Manifestation of collective effects of laser photo-plasmas in time-of-flight mass spectrometer

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Abstract. The performance of Time-of-Flight Mass Spectrometer (TOF-MS) has been studied with laser produced photoions of various densities using a reflectron TOF-MS built in our laboratory. In this, the source of atoms is a resistively heated atomic beam source. As the atomic species reach the interaction region, the interaction with pulsed laser results in ions. Samarium was used as the source element to observe all its isotopes by resonant non selective excitation of one of the ground state transitions. However, as the temperature of the source is increased, the collective plasma effect of ions and electrons becomes important. As a result of this the Time-of-Flight signal (in linear mode) of Sm isotopes became poorly resolved from a well resolved condition. The number density of the ions produced in these conditions and hence the plasma parameters were calculated. The plasma parameters like Debye length ($\lambda_D$), the number density ($N_D$), and frequency ($f_{pi}$) confirms the collective effect. In order to avoid this undesired effect, the optimum operating condition with respect to oven temperature and laser intensity was estimated.

1. Introduction

The Time-of-Flight Mass Spectrometer is well adopted worldwide in resonance ionization mass spectrometry (RIMS) [1,2] experiments for high resolution spectroscopy of atoms and molecules. Various geometrical configurations of the basic TOF-MS including the linear and the folded reflectron geometries were developed for these applications. The reflectron geometry has certain distinct advantages over the linear configuration due to the possibility of higher mass resolution achievable. Keeping these advantages in view, we have indigenously developed a reflectron Time-of-Flight Mass Spectrometer (RTOF-MS) which also incorporates a linear TOF-MS. In TOF-MS the interaction of laser with atomic beam results in ions for mass analysis. It was interesting to observe the dependence of photoionization signal on the laser intensity and the oven temperature. With either increase in laser intensity or the atom density there is increase in the number of ions (electrons) in the interaction region. It is shown that as the ion number density exceeds certain values, i.e., > $10^9$/cc, the electrons and ions behave collectively to negate the effect of external electric fields thus leading to temporal broadening of the photoionization signal which in turn deteriorates the mass resolution of the TOF-MS. Similar effects have been reported in literature earlier [3]. The contribution to the ion number density due to non-selective ionization of other species like oxides, etc has been included in our estimation of ion number density. Estimated plasma parameters like Debye length ($\lambda_D$), the number density ($N_D$), and frequency ($f_{pi}$) for a given experimental conditions also points to the collective effect. The operating conditions in one regime with respect to number density and laser intensity at the interaction region for an indigenously developed reflectron TOF-MS will be discussed.

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2. Experimental Details
The experimental set up as shown in figure 1 consists of a reflectron TOF-MS, an Nd: YAG laser pumped dye laser, a 200 MHz oscilloscope, and a fast photodiode. The above RTOF-MS was developed in our laboratory to pursue the laser spectroscopic applications using RIMS set up. The Nd: YAG laser pumped dye laser system used in these studies is a pulsed tunable laser of repetition rate 20 Hz, temporal width 8 nsec, spectral width 0.05 cm\(^{-1}\) and tuning range 555 to 570 nm. The laser beam was focused into the atomic beam in the interaction region inside the reflectron TOF-MS by a lens of focal length 280 mm. The laser system is capable of producing the intensity in the range of \(10^8\) to \(10^9\) W/cm\(^2\) in the focal spot. The mass spectrometer consists of an effusive atomic beam source, an ion source assembly, a field free flight tube (drift tube), a reflectron (ion mirror) assembly and micro channel plate (MCP) detectors. The effusive source is a resistively heated tantalum foil based high temperature cylindrical oven with a small orifice (1.5 mm) for effusion of atomic vapours. The atomic vapours effusing out of the orifice are collimated into a well defined atomic beam by fixed circular apertures placed at desired positions. The ion source assembly consisting of repeller, extractor, einzel lens and steering electrodes is used for guiding the ions into the drift tube. The extraction region is between repeller and extractor electrodes. The acceleration region is between extractor plate and the ground of the einzel lens. The applied electric fields are, 200 V/cm (extraction region), 2.03 kV/cm (acceleration region), 360 V/cm (reflectron region), -40 V/cm (vertical steering), and 74 V/cm (horizontal steering). The einzel lens voltages were 0, 358, and 0 Volts. The drift tube is of length \(\sim 1.35\) m in linear mode and \(\sim 2.38\) m in reflectron mode. The reflectron assembly consists of 20 equispaced (\(\sim 5\) mm) electrodes for reflecting back the ions at an angle set by the incoming beam. The whole assembly is enclosed in a vacuum chamber which is maintained at a pressure of \(<10^{-7}\) Torr. The atomic species reaching the interaction region are resonantly excited and ionized by single Nd: YAG pumped dye laser. The ions so formed are extracted and accelerated in the extraction and acceleration regions of the mass spectrometer. The ions are further guided by the electrostatic einzel lens and steering plates into the MCP detectors. The ion signal detected by MCP detectors is amplified by fast-amplifiers and is displayed on oscilloscope. The laser based photodiode signal is used to trigger the oscilloscope. The oscilloscope data is stored in the computer with the help of a standard software.

![Figure 1. Schematic of the experimental set up.](image-url)
A collimated Sm atomic beam generated by heating the small quantity of Sm metal in the oven to a temperature of around 1000 °C was non-selectively photoionized using single-colour three-photon photoionization scheme. Sm was chosen as a test element because of its high vapour pressure (1k Pa at 1148 °C [4]) and natural abundance of large number of its isotopes. Figure 2 shows the level scheme for the photo-ion generation.

![Figure 2. Two possible photoionization Schemes.](image)

The ground state configuration of Sm I is \{Xe\} 4f^66s^2 and the corresponding term \(7F_{1(0,6)}\) is septet. As shown in figure 2 the single-colour three-photon photoionization feature at laser wavelength 559.47nm corresponds to transition energy 17880.50 cm\(^{-1}\) originates from \(7F_2\) and \(7F_4\) sub levels as reported [5]. The one starting from \(7F_2\) is a two photon resonant excitation with near resonant in first step while the other one starting from \(7F_4\) is resonant in both first and second excitation steps. The third photon ionizes in non-resonant process in both cases. Figure 3 shows the RTOF-MS spectra of Sm I.

![Figure 3. The reflectron Time-of-Flight spectra of Sm I and its oxides.](image)
Since the laser line width (0.05cm⁻¹ or 1.5 GHz) is much larger than the Sm isotope shifts (~100MHz) all the isotopes are photoionized non-selectively. TOF spectra of Sm photoions, produced by non-isotopic selective photoionization of the Sm atