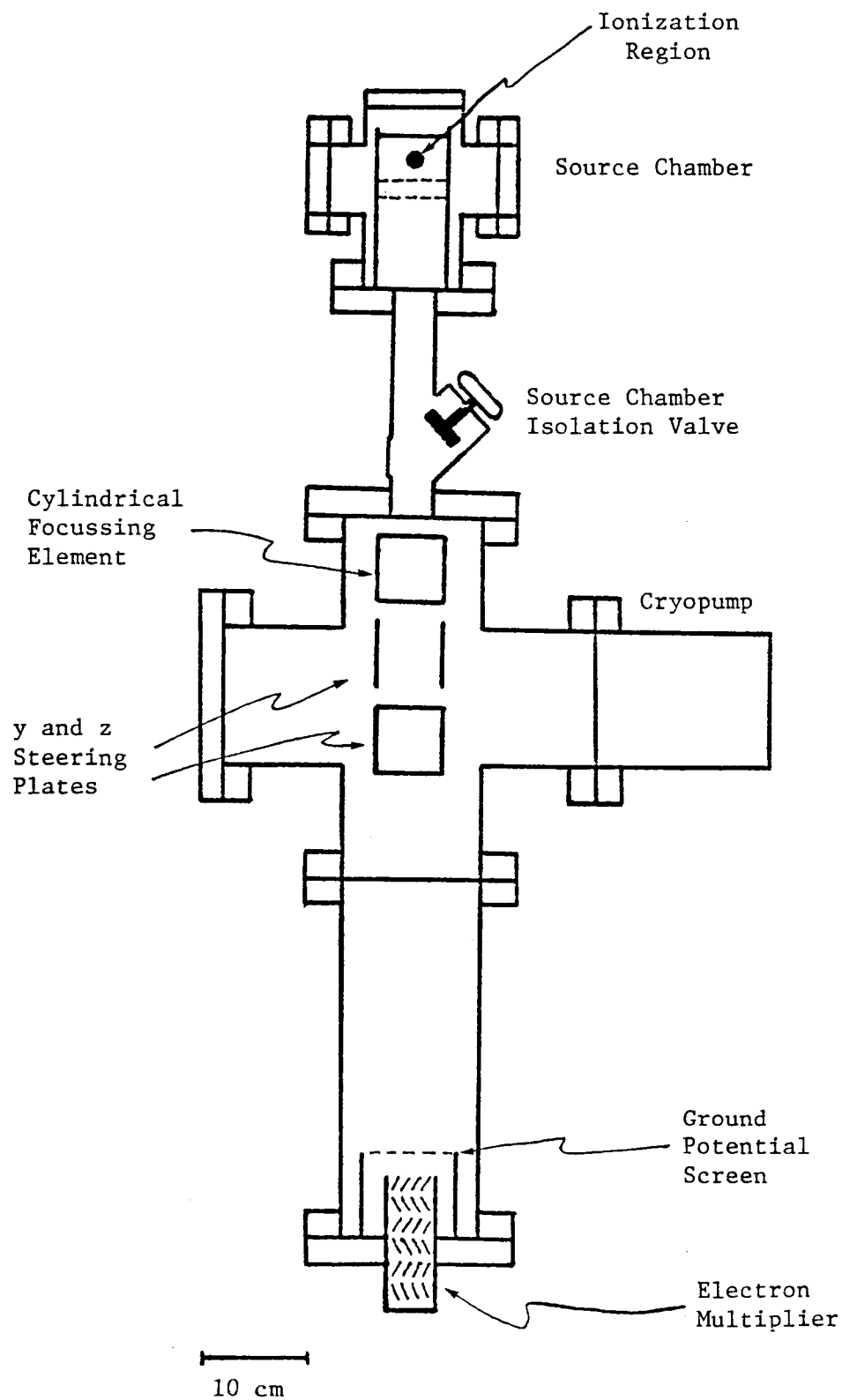


Figure 3-2. Cutaway Drawing of the TOFMS. Scale is 1.0 : 6.8.

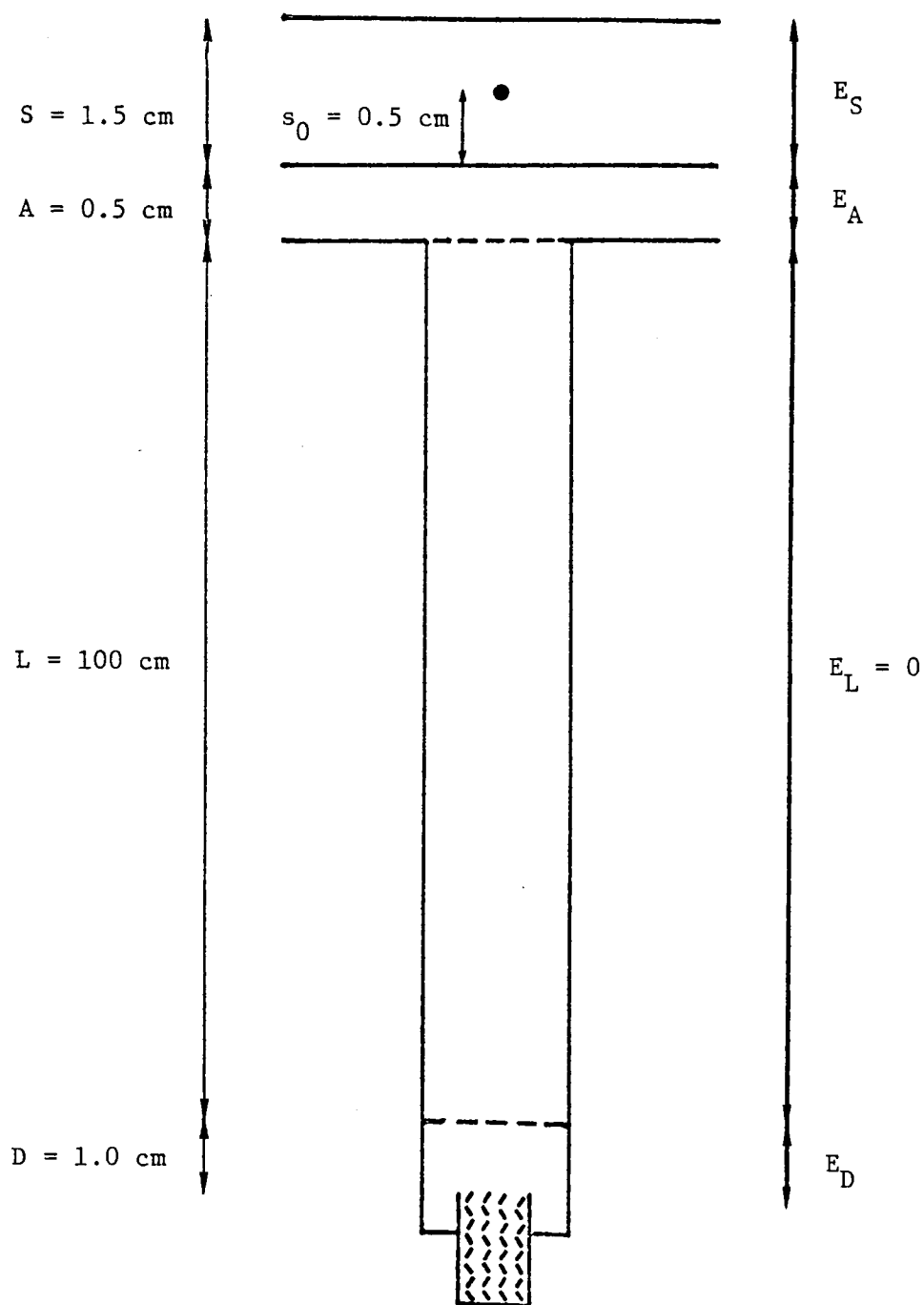


Figure 3-3. Schematic of the TOFMS, with Dimensions.

dye laser beam are accelerated by the uniform electric fields from the source region through the accelerating region and the 100 cm field-free drift region to the electron multiplier. A ground potential grid is located 1 cm in front of the detector, which is operated with the first dynode at high negative potential, thus creating a final accelerating region. The electron multiplier is an EMI-Gencom [3.7] Model 9603-2B, which produces a gain of 4×10^6 at the normal operating potential of -2.5 kV.

The TOFMS also contain ion beam steering and focussing elements, located about halfway along the flight path. The effect of these elements on the magnitude of the signal has been measured and found to be negligible except at large voltages ($> \pm 100$ V), in which case the beam is strongly de-focussed or steered away from the detector. This indicates that the ion beam is well defined by the dye laser beam and the entrance aperture in the ion source, and that the ion beam divergence is small for the 100 cm flight path. Thus the TOFMS was normally operated with the steering and focussing elements at ground potential.

The voltages for the three plates that define the source and accelerating regions are determined by the requirement for optimum spatial resolution, $(\frac{dt_T}{ds})_{s_0} = 0$, as in Eq. (2-13). The dimensions are fixed at $A = 0.5$ cm, $L = 100$ cm, and $D = 1$ cm. Typical values for the electric fields are $E_S = 150$ V/cm and $E_D = 2500$ V/cm. Using the above parameters and a particular value of s_0 , we can find a value of $R = E_A/E_S$ such that $(\frac{dt_T}{ds})_{s_0} = 0$. The function $R(s_0)$ is plotted in Figure 3-4 for $s_0 = 0$ to 1.5 cm.

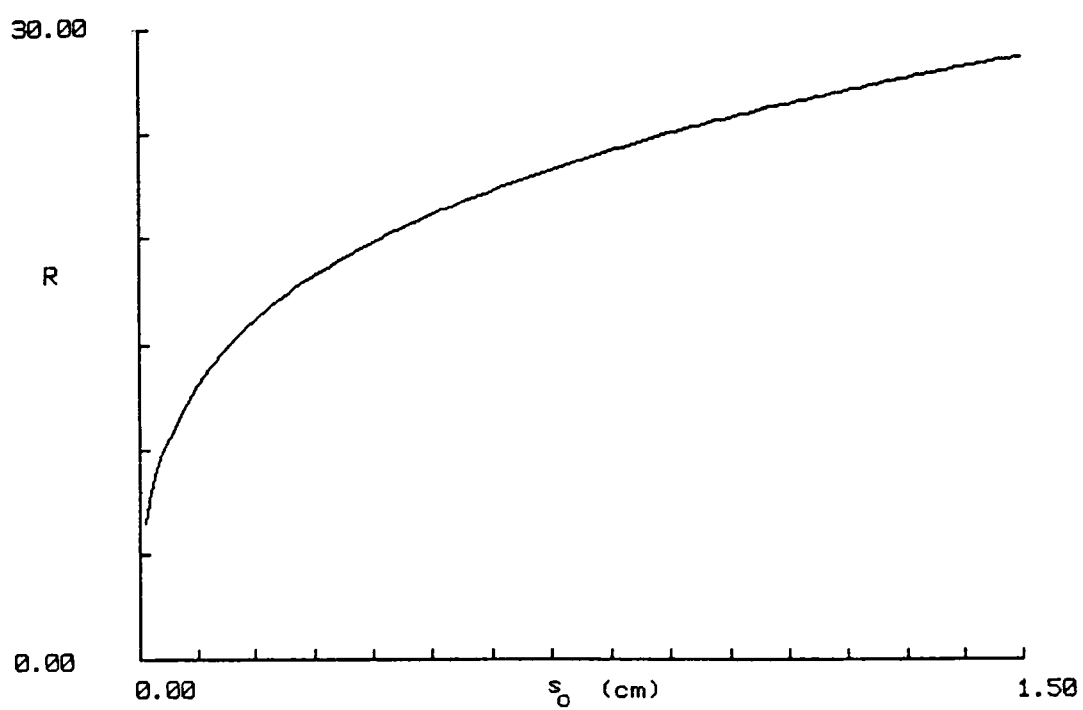


Figure 3-4. Plot of the Ratio R as a Function of s_0 for the TOFMS.

In practice, we have an ionization region of finite width and ions with slightly different initial positions. Using the parameters given above, with R appropriate to s_0 , we can find the time-of-flight for ions with any initial position s in the source region, using Eq. (2-11) with s substituted for s_0 . The results are given in Figure 3-5 for $s_0 = 0.2, 0.4, 0.8$, and 1.2 cm, and $s = 0$ to 1.5 cm. Note that each curve has a maximum at the appropriate value of s_0 . The calculations give the following values for τ_s , the contribution to the width of each mass peak due to differences in initial position, for a dye laser beam with diameter 0.2 cm ($s_0 - 0.1$ cm $< s < s_0 + 0.1$ cm): 22 ns for $s_0 = 0.2$ cm, 7 ns for $s_0 = 0.4$ cm, 2 ns for $s_0 = 0.8$ cm, and 1.5 ns for $s_0 = 1.2$ cm. For a focussed dye laser beam with diameter 0.01 cm, $\tau_s < 1$ ns for all values of s_0 .

The contribution to peak width due to initial energy of the ions is given by Eq. (2-13) as $\tau_U = \frac{2mv_0}{qE_s}$, where the velocity v_0 is along the TOFMS axis, either toward or away from the detector. The maximum axial velocity will be obtained by ions created at the top and bottom of the dye laser beam. For atoms traveling from the sample to the ionization region in 40 μ s (see Chapter IV, Section B) and for a dye laser beam with diameter 0.2 cm, we have $v_0 = 0.0025$ cm/ μ s. Using $m = 152$ amu and $E_s = 100$ V/cm, this gives $\tau_U = 0.008$ μ s = 8 ns.

Additional time spread for each mass peak will be introduced by the depth of the first dynode of the electron multiplier, ΔD . For ions with final energy of 4 keV, the final velocity is $v_f = 7.25$ cm/ μ s. The time spread for $\Delta D = 0.25$ cm is then $\tau_D = 0.035$ μ s = 35 ns.

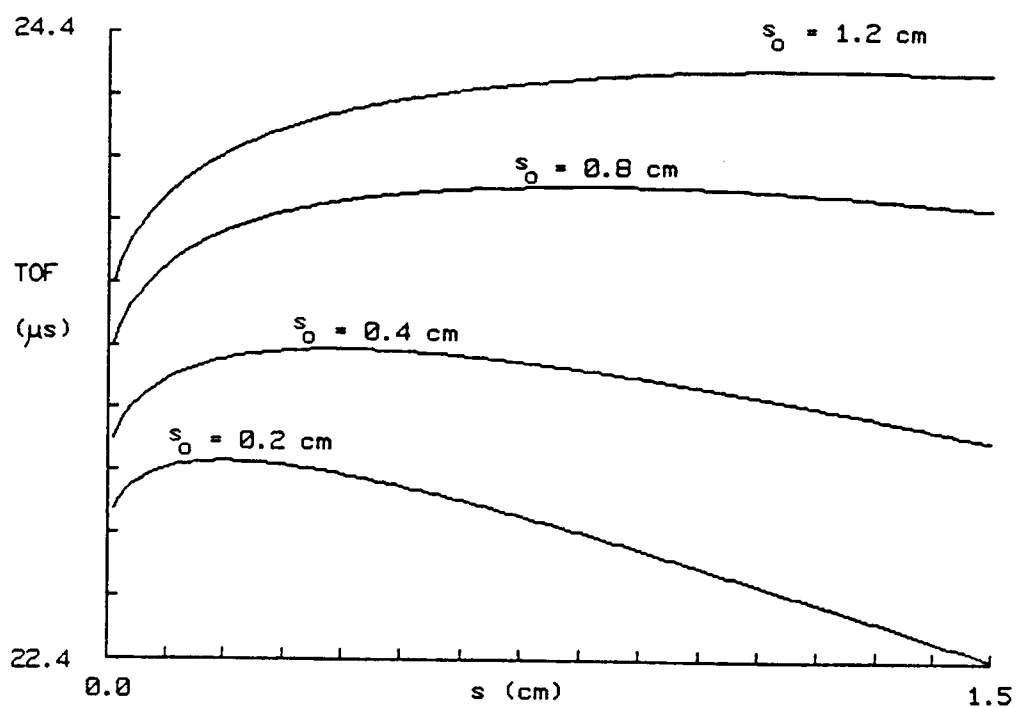


Figure 3-5. Plot of the TOF as a Function of s for $s_0 = 0.2, 0.4, 0.8$, and 1.2 cm. Here $m = 150$ amu.

The total time spread will be less than the sum of τ_U , τ_S , and τ_D . Thus $\tau_T < \tau_U + \tau_S + \tau_D = 50$ ns, using $\tau_S = 7$ ns for $s_0 = 0.4$ cm. Actual mass spectra show a peak width of about 50 ns under normal conditions. We have also observed that very strong signals (many ions) have larger peak widths, evidently due to Coulomb repulsion or distortion of the electric field in the source region of the TOFMS.

The time-of-flight for ions created at different values of s_0 can be found from Eq. (2-11). We will use $m = 152$ amu, the above values for A , L , D , and E_D , $s_0 = 0.2, 0.4, 0.8$, and 1.2 cm, and the value of R appropriate to s_0 , as found from Eq. (2-14) and Figure 3-4. Note that the absolute magnitudes of E_S and E_A are not specified in the determination of R . We will use a constant value for the energy of the ions as they enter the field-free drift region: $U_A = qE_S s_0 + qE_A A = 1500$ eV. Table 3-3 gives values of s_0 , R , E_S , E_A , the time spent in each region of the TOFMS, the total time-of-flight, and the time between mass peaks at 152 and 153 amu.

Comparing the value of the total time spread of each mass peak with the value of dt/dm from Table 3-3, we can infer that mass peaks up to at least 152 amu should be completely resolved by this instrument. This will be verified in Chapter IV.

As noted in Chapter II, Section D, the resolution of a TOFMS can be improved by the addition of a mass reflectron (see Figure 2-5, p. 28, and Ref. [2.15,16]). The optimum parameters, given in Ref. [2.16], are $B = 0.008 (L_1 + L_2)$, $R = 0.06 (L_1 + L_2)$, $qE_B = 0.7 U_A$, and $qE_R = 0.45 U_A$. We operated our system with a mass reflectron and found it to be impractical due to space limitations which restricted the detector

TABLE 3-3
PARAMETERS OF TOFMS FOR VARIOUS VALUES OF s_0

s_0 (cm)	R	E_S (V/cm)	E_A (V/cm)	t_S (μ s)	t_A (μ s)	t_L^a (μ s)	t_D^a (μ s)	t_T (μ s)	dt_T/dm (μ s)
0.2	16.106	181.75	2927.3	0.568	0.191	22.115	0.168	23.042	0.076
0.4	19.837	145.37	2883.7	0.899	0.185	22.115	0.168	23.366	0.077
0.8	24.238	116.11	2814.3	1.422	0.177	22.115	0.168	23.882	0.078
1.2	27.071	101.80	2755.7	1.860	0.172	22.115	0.168	24.315	0.080

^aNote that the times t_L and t_D are independent of s_0 since we have chosen U_A to be a constant.

size, and due to additional scattering of the ions by the screens defining the regions B and R. Since the TOFMS in the normal configuration gave adequate resolution for our purposes, we chose not to use the mass reflectron. The necessary modifications might be necessary at a later time for the analysis of heavier elements or for greater resolution in the present mass range.

D. ELECTRONICS

The data acquisition procedure for the Resonance Ionization Time-of-Flight Mass Spectrometer system is conceptually simple since the detector pulses are only amplified and digitized, with no pulse conditioning required. This technique places special requirements on the electronic components: the amplifier must be linear and must preserve the shape of pulses with risetimes and falltimes less than 10 ns, the timing of the gate pulses must be stable and precise to within 10 ns, and the ADC must be capable of digitizing fast pulses without the usual pulse-stretching electronics. Specifications are

given in Table 3-4 for the amplifiers and Table 3-5 for the delay and gate generators. Refer to Figure 3-6 for a detailed diagram of the data acquisition system.

The ADC is a LeCroy Model 2249SG, with 12 separately gated channels. Each analog input will accept signals only during the corresponding gate pulse, which may be from 10 ns to 2 μ s in duration. The unit has 10-bit (0.1%) resolution and is charge sensitive, with 256 pC producing a full-scale output. The ADC is designed to be used in a CAMAC crate, and transfers the digitized data to the host microcomputer via the CAMAC data lines.

The Kinetic Systems Corp. [3.12] microcomputer is an 8-bit microprocessor with 32K bytes of random access memory. Programming is done in FORTRAN, with two assembly language subroutines providing direct communication with the CAMAC modules. Peripheral devices are a CRT terminal, a printer, and a dual mini-floppy disk drive.

E. GENERAL PROCEDURE

Refer to Figure 3-6 for a detailed diagram of the data acquisition system, and to Figure 3-7 and 3-8 for the timing of events in the data-taking cycle.

Each data cycle begins with the firing of the Nd:YAG laser, at Point A in Figure 3-7. The Nd:YAG laser is triggered by its internal oscillator, which provides a repetition rate of 15 pulses per second. The beam is attenuated and focussed onto a solid sample, vaporizing a small portion of it (Chapter II, Section B). The internal oscillator pulse also triggers a separate delay-and-gate generator, which provides

TABLE 3-4

AMPLIFIER SPECIFICATIONS

Specification	Pulse-Shaping Amplifier	Fast Amplifier	Fan Out
Manufacturer ^a	Tennelec	LeCroy Research Systems	LeCroy Research Systems
Model	TC213	612AM	428F
Number of channels	1	6	4
Inputs per channel	1	1	4
Outputs per channel	1	2	4
Gain range	0-640	2.5-30	0.98-1.02
Gain controls	Coarse: 0-64 (binary sequence) Fine: 1-10 (continuously adjustable)	Continuously adjustable	Continuously adjustable
Maximum positive output (volts)	10	0.2	0.1
Maximum negative output (volts)	10	5	2
Nonlinearity (%)	0.2	0.2	1
Pulse shaping	Differentiating (1.2 μ s time constant)	None	None

^aSee Refs. [3.8,9] for address information.

TABLE 3-5

PULSE GENERATOR SPECIFICATIONS

Specification	Laser Trigger Generator	Digital Delay Generator	Gate Generators
Manufacturer	Rutherford Electronics	Berkeley Nucleonics	Berkeley Nucleonics
Model	B7B	7055	8010
External trigger required (volts)	± 20	± 0.2	+1
Delay range (ms)	0-10	0-10	0-100
Delay jitter	--	± 5 ns	0.1%
Delay control	Continuously adjustable	10 ns increments	Continuously adjustable
Pulse width	50 ns-10 ms	40 ns	<20 ms-1 s
Pulse width control	Continuously adjustable	None	Continuously adjustable
Pulse amplitude range (volts)	0- +50 0- -50	+4 -2	+0.5-5 -0.8 -1.5 (with -0.5 V DC offset)
Pulse amplitude control	Continuously adjustable	None	Positive: Cont. adj. Negative: Switch selectable

^aSee Refs. [3.10,11] for address information.

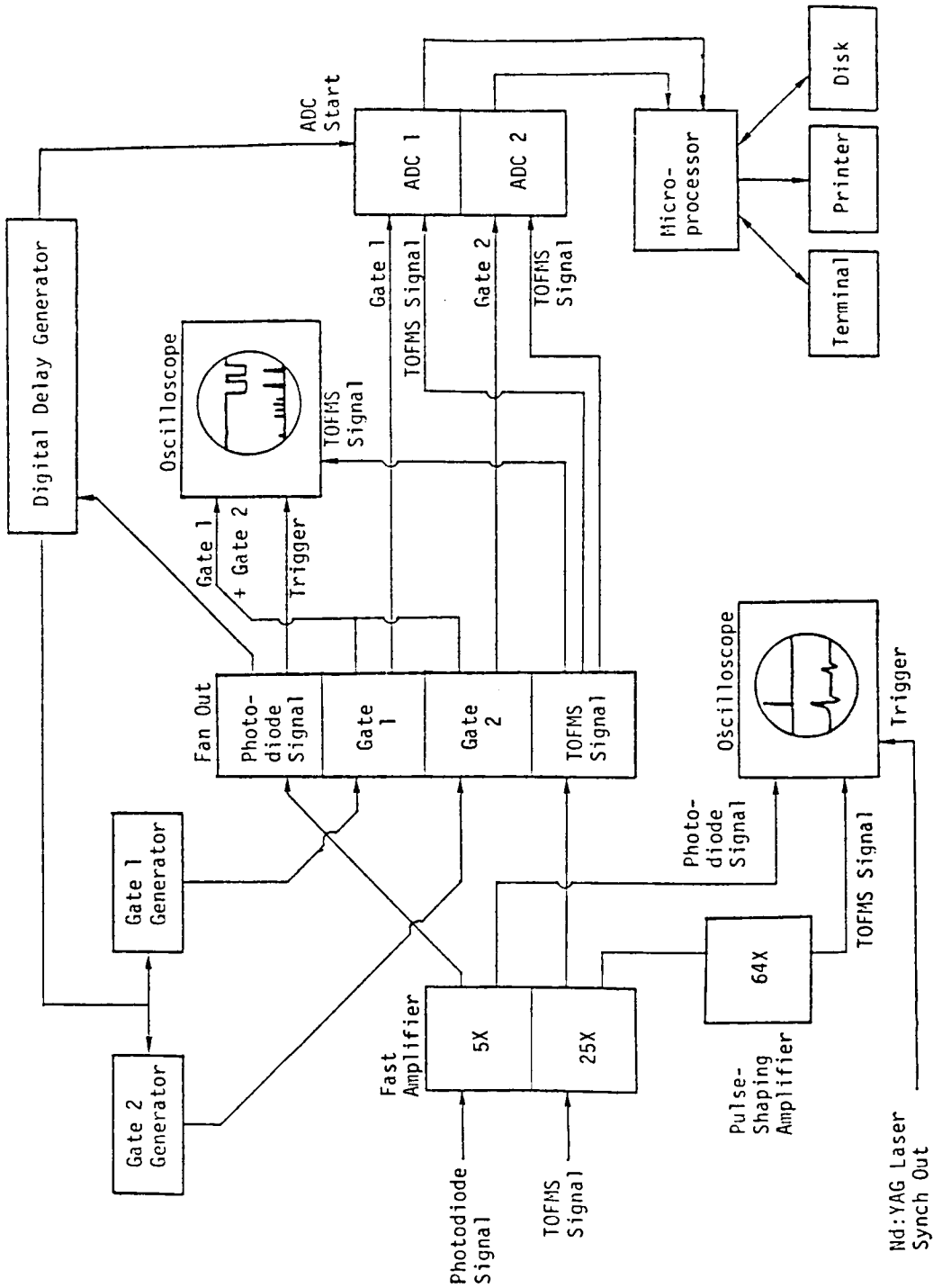


Figure 3-6. Detailed Schematic of the Data Acquisition Electronics.

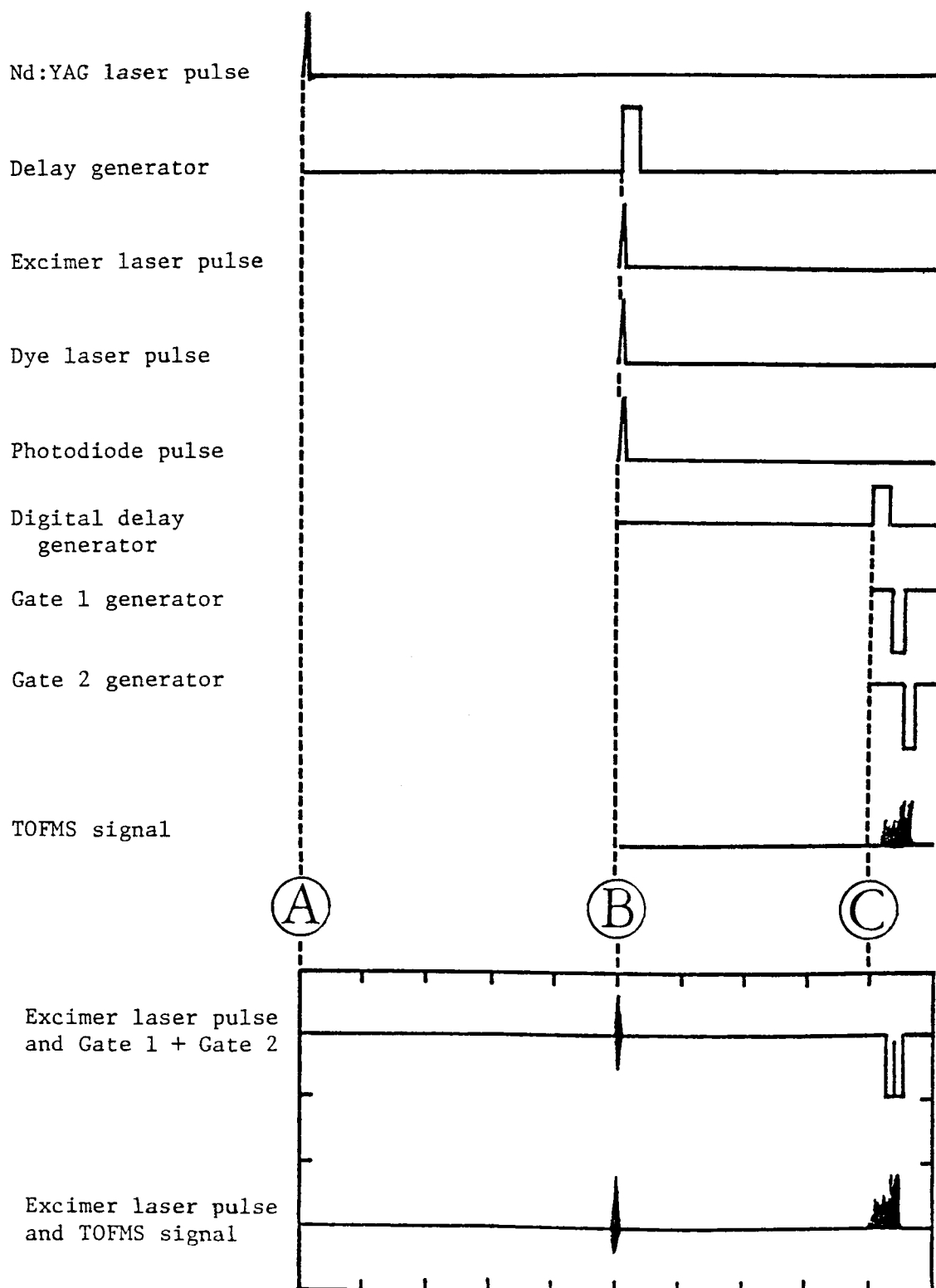


Figure 3-7. Timing Diagram for the RIMS System. Horizontal Time Scale for the Drawing is $5 \mu\text{s}/\text{div}$.

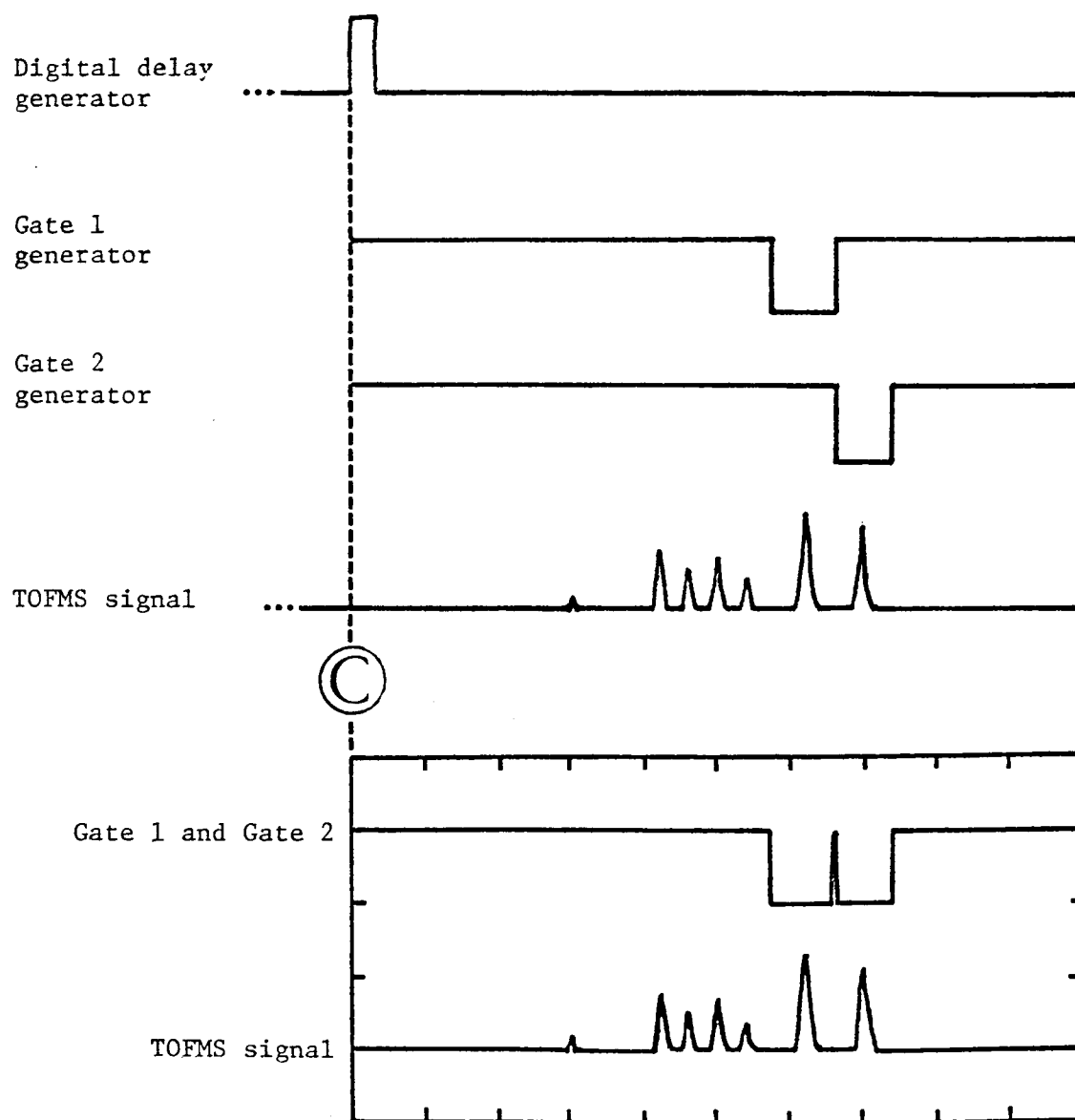


Figure 3-8. Expanded View of the Timing Diagram from Point C.
Horizontal Time Scale for the Drawing is 200 ns/div.

a variable delay—during which the vapor cloud expands into the sample chamber—then a trigger pulse for the excimer laser, at Point B of the timing diagram. The excimer laser pumps one or two dye lasers, depending on the RIS scheme chosen for the element of interest. The dye laser beams are directed through the vapor cloud at a point directly above the entrance aperture of the TOFMS, to selectively ionize atoms of a single element of the vapor (Chapter II, Section C).

A fast photodiode monitors the dye laser beam, generating a voltage pulse with duration equal to that of the dye laser pulse and magnitude proportional to the dye laser power. The photodiode signal is viewed on an oscilloscope to monitor dye laser power as a function of wavelength and as a function of time, since the gas mixture in the pump laser slowly degrades. The fast risetime of the photodiode pulse makes it an accurate means of triggering other devices at the time of the dye laser pulse, and for this purpose it is sent through the fan out to the digital delay generator and a second oscilloscope.

The digital delay generator provides a precise delay, which corresponds to the time-of-flight of the ions created by the dye laser pulse, then triggers the two gate generators (Point C, Figure 3-7). Each gate generator can set a short delay with sufficient precision to cause the gate pulse to occur simultaneously with a particular mass peak. This is shown in Figure 3-8.

The TOFMS signal is amplified by a fast amplifier which preserves the pulse shape, then is sent through the fan out to each ADC channel and to the scope, where it is displayed with the gate

pulses. After the fast amplifier, the mass spectrum may also be sent through a pulse-shaping amp to the monitor oscilloscope, to serve as an aid in positioning the dye laser beam within the TOFMS sample chamber and to qualitatively verify on- and off-resonance tuning of the dye laser wavelength. The mass peaks which coincide with a gate pulse are individually digitized by the appropriate ADC channel. The resulting data are transferred along the CAMAC data lines to the microcomputer, which reduces the data and prints the results on the terminal, printer, and disk.

The system as described above measures two isotopes at a time, but the procedure can be easily adapted to measure all isotopes of an element, given sufficient gate pulse generators and ADC modules.

Data reduction consists of using the output of the ADC modules to infer the amount of charge in the mass peaks of the TOFMS signal. This is accomplished in two steps: accounting for the response of the ADC's, and subtracting background due to electronic noise.

The response of the ADC modules is calibrated by monitoring the digital output as a function of charge input. With a constant gate width of 75 ns, and a constant ADC input impedance of 50 Ω , the input charge will be proportional to a DC voltage level at the input. The proportionality constant is 1.5 pC/mV, so a DC level of about 170 mV provides the ADC's full-scale charge of 256 pC. The response is nearly linear for each ADC, deviating slightly at the low end as shown in Figure 3-9. The slope and intercept of the response curves vary slightly with ambient temperature, etc., so both ADC's are

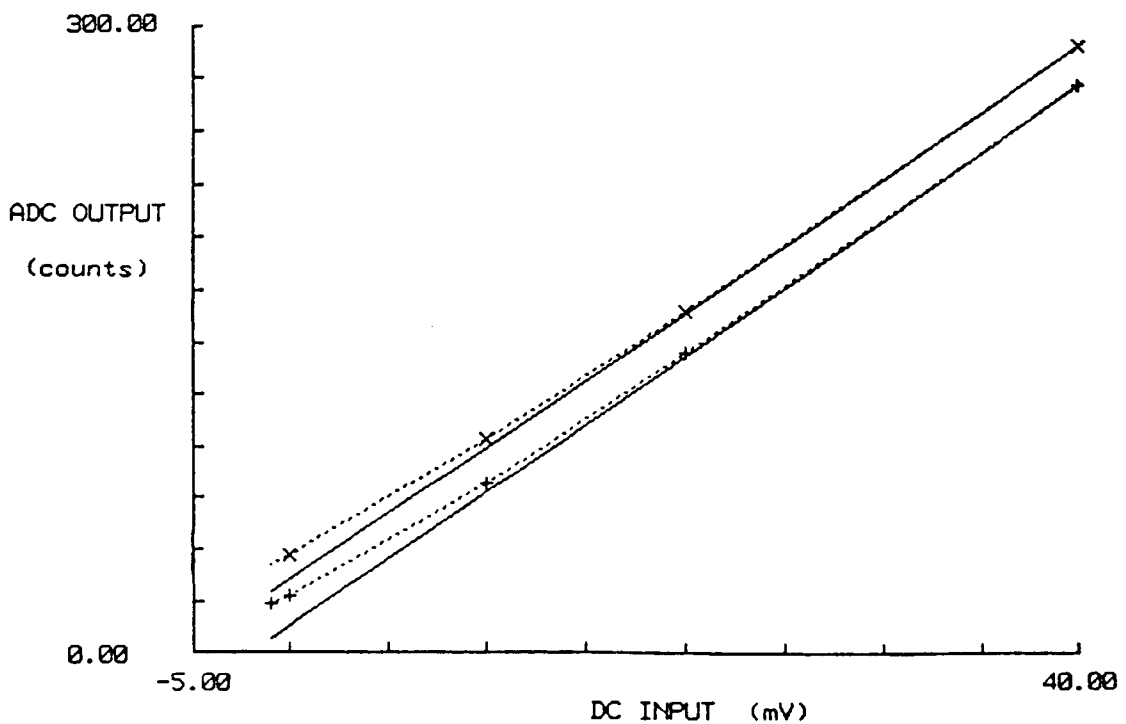
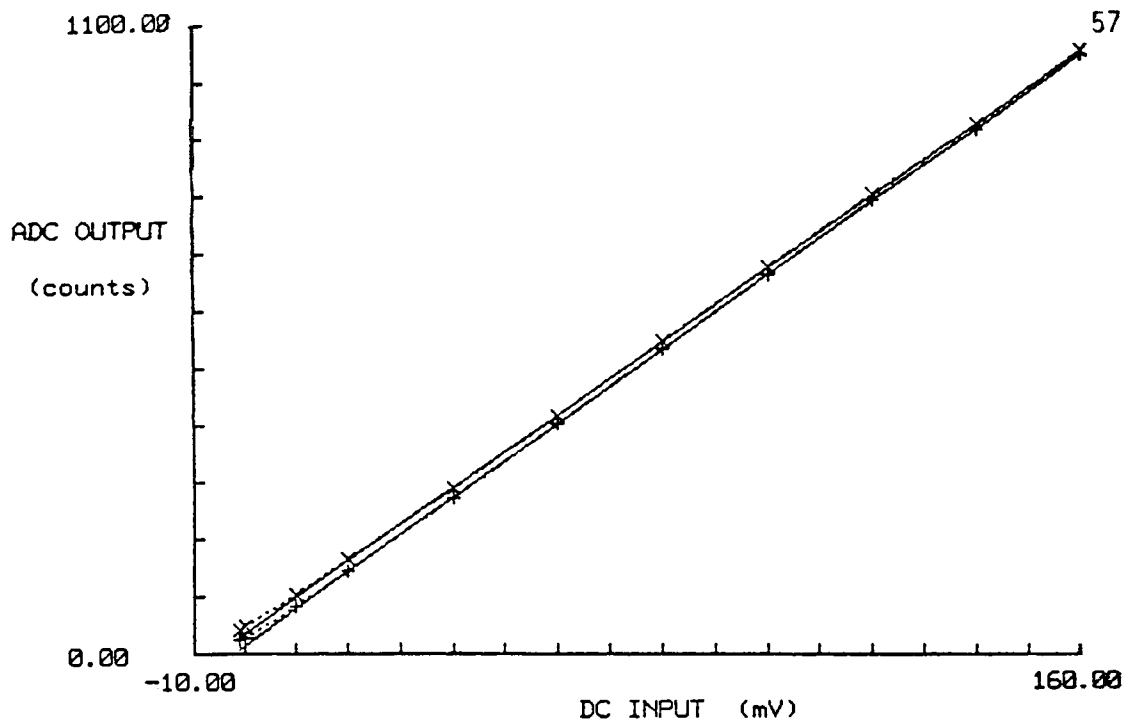


Figure 3-9. Calibration Curve for the Two ADC Modules. + : ADC 1; x : ADC 2; Dotted Line: Interpolation between Data Points; Solid Line: Extrapolation of Linear Regression for Data from 40 to 60 mV DC Input. Data Obtained with 80 ns Gates on the ADC Inputs.

calibrated immediately prior to each data run. The calibration data are entered into an interpolation program to be used during the data reduction process.

The first data set of each run measures the background due to electronic noise. Background data are acquired under actual experimental conditions except that the dye laser beam is blocked. The amount of background charge is determined from the ADC output by interpolation of the ADC calibration data.

The dye laser beam is then unblocked and individual mass peaks are measured during subsequent data sets. The interpolation program uses the raw data and the ADC calibration data to determine the total amount of charge in each mass peak. The background charge is then subtracted to give the amount of charge due to the actual signal. Using the amplifier gain, electron multiplier gain, and the detection efficiency of the electron multiplier, we can calculate the number of ions of each mass incident on the detector. The transmission coefficient of the TOFMS has not been measured, so the total number of atoms ionized by the RIS process cannot be calculated. But we estimate that at least half of the ions traverse the instrument and strike the detector.

During the data acquisition process, data are accumulated and averaged over N laser shots before intermediate values are written, where N is chosen by the operator at run time. For each N shots, the computer calculates eight values which are displayed in columns on the terminal screen and printed as shown in Figure 3-10. The first two

SM303-01 DAT

SM303-01.DAT		BACKGROUND DATA RECORD				
RAW DATA		REDUCED DATA		SD AS %	RATIO	%OT
72.10	42.90	.00	.00	8.6 15.3	1.00	0.
70.15	44.35	.00	.00	11.1 16.4	1.00	0.
72.65	41.65	.00	.00	9.1 10.7	1.00	0.
74.05	41.00	.00	.00	11.7 11.0	1.00	0.
72.65	40.45	.00	.00	10.7 11.9	1.00	0.
75.85	41.15	.00	.00	12.1 7.9	1.00	0.
69.60	41.80	.00	.00	7.8 8.2	1.00	0.
69.70	40.40	.00	.00	11.1 10.7	1.00	0.
74.25	42.85	.00	.00	9.0 13.3	1.00	0.
72.40	43.45	.00	.00	8.7 13.8	1.00	0.
71.15	42.35	.00	.00	11.6 14.3	1.00	0.
72.45	43.45	.00	.00	8.6 14.8	1.00	0.
73.00	41.45	.00	.00	13.2 15.6	1.00	0.
70.10	39.65	.00	.00	7.3 9.9	1.00	0.
71.35	39.95	.00	.00	10.7 11.2	1.00	0.
69.50	40.20	.00	.00	7.1 9.5	1.00	0.
SET:	71.93	41.69	.00	.1 .1	1.00	0. SET
ACC:	71.93	41.69	.00	10.2 12.7	1.00	0. ACC

DATA RECORD # 1

226.70	191.75	69.75	68.82	21.5 34.9	1.01	0.	
269.30	240.80	88.96	91.32	23.8 37.6	.97	0.	
271.35	218.95	89.88	81.30	32.9 26.5	1.11	0.	
234.60	186.70	73.32	66.51	18.2 40.0	1.10	0.	
266.90	184.70	87.87	65.68	24.9 29.1	1.34	0.	
242.70	208.50	76.97	76.51	20.5 39.1	1.01	0.	
256.75	231.65	83.30	87.12	31.7 30.6	.96	0.	
264.50	233.85	86.79	88.13	22.2 31.2	.98	0.	
265.85	209.60	87.40	76.55	23.4 30.5	1.14	0.	
252.55	175.40	81.41	61.33	32.8 48.7	1.33	0.	
270.50	197.20	89.50	71.32	24.8 34.6	1.25	0.	
273.00	205.85	90.62	75.29	30.0 30.1	1.20	0.	
262.95	190.40	86.09	68.20	22.2 34.6	1.26	0.	
263.85	192.60	86.50	69.21	22.9 22.7	1.25	0.	
254.05	179.70	82.08	63.30	37.2 23.9	1.30	0.	
280.15	198.70	93.85	72.01	33.0 35.1	1.30	0.	
SET:	259.73	202.85	84.64	73.91	7.8 12.3	1.15	0. SET
ACC:	259.73	202.85	84.64	73.91	27.1 34.1	1.15	0. ACC

DATA RECORD # 2

232.60	187.70	72.41	67.06	26.4 22.2	1.08	0.	
258.25	211.95	83.97	78.09	16.4 28.1	1.08	0.	
279.55	203.85	93.57	74.37	28.8 27.1	1.26	0.	
258.85	232.25	84.25	87.40	25.4 33.2	.96	0.	
242.60	178.95	76.92	62.95	24.8 19.2	1.22	0.	
248.65	201.90	79.65	73.48	25.8 31.3	1.08	0.	
261.10	207.85	85.26	76.21	27.3 36.2	1.12	0.	
248.70	175.55	79.67	61.39	38.0 34.3	1.30	0.	
259.90	212.90	94.72	78.52	18.0 29.3	1.08	0.	
268.40	199.50	88.55	72.38	32.9 36.9	1.22	0.	
230.75	197.40	71.58	71.42	23.5 26.5	1.00	0.	
286.65	217.70	96.78	80.73	25.5 30.1	1.20	0.	
277.40	187.10	92.61	66.69	24.0 34.6	1.39	0.	
279.85	199.55	93.71	72.40	30.6 22.5	1.29	0.	
234.65	195.75	73.34	70.66	30.3 25.0	1.04	0.	
257.85	212.10	83.79	78.16	26.6 27.8	1.07	0.	
SET:	257.87	201.37	83.80	73.24	9.4 9.2	1.14	0. SET
ACC:	258.80	202.12	84.22	73.58	27.1 32.0	1.14	0. ACC

Figure 3-10. Sample of Computer Printout Obtained During Data Acquisition. Data Identified in the Text.

columns show the averaged ADC output for each mass peak. The next two columns show the averaged reduced data, followed by the standard deviation of the raw data for each mass, which is calculated as a percentage of the averaged raw data value. The ratio of the averaged reduced data is given in column seven, and the final column indicates the percentage of laser shots for which one or both ADC's produced a value greater than a prescribed limit. This limit is set equal to the maximum of the calibration data to avoid extrapolation while using nearly all of the dynamic range of the ADC's. For laser shots which produce an overflow value in either ADC or both, the data for both ADC's are ignored and the counter index is not incremented. Therefore, good data are obtained for N laser shots for every intermediate value displayed.

Each data set is comprised of 16 intermediate values, which are then used to find an average value for the entire data set for each of the eight quantities described above. Here the standard deviation refers to the 16 intermediate values of the reduced data, and is given as a percentage of the average reduced data for the set. Overall averages for each quantity, representing all data accumulated after the background set, are also calculated and displayed following each data set.

The data acquisition program pauses after each data set to allow for the change of an experimental parameter, such as dye laser wavelength, and continuation or termination of data acquisition. A complete data run thus produces two groups of data points, each representing for a particular isotope the relative number of ions produced as a function of the experimental variables. Each data point

is the average value for one data set, or $16 \times N$ laser shots. Since the lasers operate at 15 Hz, N is usually chosen to be 50, thus producing an intermediate value about every 3 seconds, while a data set (800 laser shots) is completed in just less than a minute.

CHAPTER IV

EXPERIMENTS

A. INTRODUCTION

In this chapter we discuss in detail the experiments performed with the apparatus and general procedure described in Chapter III. The results of these experiments are analyzed in terms of the theoretical development given in Chapter II.

In Section B, a procedure is given for the calibration of the dye laser wavelength. Since the calibration depends on the alignment of optical components in the dye laser, the procedure was performed after each realignment of the dye laser optics.

The following section describes the measurement of the kinetic temperature of a Sm vapor cloud produced by the Nd:YAG laser microprobe.

Section D describes the measurement of the relative population of thermally populated ground levels in Sm. The ratios of these relative populations are used to calculate the excitation temperature of the vapor cloud.

Section E gives qualitative results for the selective detection of Cr from a stainless steel sample, and for the detection of Nd and Sm separately from a Nd-Sm alloy.

The final section describes the measurement of isotope shifts in Nd and Sm, and the effects of these shifts on isotope ratio measurements.

B. DYE LASER CALIBRATION

The first step in the RIS process is a laser-induced resonance excitation. The selection of a specific transition requires accurate knowledge of the laser wavelength. Wavelengths of atomic transitions, as determined by emission spectra, are listed to six significant figures in NBS Monograph 145 [4.1], hereafter referred to as NBS 145. Matching experimentally observed resonances to published data thus provides an accurate calibration of the dye laser wavelength. This procedure is, in principle, sufficiently simple to be performed after every realignment of the dye laser optics, as is required.

However, heavy elements such as Nd and Sm have many transitions in the wavelength range used in RIS Scheme 1 (380-460 nm for Nd and Sm), and RIS often detects resonances not listed in the literature [4.2,3]. Therefore, experimentally observed resonances cannot always be matched to published spectra. Better materials for calibration purposes would be lighter elements with a few resonances in the wavelength range of interest.

To calibrate the dye laser wavelength for RIS with Nd and Sm, we use the chromium lines at 425.435, 427.480, and 428.972 nm, all of which are transitions from the ground state of Cr to intermediate states at about 2.9 eV. Each line has a high intensity in the arc emission data [4.4] and a strong RIS signal, although this correlation does not always hold [4.2,3]. Due to the high ionization potential of Cr (6.8 eV), two photons at any of the above wavelengths will not produce Cr ions. Therefore, we use RIS Scheme 1A (Figure 2-3, p. 20),

with the excimer laser providing photons with wavelength 308 nm (4.0 eV) for the ionization step. This requires a beamsplitter between the excimer and dye lasers to pick off about 10% of the excimer beam, which is then reflected into the sample chamber in the opposite direction to and collinear with the dye laser beam. The observed resonances are easily matched with published Cr spectral data [4.4] to give a correction factor for the dye laser wavelength readout.

Implicit in this calibration procedure is the assumption that the dye laser realignment introduces only an offset error in the indicated wavelength. This has been checked by applying the measured correction factor to subsequent observation of Nd and Sm resonances and verifying good correlation of corrected experimental wavelengths with published data.

C. KINETIC TEMPERATURE

We have determined the kinetic temperature of a laser-produced samarium vapor cloud by measuring the relative number density of neutral atoms within a specified region as a function of time. This was accomplished by resonantly ionizing the samarium atoms in a region defined by the cross section of the ionizing laser beam and the entrance aperture of the mass spectrometer. The RIS signal was monitored as a function of the delay time between the vaporizing laser pulse and the ionizing laser pulse, which is the time-of-flight (TOF) for the ionized atoms. Note that here TOF refers to the time required for an atom to

travel from the sample to the ionization region. The general procedure of Chapter III, Section E, was followed, with data accumulated for one data record (800 laser shots) for delay times between 20 and 200 μs . This established the experimental TOF distribution function.

The kinetic temperature is defined by the Maxwell speed distribution function, Eq. (2-2), but for comparison with experimental data we will use Eq. (2-5):

$$g'(t,u) = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2kT_k} \right)^{3/2} \int_{\ell_0}^{\ell_0 + \Delta \ell} \exp \left[\frac{-m}{2kT_k} \left(\frac{\ell}{t} - u \right)^2 \right] \frac{\ell^2 d\ell}{t^3}.$$

To match the experimental data to Eq. (2-5), a brute force least-squares method was used, with the kinetic temperature T_k , the hydrodynamic velocity u , and the data normalization constant C as adjustable parameters. The sum of the squared errors between each experimental point and the corresponding calculated value was evaluated for various combinations of T_k , u , and C . The program then reported the combination which produced the least value for the sum of squared errors. The TOF distribution function was calculated with the parameters as determined above for graphic comparison to the experimental data.

Figures 4-1 and 4-2 show the data and calculations for the TOF distribution functions measured in two data runs. The values of the parameters used for the calculated TOF distribution function are also given in the figures.

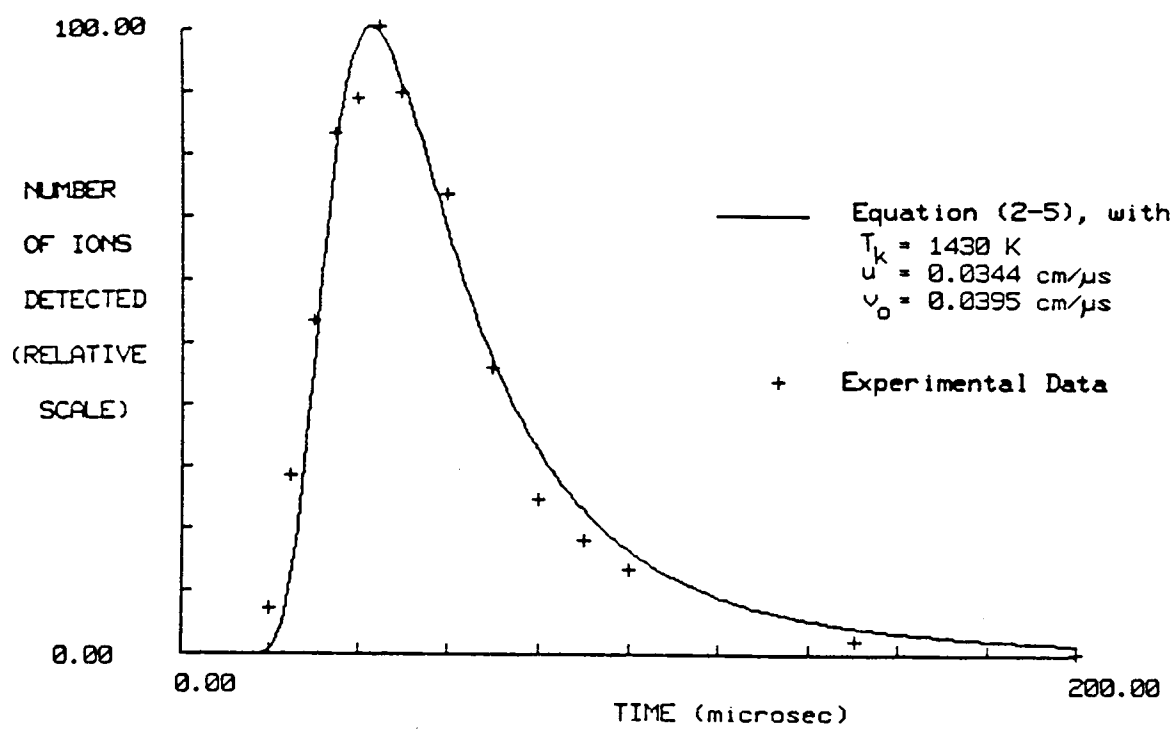


Figure 4-1. Velocity Distribution Data Set 1 and Calculations.

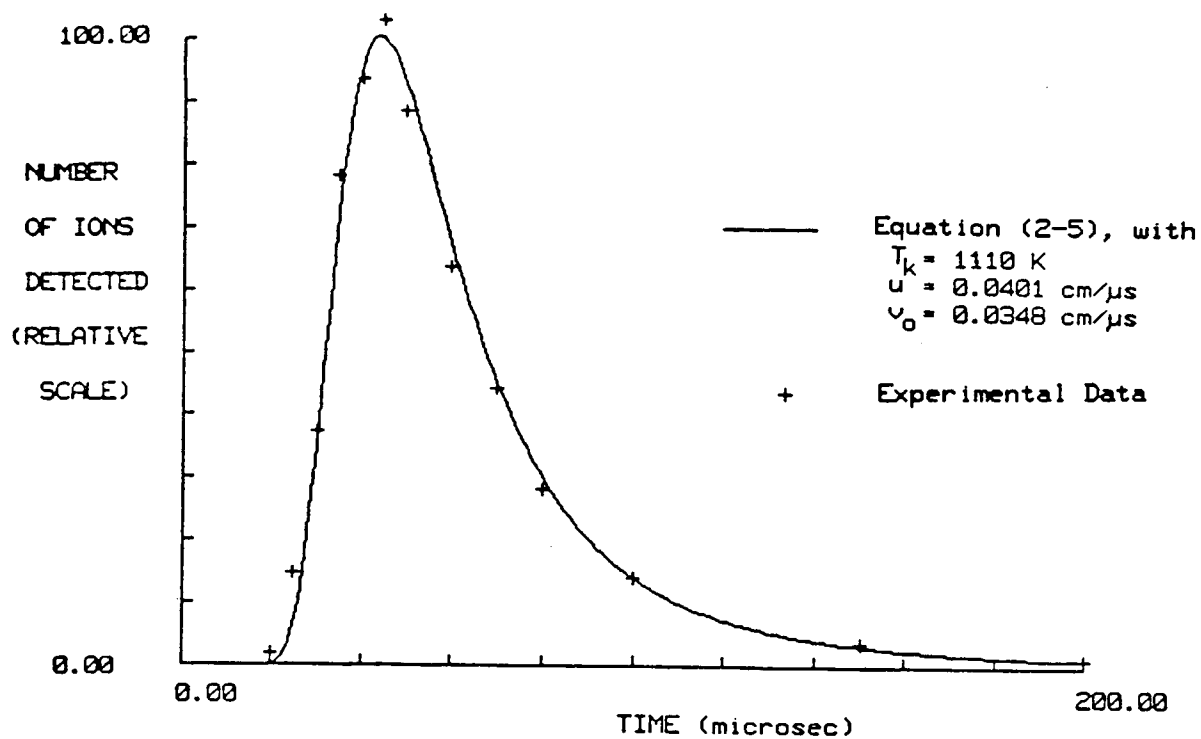


Figure 4-2. Velocity Distribution Data Set 2 and Calculations.

One interesting feature of the data is the surplus of atoms with short TOF (high speed). This can be seen in the first two data points of each figure. This indicates that the fast atoms quickly escape from the vapor cloud while the collision frequency is still high. The remaining atoms then establish a thermal equilibrium at a slightly lower temperature.

The estimated error in the kinetic temperature determination is ± 200 K and is primarily due to variations in the laser beam interaction with the solid sample resulting from changes in the surface profile during the data run and to 10% uncertainty in the TOF.

D. EXCITATION TEMPERATURE

The relative population of thermally populated levels may be calculated as a function of excitation temperature from Eq. (2-1). Figures 4-3 and 4-4 show the relative populations for the lowest energy levels of Nd and Sm, respectively, for excitation temperatures of 1200, 1600, and 2000 K.

Note that the ground level of Nd has the greatest population for each of these temperatures, while for Sm the greatest population is in the second or third level. The difference can be explained by Eq. (2-1) and the values of Tables 4-1 and 4-2. For Nd, the levels are widely separated and the exponential factor of Eq. (2-1) is more important than the ratio of the degeneracies. For Sm, the energy levels are closely spaced and the exponential term changes slowly, while the ratio of degeneracies is large for the first few levels.

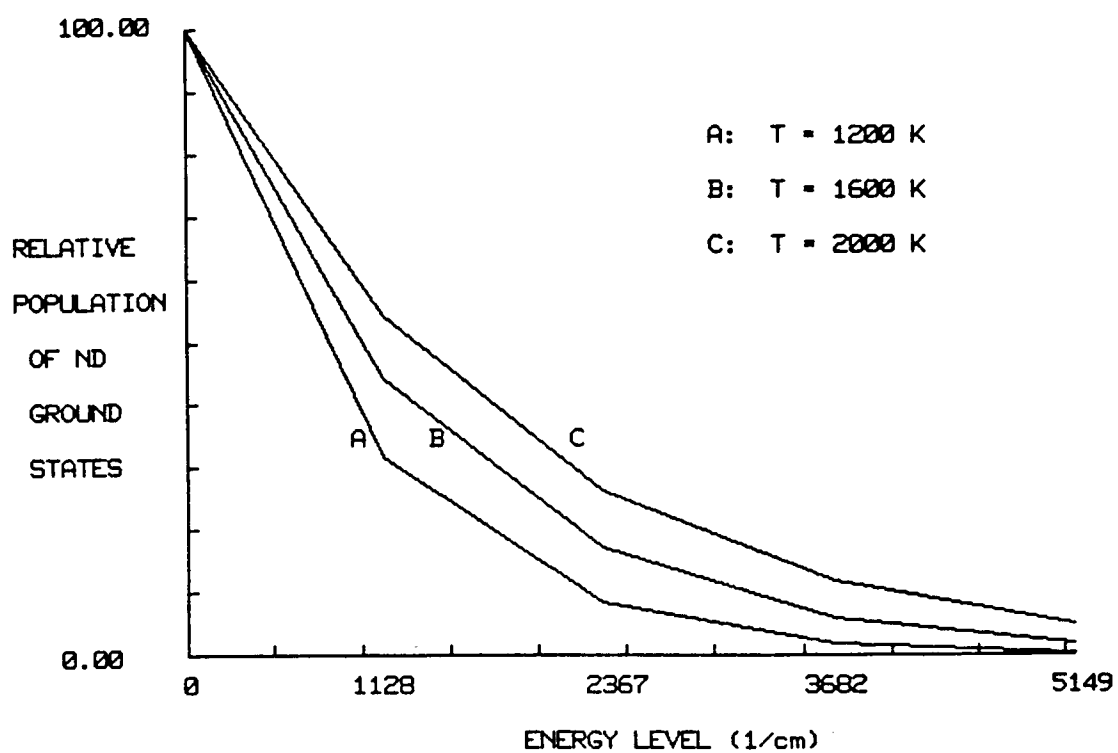


Figure 4-3. Relative Populations of Nd Ground State Levels.

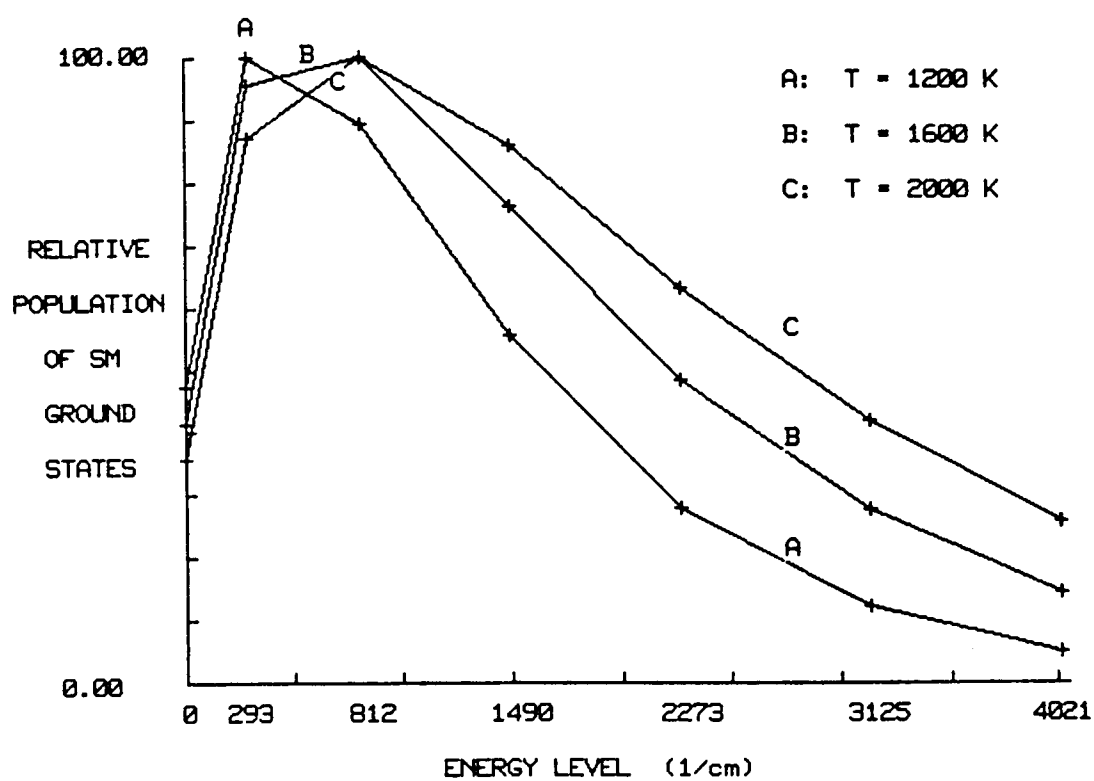


Figure 4-4. Relative Populations of Sm Ground State Levels.

TABLE 4-1

J-VALUE, DEGENERACY, AND RELATIVE POPULATION OF Nd ENERGY LEVELS

Energy Level (cm^{-1})	J	Degeneracy	Relative Population		
			T = 1200 K	T = 1600 K	T = 2000 K
0.00	4	9	100	100	100
1128.06	5	11	32	44	54
2366.60	6	13	9	17	26
3681.70	7	15	2	6	12
5048.60	8	17	0.4	2	5

TABLE 4-2

J-VALUE, DEGENERACY, AND RELATIVE POPULATION OF Sm ENERGY LEVELS

Energy Level (cm^{-1})	J	Degeneracy	Relative Population		
			T = 1200 K	T = 1600 K	T = 2000 K
0.00	0	1	47	42	36
292.58	1	3	100	96	87
811.92	2	5	89	100	100
1489.55	3	7	56	76	86
2273.09	4	9	28	48	63
3125.46	5	11	12	28	42
4020.66	6	13	5	15	26

We have determined the excitation temperature of a laser-produced Sm vapor cloud by measuring the relative population of three thermally populated levels. The general procedure of Chapter III, Section E, was used with RIS scheme 1B. For this scheme we use a low-power excitation laser beam tuned to a resonant transition and a high-power ionizing laser beam tuned off-resonance, as shown in Figure 4-5. The delay time between vaporization and ionization was 45 μ s, corresponding to the maximum in the velocity distribution.

The excitation laser was tuned successively to the wavelengths 429.914, 439.734, and 453.244 nm to produce excitations from levels at 293, 812, and 1490 cm^{-1} , respectively, to the intermediate state at 23547 cm^{-1} [4.5]. In each case, ionization from the intermediate state by a second photon from the excitation laser pulse is energetically possible. However, the power density was adjusted to 10^4 W/cm^2 ($\phi_1 = 10^{14} \text{ photons cm}^{-2}$) for each wavelength, which makes the ionization probability $\phi_1 \sigma_I$ much less than one. This avoided errors due to the possible wavelength dependence of the photoionization cross section from the intermediate state. The excited atoms were ionized by photons from the high-power dye laser tuned to 421 nm. The ionizing laser power density was 10^7 W/cm^2 ($\phi_2 = 10^{17} \text{ photons cm}^{-2}$), so the ionization probability from the intermediate state was constant and approached one for this case.

The condition $\phi_1 \sigma_I \ll 1$ was verified by blocking the ionizing laser beam and noting the disappearance of the RIS signal. The non-resonant condition for the ionizing laser beam was verified by blocking the excitation laser beam and again noting the disappearance of the RIS

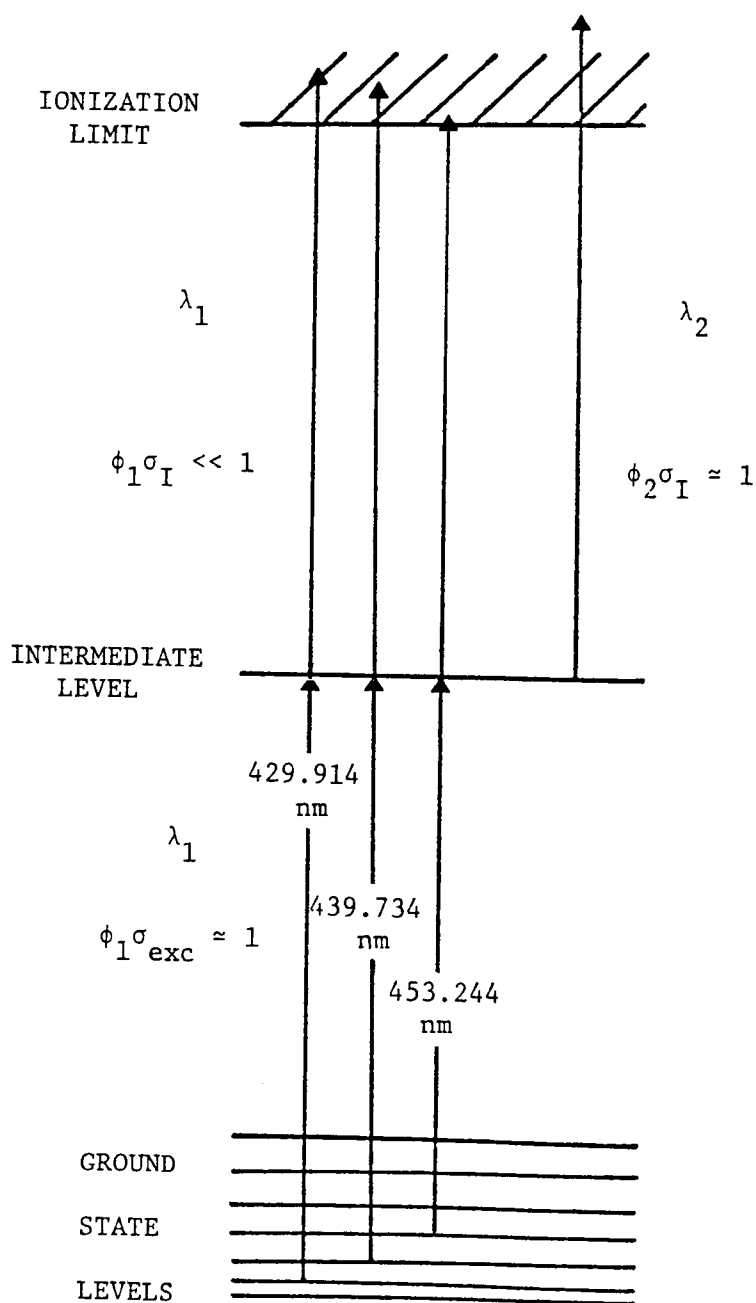


Figure 4-5. RIS Scheme 1A for Sm. Here λ is the Photon Wavelength, ϕ is the Photon Flux (Photons/cm²), σ is the Transition Cross Section, and $\phi\sigma$ is the Transition Probability.

signal. A single Sm isotope (^{152}Sm) was digitized by the TOFMS detection electronics to provide the data.

Since the excitation dye laser beam was linearly polarized, the degeneracies g_i of the electronic levels must be replaced by the effective degeneracies g'_i , as in Chapter II, Section C. Then Eq. (2-1) for the relative population of thermally populated levels is replaced by the following expression for the effective relative populations N'_m and N'_n :

$$\frac{N'_m}{N'_n} = \frac{g'_m}{g'_n} \exp \left[- \frac{hc}{k} \frac{(\tilde{\nu}_m - \tilde{\nu}_n)}{T_{\text{exc}}} \right]. \quad (4-1)$$

We can use this equation to obtain an expression for the excitation temperature in terms of the experimentally determined ratio N'_m/N'_n :

$$T_{\text{exc}} = - \frac{hc}{k} \frac{(\tilde{\nu}_m - \tilde{\nu}_n)}{\ln \left(\frac{N'_m}{N'_n} \frac{g'_n}{g'_m} \right)}. \quad (4-2)$$

The effective degeneracies for some thermally populated Sm levels are given in Table 4-3 for transitions to intermediate states with $J' = 1, 2, 3, 4$, or 5 from initial states with $J - J' = \Delta J = -1, 0, +1$ or $J = J' - 1, J', J' + 1$. The effective relative populations, along with the actual relative populations, are given in Table 4-4 for $T_{\text{exc}} = 1600 \text{ K}$ and energy levels with the same values of J and J' as above.

TABLE 4-3

J-VALUE, DEGENERACY, AND EFFECTIVE DEGENERACY OF Sm ENERGY LEVELS

Energy Level (cm^{-1})	J	Degeneracy	Effective Degeneracy				
			J'=1	2	3	4	5
0	0	1	1				
293	1	3	3	3			
812	2	5	3	5	5		
1490	3	7		5	7	7	
2273	4	9			7	9	9
3125	5	11				9	11
4021	6	13					11

TABLE 4-4

ACTUAL AND EFFECTIVE RELATIVE POPULATION OF Sm ENERGY LEVELS

Energy Level (cm^{-1})	Actual Relative Population (T=1600 K)	Effective Relative Population ($T_{\text{exc}}=1600$ K)				
0	42	42				
293	96	96	96			
812	100	60	100	100		
1490	76		54	76	76	
2273	48			38	48	48
3125	28				23	28
4021	15					12

The data obtained from the effective relative population experiment is given in Table 4-5 for two data cycles, with each data cycle consisting of a background set and two data sets for each of the three wavelengths given above. The intermediate values of each data set were averages over 20 laser shots for this data run. With 16 intermediate values per data set, this means each data value in the table represents an average over 640 laser shots.

TABLE 4-5
EXPERIMENTAL DATA FOR THE EFFECTIVE RELATIVE
POPULATION OF Sm ENERGY LEVELS

Energy Level (cm^{-1})	Effective Relative Population Data	
	Data Cycle 1	Data Cycle 2
293	156.74	116.77
812	165.04	126.40
1490	89.90	68.58

For each cycle, the data values for the three energy levels are taken in pairs as N_m and N_n in Eq. (4-2) to calculate the excitation temperature. The three data values may be taken in pairs three ways, thus giving three results for the excitation temperature for each data cycle, as given in Table 4-6. The average temperature for the first data cycle is $1616 \text{ K} \pm 0.6\%$, and for the second data cycle $1659 \text{ K} \pm 4\%$. Thus the data give results that are consistent within each data cycle and also between data cycles.

TABLE 4-6
EXCITATION TEMPERATURE OF Sm VAPOR CLOUD AS CALCULATED
FROM EXPERIMENTAL DATA

Energy Levels (cm^{-1})	Excitation Temperature (Kelvin)	
	Data Cycle 1	Data Cycle 2
293 and 812	1626	1730
812 and 1490	1606	1595
1490 and 293	1615	1651
Average:	1616	1659

E. ELEMENT SEPARATION

The main advantage of Resonance Ionization Mass Spectroscopy is the ability to analyze a single element of a sample containing many elements. To demonstrate this advantage, we have obtained mass spectra for Cr from a sample of Type 304 stainless steel [4.6], and for Nd and Sm individually from an alloy of the two metals. The general procedure of Chapter III, Section E, was followed, using various RIS schemes.

The elemental composition of Type 304 stainless steel [4.7] is given in Table 4-7, along with the natural isotopic composition of each element [4.8]. Figure 4-6 shows the mass spectrum resulting from the laser-vaporized steel nonresonantly ionized by the excimer beam at 10^8 W/cm^2 . The mass spectrum shows evidence of the following isotopes: $^{50}\text{Cr} + ^{50}\text{V}$, ^{51}V , ^{52}Cr , ^{53}Cr , $^{54}\text{Cr} + ^{54}\text{Fe}$, ^{56}Fe , and ^{59}Co . The trace isotope ^{58}Fe should also be present but is not detected here. The absence of Ni cannot be explained.

Vanadium is the only element with an isotope of mass number 51, so the presence of a significant mass peak at 51 amu is unexpected, since vanadium is not listed as a component of Type 304 stainless steel. This may be explained by the vanadium transition at 308.211 nm [4.9] from the thermally populated state at 553 cm^{-1} to an intermediate state over halfway to the ionization limit. This transition is resonant with the XeCl excimer laser line at 308.21 nm, which contains about 40% of the laser power (with 50% at 307.96 nm, 5% at 307.70 nm,

TABLE 4-7
ELEMENTAL AND ISOTOPIC COMPOSITION OF TYPE 304 STAINLESS STEEL IN THE RANGE 50-64 amu

Element	Abundance (%)	Mass Number:	Isotopic Abundance (%)														
			50	51	52	53	54	55	56	57	58	59	60	61	62	63	64
V	--		V (0.2)	V (99.8)													
Cr	18-20		Cr (4.3)		Cr (83.8)	Cr (9.5)	Cr (2.4)										
Mn	<2							Mn (100)									
Fe	65-71						Fe (5.8)		Fe (91.7)	Fe (2.2)	Fe (0.3)						
Co	--											Co (100)					
Ni	8-12										Ni (68.3)		Ni (26.1)	Ni (1.1)	Ni (3.6)		Ni (0.9)

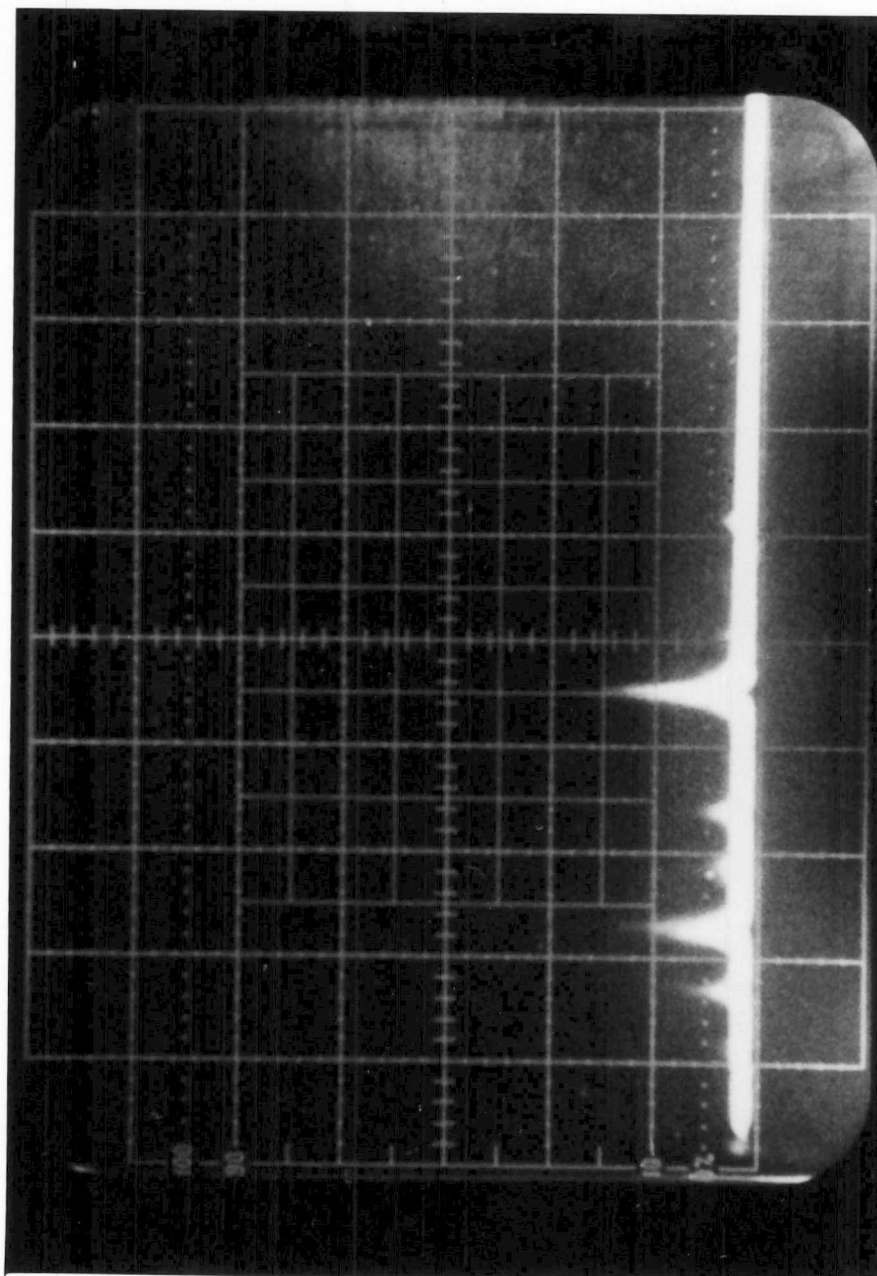


Figure 4-6. Mass Spectrum Obtained by Nonresonant Ionization of Type 304 Stainless Steel. Individual Mass Peaks are Identified in the Text.

and 5% at 308.46 nm) [4.10,11]. Therefore, any trace amounts of vanadium that are present will be resonantly ionized by RIS Scheme 1 with much greater efficiency than the nonresonant ionization of the other elements.

Figure 4-7 shows the mass spectrum obtained by using RIS Scheme 1A (Figure 2-3, p. 20) to resonantly ionize Cr atoms from the laser-vaporized steel. Here the excitation laser was tuned to 425.375 nm with a power density of 10^5 W/cm², while the excimer laser power density was reduced to 10^6 W/cm² to ionize excited Cr atoms while decreasing the nonresonant ionization probability for the other elements. Note that a small peak due to ⁵⁶Fe is still discernible, so the excimer laser power density should be reduced even further for more complete separation.

The vertical scales of Figures 4-6 and 4-7 are different, such that the largest peak in Figure 4-6 represents about 70 ions per laser shot for ⁵⁶Fe (60% of the sample), while the largest peak in Figure 4-7 represents 300 ions per laser shot of ⁵²Cr (16% of the sample).

The lanthanide elements Nd and Sm have isobars at 144, 148, and 150 amu, as shown in Table 4-8. This produces complications for conventional isotopic analysis. The RIS technique has the ability to cleanly separate each element from a mixture of the two metals. Figures 4-8 and 4-9 show the mass spectra of Nd and Sm, respectively, each obtained from a sample consisting of about 50% of each element. The dye laser wavelength was tuned to 456.233 nm to obtain the mass spectrum of Nd and 442.339 nm for Sm. Again, the delay between vaporization and ionization corresponded to the maximum in the velocity

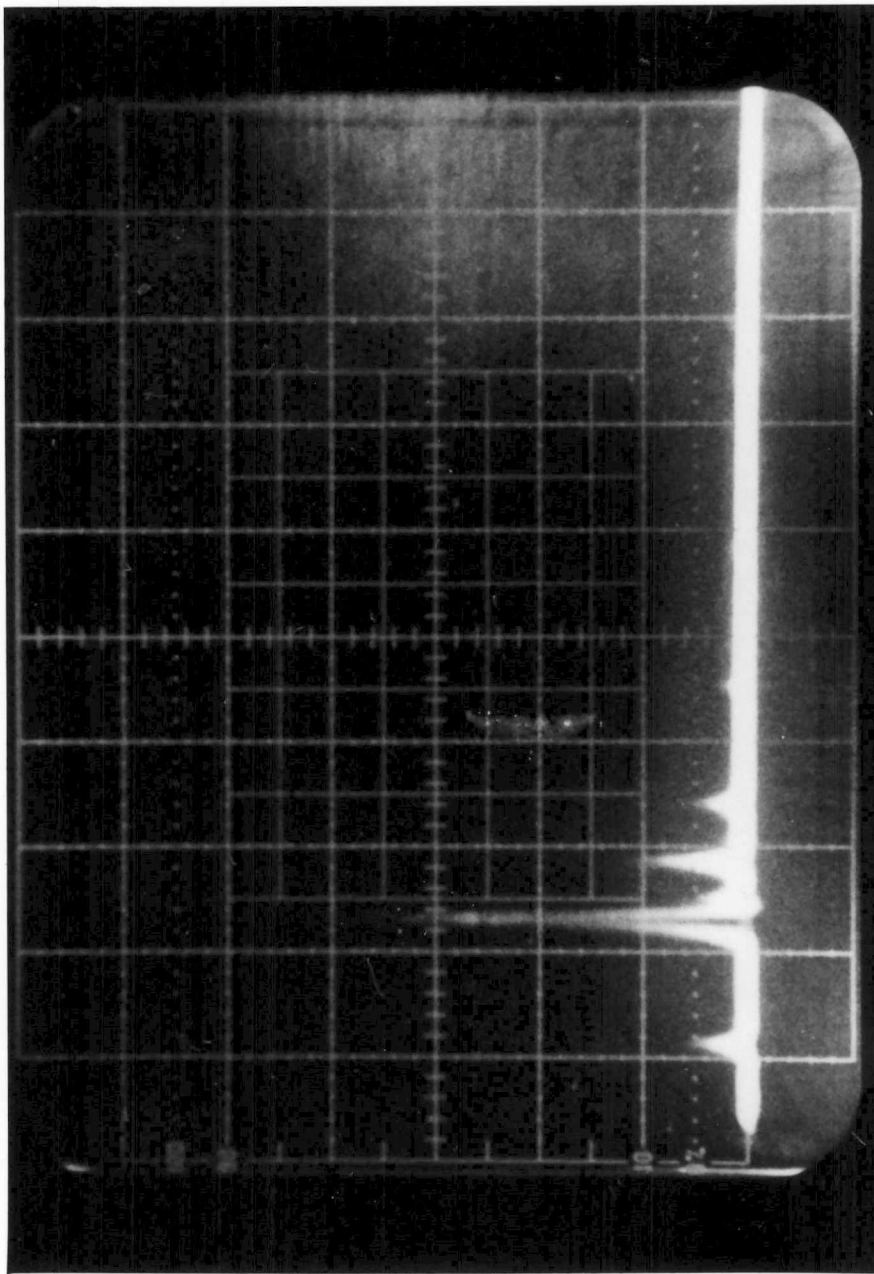


Figure 4-7. Mass Spectrum Obtained by Resonance Ionization of Cr Using Type 304 Stainless Steel Sample. Mass Peaks 50, 52, 53, and 54 amu.

TABLE 4-8
NATURAL ISOTOPIC ABUNDANCE OF Nd AND Sm

Element	Mass Number:	Isotopic Abundance (%)												
		142	143	144	145	146	147	148	149	150	151	152	153	154
Nd		27.13	12.20	23.87	8.30	17.18		5.72		5.60				
Sm				3.16			15.07	11.27	13.84	7.47		26.63		22.53

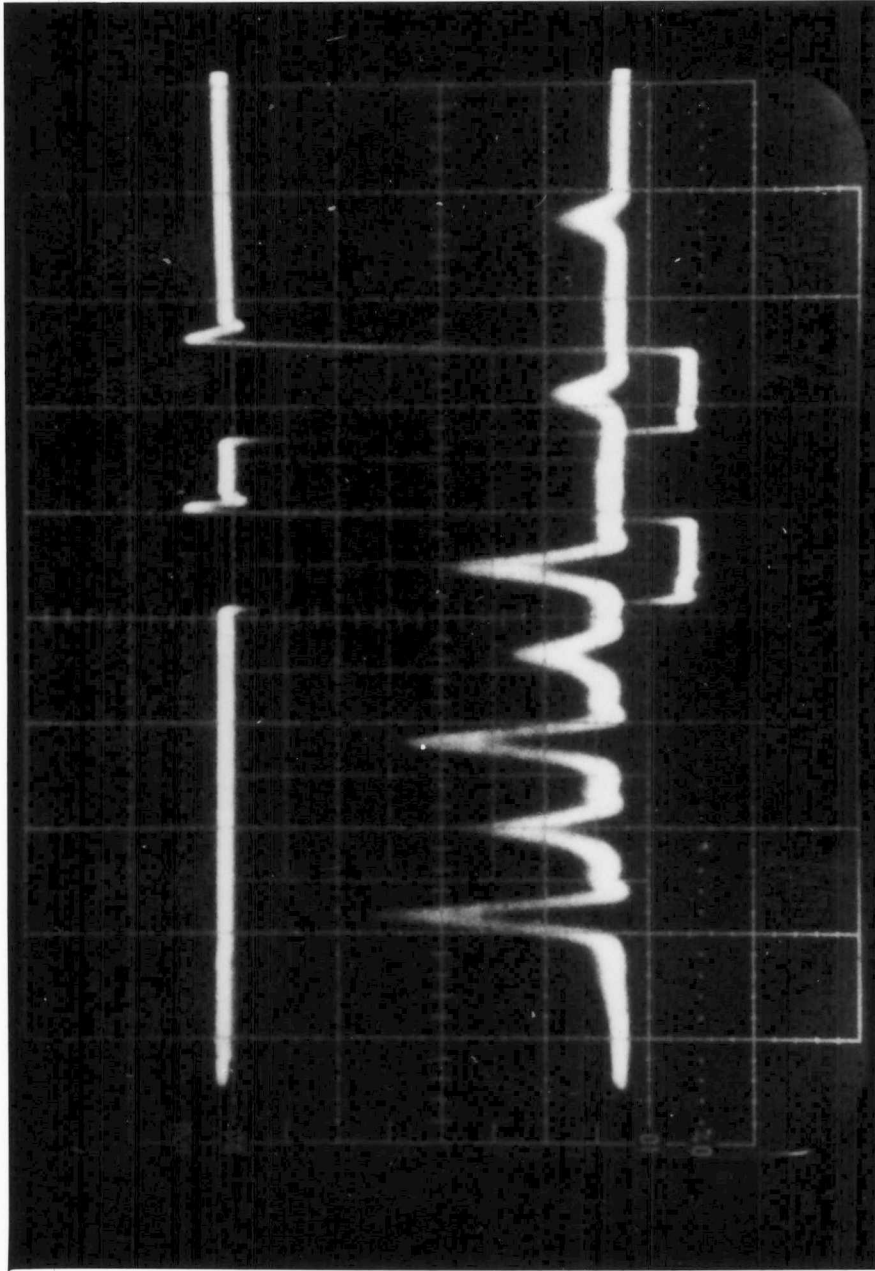


Figure 4-8. Nd Mass Spectrum Obtained by Resonance Ionization Using Nd-Sm Alloy Sample. Mass Peaks 142, 143, 144, 145, 146, 148, and 150 amu,

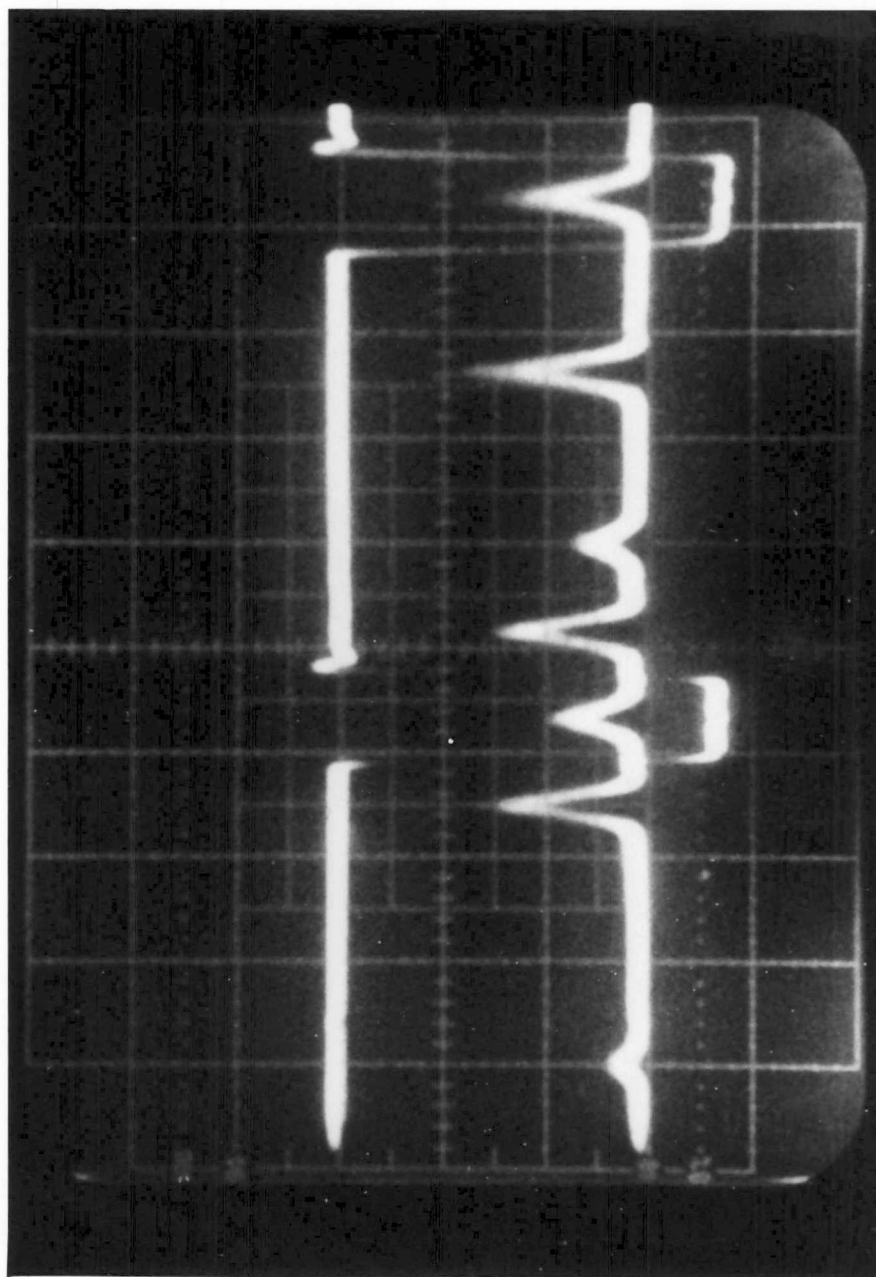


Figure 4-9. Sm Mass Spectrum Obtained by Resonance Ionization Using Nd-Sm Alloy Sample. Mass Peaks 144, 147, 148, 149, 150, 152, and 154 amu.

distribution. The top trace of each figure shows the gate pulses used to admit only one mass peak into each ADC, as described in Chapter III, Section E. Note that no Sm is observed at 147 or 149 amu in Figure 4-8, and no Nd is observed at 145 or 146 amu in Figure 4-9. Note also that the areas of the mass peaks in Figure 4-8 correspond qualitatively to the isotope abundances given in Table 4-8, while Figure 4-9 shows a bias for the lighter isotopes. The bias is due to the isotope shift of the transition, as will be discussed in the following section.

The selectivity of the RIS process for Nd and Sm could not be measured by our system since the unselected element could not be detected. However, this fact may be used to estimate a lower limit. It was observed that the strongest Nd resonances were much weaker than the strongest Sm resonances. This is due in part to differences in excitation and ionization cross sections, but a larger effect is probably the difference in vapor pressures, as shown in Figure 4-10 [4.12,13]. We will assume here that the observed excess of vaporized Sm atoms over Nd atoms implies the vaporization mechanism is simply heating and evaporation of the sample material, rather than the compression and heating of the material beyond the thermodynamic critical point, followed by explosive expansion of the compressed material (see Chapter II, Section B). The latter mechanism has been shown to produce vapor clouds with composition similar to that of the solid sample [4.14,15]. For a vapor cloud temperature of 1600 K (as determined by the measurements of Chapter IV, Sections C and D), the vapor pressure of Sm is 3000 times greater than the vapor pressure of Nd. Thus the number of Sm atoms available for ionization is 3000 times greater than

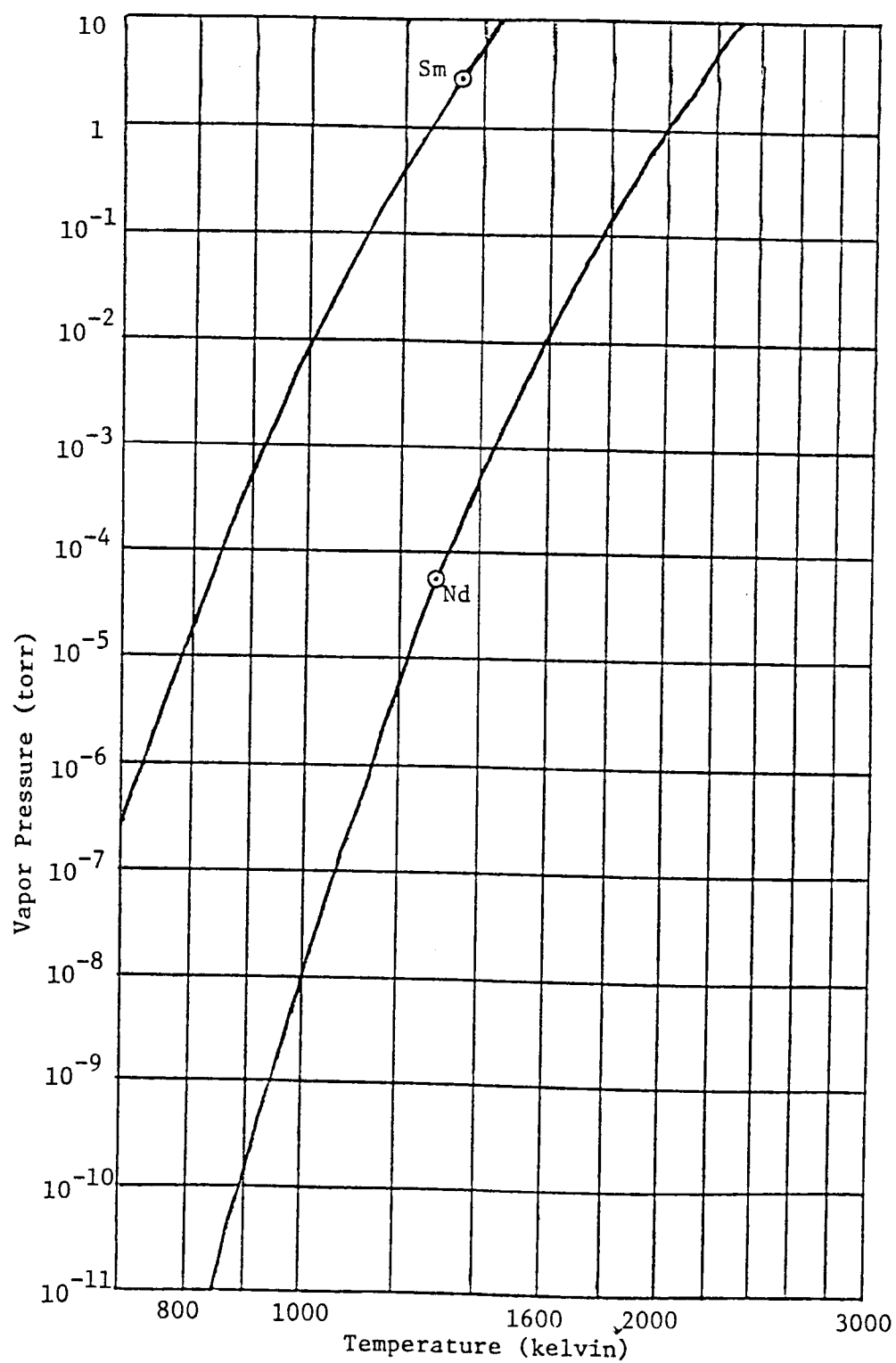


Figure 4-10. Vapor Pressure of Nd and Sm as a Function of Temperature. The Dot Indicates the Melting Point.

the number of Nd atoms. Since the smallest Nd peak in Figure 4-8 represents about 100 ions per laser shot and even the most abundant Sm isotope cannot be observed, the selectivity of Nd over Sm must be much greater than 3×10^5 .

It should be noted that in any RIS experiment the selectivity will depend on the relative abundances and ionization potentials of the other elements present. The selectivity can be maximized by the choice of resonant transition for the selected element, to avoid near-resonances in other elements, and by adjustment of the power density of the dye laser beam, to minimize the nonresonant ionization of other elements.

Tables of spectral lines (e.g., Ref. [4.1]) list for Nd and Sm many strong transitions which could be used for RIS Scheme 1, with few overlapping wavelengths. We have found, however, many resonances which do not correspond to tabulated transitions, such as the Nd resonance at 456.233 nm used to obtain Figure 4-8. Young and Donohue [4.2] have performed a systematic survey of Nd and Sm resonances from 423 to 463 nm using RIS Scheme 1 and a low-power (300 μ J) dye laser with 0.03 nm linewidth. They made tentative correlations of observed resonances with allowed transitions between known energy levels for all observed Sm resonances, but only half of their observed Nd resonances. Since our dye laser has more power and narrower linewidth, we were able to detect and resolve additional resonances, as shown in

Table 4-9 for the wavelength range 455.4 to 456.7 nm. The intensity of the resonance signal is given as strong (S), medium (M), or weak (W). The table also gives wavelengths and intensities for transitions tabulated in NBS 145 [4.16]. The last column gives wavelengths and the associated energy levels for allowed Nd transitions identified by a simple computer program called TRANS which uses the energy levels and J-values of NSRDS-NBS Monograph 60 [4.17] and the selection rule $\Delta J = -1, 0, +1$ (but not $J = 0$ to $J = 0$). For each transition, the energy difference between the two levels is converted to wavelength of the associated photon by the formula

$$\lambda = \frac{hc}{(E_2 - E_1)} \frac{1}{n}$$

where λ is the wavelength in air, h is Planck's constant, c is the speed of light, E_i is the energy of level i , and n is the refractive index of air. The energy of each level is given in NBS 60 as E/hc in cm^{-1} , referred to the ground level. The refractive index of air is calculated as a function of wavenumber by Edlen's formula [4.18,19]

$$(n-1) \times 10^8 = 8.34213 \times 10^3 + \frac{2.406030 \times 10^6}{(130 - \tilde{\nu}^2)} + \frac{1.5997 \times 10^4}{(38.9 - \tilde{\nu}^2)}$$

where $\tilde{\nu} = (E_2 - E_1)/hc$ is the vacuum wavenumber of the transition, in μm^{-1} .

TABLE 4-9

Nd TRANSITIONS IDENTIFIED BY VARIOUS SOURCES

This Work		Young and Donohue		NBS 145		NSRDS-NBS 60	
Wavelength (nm)	Intensity	Wavelength (nm)	Intensity	Wavelength (nm)	Intensity	Wavelength (nm)	Transition Levels (cm ⁻¹)
455.41	M	455.3	S	--	--	455.415	0.0-21951.9
455.77	W	--	-	--	--	--	--
455.92	W	--	-	--	--	455.917	3681.7-25609.4
455.97	M	455.8	S	455.967	M	455.966	2366.6-24291.9
456.04	W	--	--	456.042	W	456.042	1128.1-23049.8
456.18 ^a	W	--	--	{ 456.186	--	456.176	3681.7-25596.9
456.23	S	456.1	W		W	456.185	3681.7-25596.5
--	--	456.5	W	--	--	456.233	1128.1-23040.5
456.72	W	--	--	--	--	456.408	2366.6-24270.7
				--	--	456.734	1128.1-23016.5

^aPossible unresolved doublet.

Several observations can be made concerning the data of Table 4-9:

1. The use of different dye lasers results in the detection of different RIS resonances and different intensities for those resonances detected by both systems. The most important laser parameters are probably linewidth and power density.

2. Tabulated spectral lines, as in NBS 145, do not completely correspond to RIS resonances. This can cause problems especially in checking for interferences from other elements, since such tabulations are poor indicators of the lack of RIS resonances in a certain wavelength region.

3. The best indicator for RIS resonances could be a list of allowed transitions, as determined by a computer program similar to that described above. For this, an accurate tabulation of energy levels and J-values is necessary (see Ref. [4.20-28]). Note, however, that there are several discrepancies between our data and our list of allowed transitions for Nd.

To our knowledge, no recent compilation or even bibliography of experimentally observed RIS resonances exists (see, however, Ref. [2.12], p. 775). Thus, the only definite method of locating RIS resonances is actual experiment. This should include not only the element of interest, but also those elements which may produce interferences.

F. ISOTOPE SHIFTS

The most valuable application of resonance ionization mass spectroscopy is the measurement of isotope ratios in systems having isobaric interferences, most notably the lanthanide elements. To make such measurements directly, the isotopes must be ionized with equal probability by the laser. This will occur if the laser line-width is much greater than the isotope shift, such that the laser intensity is approximately constant over the wavelength range corresponding to the isotope shift, or if the laser intensity is greater than that required to saturate the RIS process over the wavelength range of the isotope shift.

Neodymium and samarium have isotope shifts in the range 0.003-0.007 nm for transitions used in RIS Scheme 1 [4.29-32]. As mentioned in Chapter II, Section E, the isotope shift of a spectral line depends both on the mean square nuclear radius $\langle r^2 \rangle$, determined by atomic mass number, shell model effects, and nuclear deformity, and on the relative electron density inside the nucleus, $(-e)|\psi(0)|^2$, for the two levels of the transition, which is determined by their respective valence electron configurations. Electron configurations have been assigned to only a few percent of the intermediate neodymium levels which are used in RIS. For samarium, however, most intermediate energy levels have been identified as a mixture of valence electron configurations. The composition of each level is specified by giving the percentage for each of the leading terms, usually $4f^6 6s 6p$ and $4f^5 5d 6s^2$ for samarium and neodymium [4.17].

To approximate the isotope shift for a transition between two pure configurations, we use Eq. (2-17) and the uniformly charged sphere model of the nucleus, as in Figure 2-6 (p. 32). For a point nucleus, the electrostatic potential at all points is $V(r) = q/r$, where $q = Ze =$ charge of nucleus. For a uniformly charged spherical nucleus of radius a , the potential is:

$$V'_{in}(r) = \frac{3q}{2a} - \frac{qr^2}{2a^3} \quad \text{for } r \leq a$$

$$V'_{out}(r) = \frac{q}{r} \quad \text{for } r \geq a$$

Assuming the electronic charge density is constant within the nucleus and defining

$$\rho_c = \frac{-e}{4\pi} \left[4\pi |\psi(0)|^2 \right]_c$$

where c denotes the electron configuration, we have for the shift of the energy levels from the reference energy levels:

$$(E' - E)_{c,A} = \rho_c \int_0^a [V'_A(r) - V(r)] 4\pi r^2 dr = 4\pi q \rho_c \left(\frac{-a^2}{10} \right)$$

where A is the mass number. Converting to MKS units by inserting $1/(4\pi\epsilon_0)$, using $a = A^{1/3}R_0$ and using the definitions of q and ρ , we obtain:

$$\begin{aligned}
 (E' - E)_{c,A} &= \frac{1}{4\pi\epsilon_0} (4\pi Ze) \frac{-e}{4\pi} \left(\frac{4\pi |\psi(0)|^2}{a_0^3} \right) \left(\frac{-a^2}{10} \right) \\
 &= \frac{Ze^2 R_0^2}{40\pi\epsilon_0 a_0^3} (4\pi |\psi(0)|^2_c A^{2/3}) \quad (4-3)
 \end{aligned}$$

The coefficient is a constant for each element and is evaluated using

$$Z = 62 \text{ for samarium}$$

$$e = 1.602 \times 10^{-19} \text{ C}$$

$$R_0 = 1.2 \times 10^{-15} \text{ m}$$

$$\epsilon_0 = 8.854 \times 10^{-12} \text{ (C/Vm)}$$

$$a_0 = 5.292 \times 10^{-11} \text{ m}$$

Then

$$C = \frac{Ze^2 R_0^2}{40\pi\epsilon_0 a_0^3} = 8.675 \times 10^{-8} \text{ eV.}$$

The largest uncertainty in C is due to R_0 , which has ~10% uncertainty.

The energy level shift is then calculated from Eq. (4-3) by inserting the values of $4\pi|\psi(0)|^2$ for the proper electron configuration, and the value of A for each isotope. Wilson [4.33] has calculated Hartree-Fock values of $4\pi|\psi(0)|^2$ for s-electrons in various valence electron configurations in samarium and europium. His results for selected configurations are given in Table 4-10. Table 4-11 gives the energy level shifts for ^{144}Sm and ^{154}Sm as calculated by Eq. (4-3), and the isotope shift for transitions from

TABLE 4-10

ELECTRON DENSITY^a OF ns-ELECTRONS FOR VARIOUS VALENCE ELECTRON CONFIGURATIONS IN Sm

Configuration	$4f^6 6s^2 (=GS)$	$4f^6 6s 6p$	$4f^5 5d 6s^2$	$4f^5 5d^2 6s$
1s	936674	936675	936671	936672
2s	100913	100912	100903	100903
3s	21253	21253	21250	21249
4s	4813	4812	4843	4842
5s	703	701	748	737
6s	46	52	54	43
Total	2128803	2128758	2128941	2128849
$\Delta \frac{4\pi \psi(0) ^2}{4\pi \psi(0) _{GS}^2}$	0	-2×10^{-5}	$+6 \times 10^{-5}$	$+2 \times 10^{-5}$

^aElectron density given in units of a_0^{-3} , where $a_0 = 0.053$ nm = Bohr radius.

TABLE 4-11
ENERGY LEVEL SHIFTS AND ISOTOPE SHIFTS IN Sm^a

Configuration	$4f^6 6s^2 (=GS)$	$4f^6 6s 6p$	$4f^5 5d 6s^2$	$4f^5 5d^2 6s$
Energy Level Shift A=144:	5.0736489	5.0735397	5.0739756	5.0737567
A=154:	5.3059006	5.3057871	5.3062425	5.3060136
Isotope Shift (eV):	--	-4.3×10^{-6}	$+1.5 \times 10^{-5}$	$+5.2 \times 10^{-6}$
(cm ⁻¹):	--	-0.035	+0.12	+0.042
(nm at 442 nm):	--	-0.0007	+0.0024	+0.0008

^aEnergy level shifts calculated from Eq. (4-3), and isotope shifts are calculated for transitions from the ground state configuration.

the ground state to each of the other configurations. The isotope shift ϵ is calculated from the energy shifts by

$$\epsilon_{C,A,A'} = [(E' - E)_{C,A} - (E' - E)_{GS,A}] - [(E' - E)_{C,A'} - (E' - E)_{GS,A'}]. \quad (4-4)$$

This model should give the correct order of magnitude for the isotope shift. More detailed calculations use various other charge distributions and account for quadrupole deformation and shell model effects on the mean square nuclear radius [4.34 and references therein].

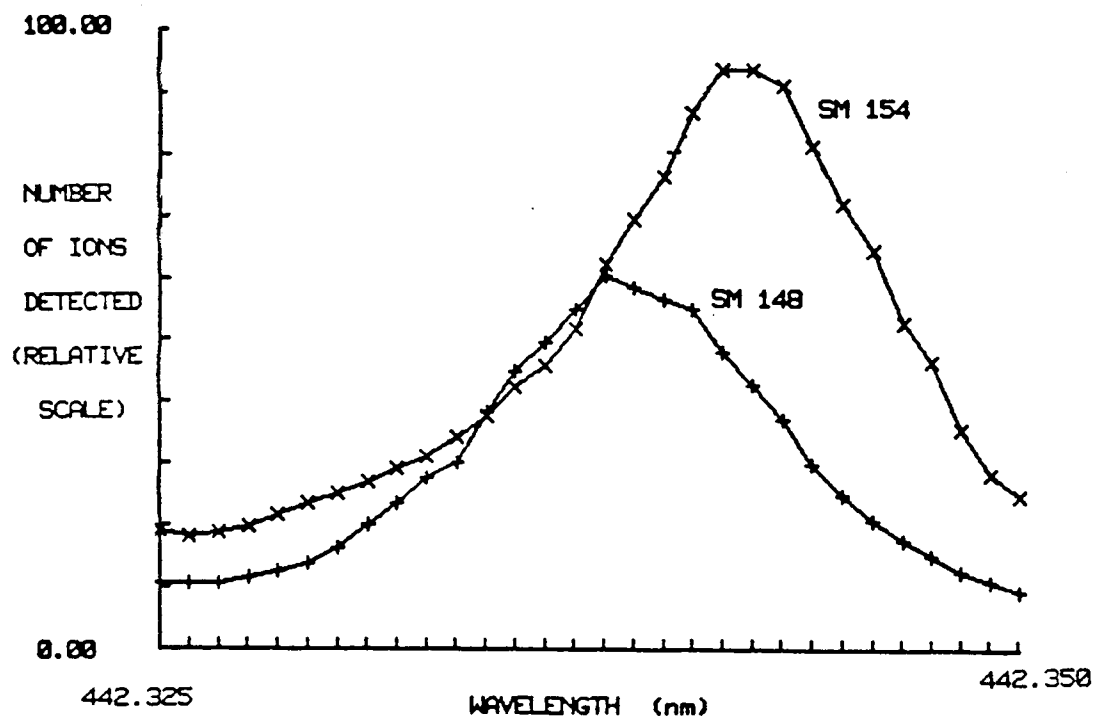
We have used the Resonance Ionization Time-of-Flight Mass Spectrometer system to measure the isotope shift of four Sm transitions and one Nd transition. The general procedure of Chapter III, Section E, was followed, with the dye laser wavelength scanned in small steps over the transition. The dye laser linewidth was 0.007 nm and the scan step size was 0.0007 nm, except for the Sm transition at $\lambda = 440.1$ nm, for which the step size was 0.0014 nm. Table 4-12 summarizes important parameters of each data set.

The data for Sm transitions at $\lambda = 442.338$ nm and 450.443 nm are plotted in Figure 4-11 A and B, respectively. For both transitions, the width of the resonance line for each mass is approximately equal to the dye laser linewidth, thus indicating that the resonance lines themselves are much narrower. This is true even for the odd isotope ^{147}Sm in Figure 4-11B, so the hyperfine splitting must also be much smaller than the dye laser linewidth. Note that the isotope shift in Figure 4-11A is negative (heavier isotope shifted toward lower

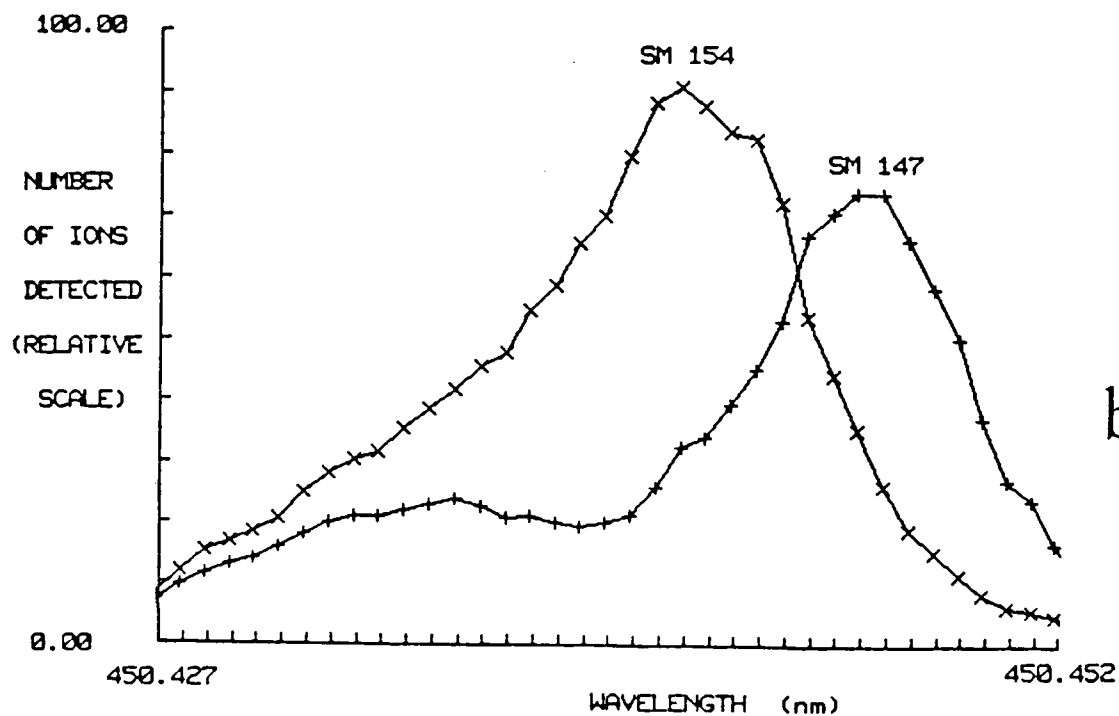
TABLE 4-12
SUMMARY OF ISOTOPE SHIFT DATA FOR FOUR Sm TRANSITIONS AND ONE Nd TRANSITION

Element	Sm	Sm	Sm	Sm	Nd
Wavelength (nm)	435.584 ^a	440.117	442.338	450.443 ^a	456.233 ^a
Ground State					
Energy Level (cm ⁻¹)	293	3125	293	2273	1128
Configuration	95% 4f ⁶ 6s ²	98% 4f ⁶ 6s ²	95% 4f ⁶ 6s ²	98% 4f ⁶ 6s ²	99% 4f ⁴ 6s ²
Intermediate State					
Energy Level (cm ⁻¹)	23244	25840	22893	24467	23041
Configuration	67% 4f ⁵ 5d 6s ²	40% 4f ⁶ 6s 6p 17% 4f ⁵ 5d 6s ²	44% 4f ⁶ 6s 6p 29% 4f ⁵ 5d 6s ²	26% 4f ⁵ 5d 6s ²	--
Mass Numbers	148, 154	148, 154	148, 154	147, 154	142, 148 142, 150
Measured Isotope Shift (nm)	+0.004	+0.003	-0.003	+0.005	-0.002 -0.003
Measured Full-Width Half-Maximum (nm)	148 _{Sm} : 0.016 154 _{Sm} : 0.018	148 _{Sm} : 0.018 154 _{Sm} : 0.018	148 _{Sm} : 0.008 154 _{Sm} : 0.009	147 _{Sm} : 0.008 154 _{Sm} : 0.010	142 _{Nd} : 0.007 148 _{Nd} : 0.006 142 _{Nd} : 0.007 150 _{Nd} : 0.009

^aTransitions not listed in NBS 145; identified by program TRANS as allowed transitions between energy levels of NBS 60.



a



b

Figure 4-11. Isotope Shift Data: a) $\lambda = 442.34$ nm, ^{148}Sm and ^{154}Sm ; b) $\lambda = 450.44$ nm, ^{147}Sm and ^{154}Sm .

energy), while the shift in Figure 4-11B is positive. This is in accordance with the configuration assignments shown in Table 4-11, the calculations based on Eq. (4-4), as shown in Table 4-10, and the trends of previous isotope ratio measurements [4.30-32].

A second resonance is clear in the ^{147}Sm data of Figure 4-11B, while this is evidenced in the ^{154}Sm data only as a small increase in linewidth. NBS 145 lists a resonance line at 450.431 nm, which agrees with the ^{147}Sm data. The transition is between the initial level at 2273 cm^{-1} ($4f^6\ 6s^2$) and the excited level at 22468 cm^{-1} , which has been assigned the tentative configuration $4f^5\ 5d^2\ 6s$. Table 4-10 indicates this transition would have a small positive isotope shift. The data show no sign of a positive isotope shift and would be better explained by a negative isotope shift for this transition, but the evidence is not sufficiently strong to justify this conclusion.

Figure 4-12 shows the data for Sm transitions at $\lambda = 435.584\text{ nm}$ and 440.118 nm . The most striking difference from the data of Figure 4-11 is the increased width of the resonance lines, here well over twice the dye laser linewidth. The linewidth, the convex line-shape in Figure 4-12A, and the structure of the lines in Figure 4-12B strongly suggest the possibility of unresolved multiple resonance lines. Although the transition at 435.584 nm is not listed in NBS 145, it has been identified as an allowed transition by the program TRANS (described in Chapter IV, Section E), which matches any two energy levels having opposite parity which satisfy the selection rule $\Delta J = -1, 0, +1$, but not $J = 0$ to $J = 0$. Neither NBS 145 nor the program

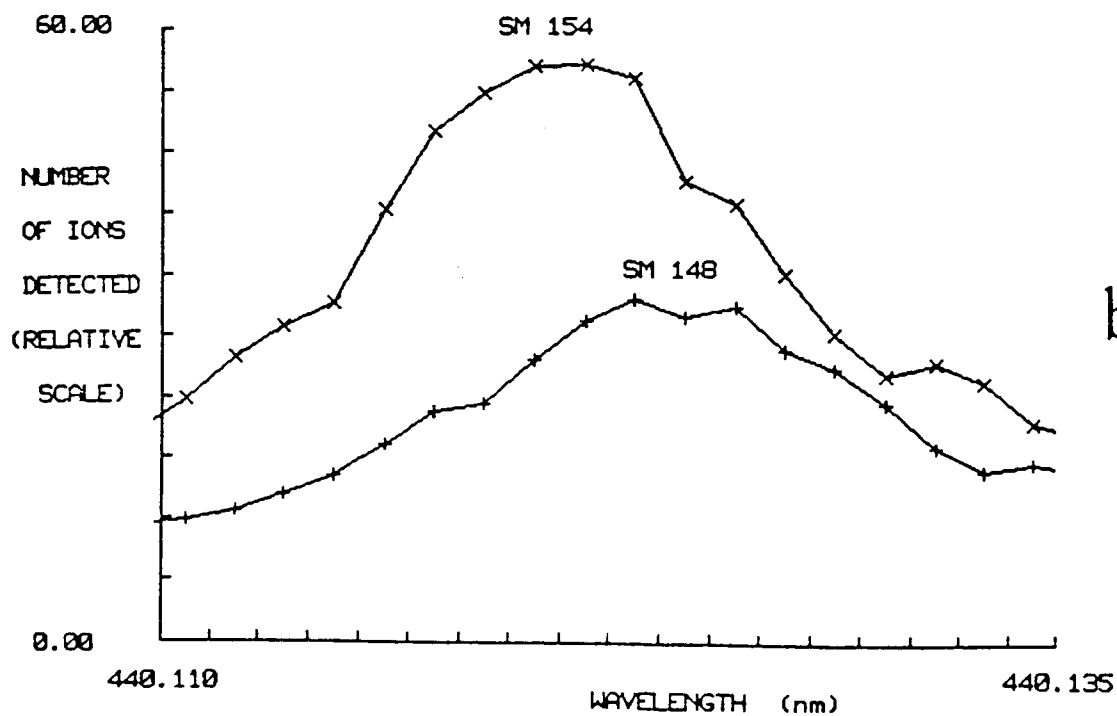
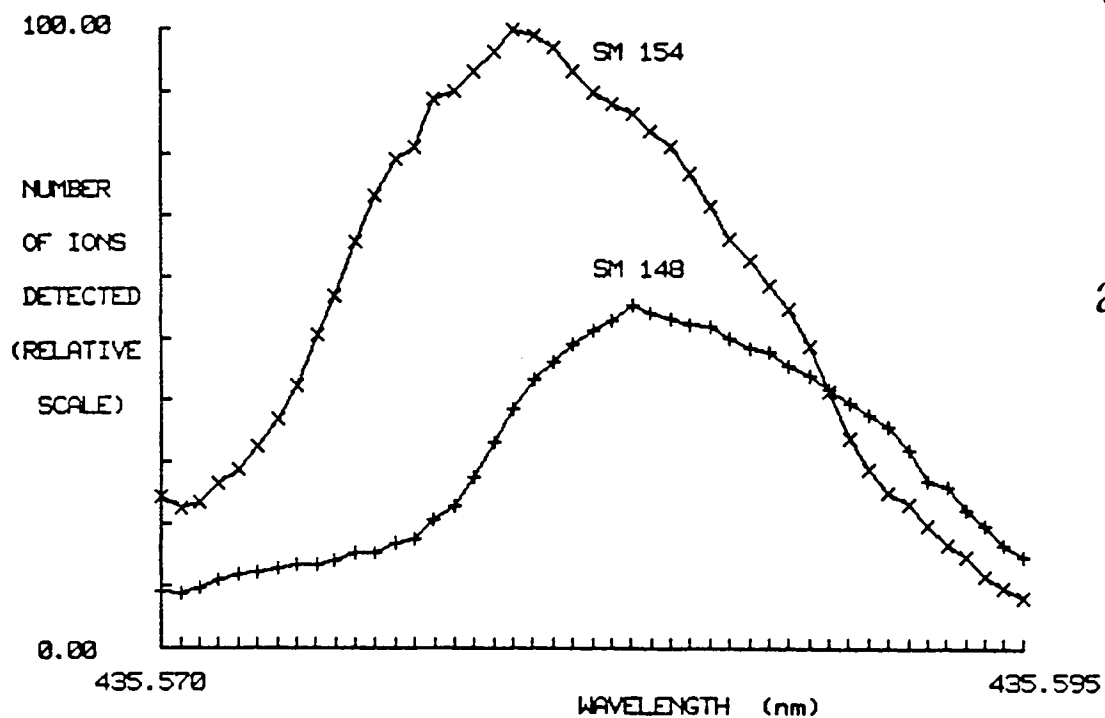


Figure 4-12. Isotope Shift Data, ^{148}Sm and ^{154}Sm : a) $\lambda = 435.58 \text{ nm}$; b) $\lambda = 440.12 \text{ nm}$.

TRANS identify any other resonances in the immediate neighborhood of 435.584 or 440.117 nm.

It should be noted that the positive isotope shift of the transition at $\lambda = 440.117$ nm does not follow the pattern noted earlier for transitions from $4f^6 6s^2$ to $4f^6 6s 6p$. From the configuration assignments of Table 4-11, one would expect a substantial negative shift, larger than that of the 442.338 nm transition. The explanation may lie with the large percentage of the configuration left unspecified. Striganov [4.31] also measured a positive isotope shift for a similar transition, from the $4f^6 6s^2$ ground state to the 23996 cm^{-1} level, which is assigned 35% $4f^6 6s 6p$ + 14% $4f^5 5d 6s^2$. Again, a large percentage is left unspecified.

Figure 4-13 shows the data for the Nd transition at 456.233 nm. The transition is also not listed in NBS 145, but the program TRANS (Chapter IV, Section A) identified this as an allowed transition. We see that the width of each resonance line is nearly equal to the dye laser linewidth, and that the isotope shift is negative and larger for the ^{142}Nd - ^{150}Nd data than for the ^{142}Nd - ^{148}Nd data. No valence electron configuration has been assigned to the 23041 cm^{-1} upper level of the transition, but other investigators find negative isotope shifts in nearly all Nd transitions [4.30].

G. ISOTOPE RATIOS

Figures 4-11 through 4-13 also show the isotope ratio as a function of wavelength, as measured by our system. The measured ratio

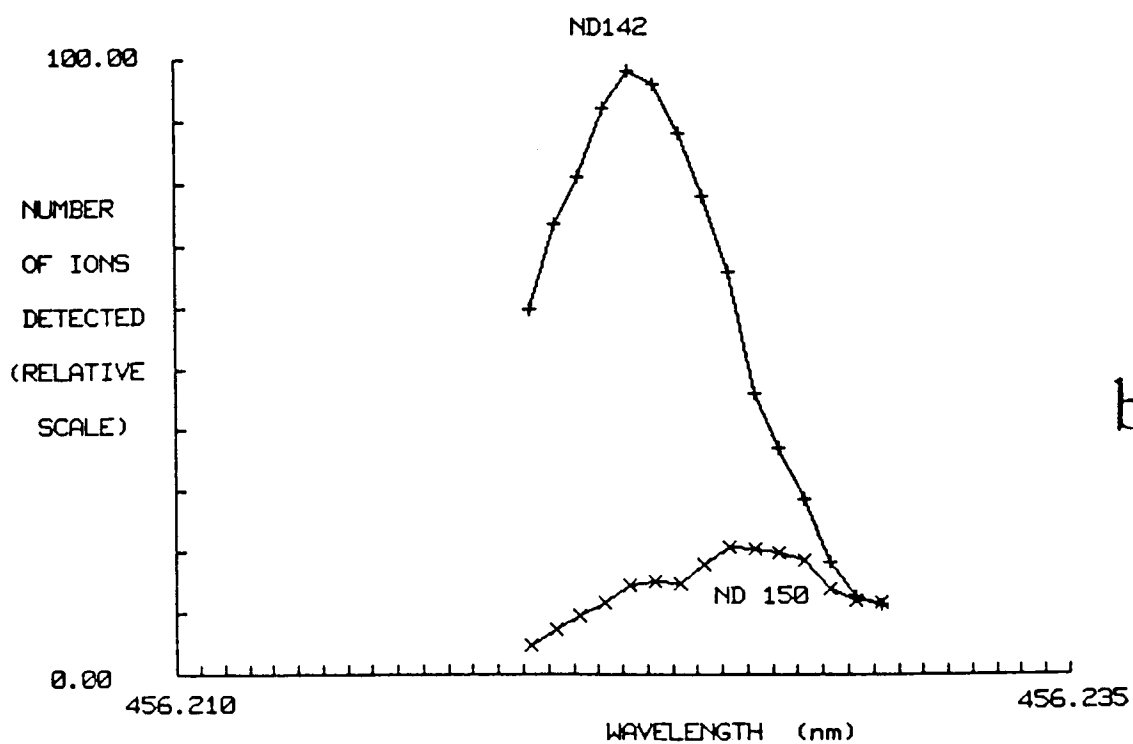
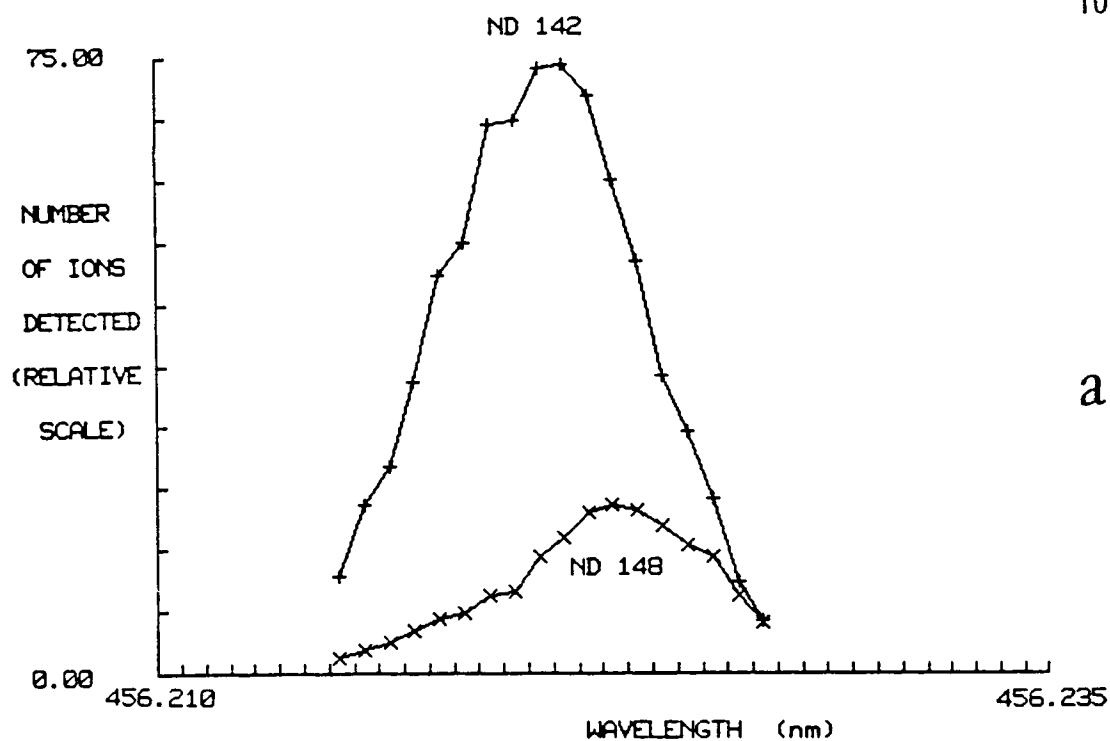


Figure 4-13. Isotope Shift Data, $\lambda = 456.22$ nm: a) ^{142}Nd and ^{148}Nd ; b) ^{142}Nd and ^{150}Nd .

depends strongly on the wavelength, because the dye laser linewidth is smaller than the isotope shift for each transition. With such a laser system, it is not possible to assure equal power levels at the transition wavelength of each isotope. Thus this laser system is not the optimum choice for making isotope ratio measurements.

One possible method of making isotope ratio measurements using the present laser system is to measure the signal for each isotope at the transition wavelength for that isotope, although this nullifies the advantage gained by using the TOFMS to detect all isotopes for each laser shot. The necessary information is available in Figures 4-11 through 4-13 as the ratio of peak heights in each graph. The isotope ratios measured in this way are compared to the standard values [4.8] in Table 4-13. In each case the measured ratio of the more abundant isotope to the less abundant isotope is too low.

One problem might be the previously mentioned unresolved multiple transitions which could make unequal contributions to the signal for each isotope. This should not be a problem for the Nd data, which implies a single, isolated transition. However, the two Nd isotope ratios measured for this transition give -24% and -2.5% error. Further investigations would be necessary if this method is to be used for isotope ratio measurements.

TABLE 4-13
MEASURED Nd AND Sm ISOTOPE RATIOS

Isotopes	Transition Wavelength (nm)	Ratio		
		Standard ^a	Measured ^b	Error
$\frac{^{154}\text{Sm}}{^{147}\text{Sm}}$	450.443	1.50	1.24	-17%
$\frac{^{154}\text{Sm}}{^{148}\text{Sm}}$	442.338	2.00	1.56	-22%
$\frac{^{154}\text{Sm}}{^{148}\text{Sm}}$	435.584	2.00	1.82	-9%
$\frac{^{154}\text{Sm}}{^{148}\text{Sm}}$	440.118	2.00	1.67	-17%
$\frac{^{142}\text{Nd}}{^{148}\text{Nd}}$	456.233	4.74	3.60	-24%
$\frac{^{142}\text{Nd}}{^{150}\text{Nd}}$	456.233	4.85	4.73	-2.5%

^aSee Ref. [4.8].

^bUsing peak heights of Figures 4-11 through 4-13.

CHAPTER V

SUMMARY, CONCLUSIONS, AND DISCUSSION

A. INTRODUCTION

This chapter presents a brief summary of the results of experiments performed on our Resonance Ionization Mass Spectrometer (RIMS) system, including conclusions based on those results. Implications for the design of other RIMS systems are discussed, along with recommendations for extensions of this work and suggestions for other investigations which could be performed with this system.

B. SUMMARY AND CONCLUSIONS

We have assembled a RIMS system consisting of a Nd:YAG laser for vaporization of solid samples, an ionizing laser system composed of two tuneable dye lasers pumped by a single excimer laser, a time-of-flight mass spectrometer (TOFMS), and a novel computer-based data acquisition system with separately gated ADC modules.

We used this system to measure the neutral atom kinetic temperature and the excitation temperature of a laser-produced Sm vapor cloud. For two measurements of the kinetic temperature, the results were 1430 K and 1110 K, with an estimated error of ± 200 K. The excitation temperature was also measured twice, with results of 1616 ± 10 K and 1659 ± 66 K.

Note that the measured excitation temperatures fall at the upper limit of the estimated error in the measured kinetic temperature. We conclude that a real difference exists between the two temperatures for our experimental conditions, although the magnitude of this difference cannot be accurately determined with the available data.

An analysis of the mechanisms involved in the development of the vapor cloud makes the difference in temperatures plausible [5.1]. As the vaporizing laser beam strikes the solid sample, the initial result is a dense, highly ionized plasma. The ions and electrons recombine mainly due to three-body collisions, with another electron receiving the recombination energy. This energy is efficiently distributed among free and bound electrons, thus establishing the excitation temperature in equilibrium with the electron temperature. The recombination energy is less efficiently shared with the ions and neutral atoms due to the large difference in mass. The neutral atom kinetic temperature will then decrease more rapidly than the excitation temperature as the vapor cloud expands.

To fit a velocity distribution function to the kinetic temperature data, it was necessary to include a hydrodynamic velocity [5.2] approximately equal to the thermal velocity. The excitation temperature data for the measured relative population of $5m$ energy levels were matched to calculated Boltzmann factors using effective degeneracies for the levels, which differ from actual degeneracies due to the linear polarization of the excitation dye laser (see Chapter II, Section C).

The selectivity of Resonance Ionization Spectroscopy (RIS) was qualitatively demonstrated in two experiments. First, the mass spectrum of Cr was obtained from a sample of stainless steel, using RIS scheme 1B (Figure 4-5, p. 73). Using Table 4-7 (p. 79) and Figure 4-7 (p. 82), we can estimate that the selectivity in this case was about 1000 (the ionization probability of Cr was 1000 times greater than that of Fe). This is a low selectivity for a RIS experiment. The problem is inherent in RIS scheme 1B, since the ionization step requires a high density of high energy photons. This will always produce some nonresonant ionization, which is the limiting factor here. The selectivity would be greater with lower density of the high energy photons, although this would also decrease the signal. Another problem encountered in this experiment was the unintended resonance ionization of vanadium, which has a transition at the fixed wavelength of the excimer ionizing laser. This is always a potential problem when using fixed wavelength lasers, and can be avoided if photons of appropriate wavelength and flux can be provided by a tuneable laser.

The other demonstration of RIS selectivity was the detection of Nd and Sm individually from a 1:1 alloy of the two metals. In this experiment, the separation was essentially complete. However, the selectivity could not be quantified, because the unselected element was not observed at all. This was especially impressive for the detection of Nd, since we observed that the vapor cloud produced by the laser microprobe contained much more Sm than Nd. This is due to

the much higher vapor pressure of Sm over the temperature range of the sample during laser vaporization (see Figure 4-10, p. 87).

We have then conflicting data as to the mechanism responsible for vaporization of the sample. The kinetic temperature experiment required the use of a hydrodynamic velocity to fit theory with data. This favors the mechanism in which high laser power densities heat and compress the solid beyond the critical point, after which the material expands explosively [5.3]. But this mechanism has been shown to produce a vapor cloud representative of the sample [5.4], which in this case is Nd and Sm in equal amounts. The difference in vapor pressure of the two elements and the observed excess of Sm in the vapor cloud implies the mechanism is simply heating and evaporation of the sample material.

We conclude that we are operating in an intermediate regime, in which the solid is vaporized to a certain depth before the material has time to expand. The material below the surface then exerts a pressure on the surface material, which produces the hydrodynamic velocity. The pressure is not sufficient, however, to significantly change the relative vapor pressure of Nd and Sm.

We have also measured the isotope shift for four Sm transitions and one Nd transition. We found both positive and negative shifts, with magnitude 0.002 to 0.005 nm (0.1 to 0.25 cm^{-1}). The measurements were not precise because the dye laser linewidth was 0.007 nm. The laser linewidth was also too large to resolve the selected resonance in several cases, so other transitions contributed to the excitation and ionization.

However, the dye laser linewidth was too small to accurately measure isotope ratios. Since the linewidth was only twice the average isotope shift, the power level varied considerably over the wavelength range of the isotope shift.

C. DISCUSSION

Since we observed that the composition of the vapor cloud was not representative of the sample composition at the vaporizing laser power density used here, we suggest that higher power density ($>10^{10}$ W/cm²) be used in future work. The determination of appropriate power density would be a project in itself, but any increase would require modifications to the TOFMS source region to allow for the greater number of ions created. The plates and screens used to define the source and accelerating regions of the TOFMS (see Figure 3-3, p. 42) must be shielded from these ions to prevent sparking from the high potential on these plates to the grounded sample.

The size and separation of the plates could be reduced to increase the distance from the plates to the sample. This would also allow the sample to be moved closer to the ionization region, thus increasing the number of atoms within that region as a function of time.

Other investigations concerning the vaporization process include measurement of the vapor cloud composition as a function of the total number of vaporization laser pulses on a particular sample spot, for various vaporization laser power densities, the measurement

of the vapor cloud composition as a function of vaporization-to-ionization delay time, and measurement of the excitation temperature versus vaporization-to-ionization delay time.

Another problem encountered with the current system was the difficulty in verifying the saturation of the RIS process, caused by the Gaussian spatial distribution of the dye laser beam (see Chapter II, Section C). A constant spatial distribution is not easily obtained, but a circular aperture (or two) would provide a much sharper cutoff of the radial power distribution. Similarly, it is desirable to have a constant longitudinal power distribution, i.e., a collimated beam rather than a focussed beam. Thus two lenses arranged as a beam reducer are better than a single focussing lens.

With nearly constant radial and longitudinal power distributions for the dye laser beam, it would be possible to clearly demonstrate saturation of the RIS process and also the saturation of each transition separately. This would allow the measurement of relative cross sections and, with careful calibration, absolute cross sections for excitation and ionization.

The dye laser linewidth is another important parameter of the RIMS system. A narrow linewidth is required for high resolution spectroscopy, such as the measurement of isotope shifts and the identification of specific transitions. A large linewidth is necessary for isotope ratio measurements, so that the power level would be approximately equal, or above the saturation level, at the resonance wavelength of each isotope.

The most appropriate dye laser for an RIMS system depends on the type of experiment to be performed. A flexible system would use two dye lasers, one with narrow linewidth ($\sim 5 \times 10^{-4}$ nm or 0.03 cm^{-1}) and the other with large linewidth (~ 0.03 nm or 1.5 cm^{-1}). For spectroscopic experiments, the narrow linewidth laser would be used at low power for the resonance excitation step, while the large linewidth laser would be used at high power for the ionization step. The spectroscopic information allows the choice of an appropriate transition for isotope ratio measurements (no other transitions within 0.05 nm). The two lasers could then exchange roles: the large linewidth laser would resonantly excite all isotopes of the selected element with equal probability, and the narrow linewidth laser would be used at high power for ionization. The above experiments would best be done using RIS scheme 1A (Figure 2-3, p. 20), with the ionization laser operating at photon energies less than half of the ionization potential to reduce the nonresonant ionization background. A two dye laser system could also use RIS scheme 3 (see Figure 2-1, p. 13), which has two successive resonance excitations followed by ionization from the second excited state.

Another aspect of our work suggests that the current design could be improved by using a flat detector in the TOFMS. We determined that the observed time spread of each mass peak was much larger than that provided by the two-stage ion acceleration system with properly adjusted voltages, due to the depth of the first dynode of the venetian-blind type electron multiplier. A channel plate is essentially flat and would eliminate nearly all of this contribution

to the time spread of the mass peaks, resulting in a peak width of about 15 ns rather than the current 50 ns.

Another possible modification to the RIMS system would make use of a transient digitizer instead of the gated ADC's to quantify the TOFMS signal. Transient digitizers use voltage comparators to digitize the entire mass spectrum at intervals as short as 2 ns. This gives more complete information about the TOFMS signal and simplifies data acquisition, although the data analysis is correspondingly more complex.

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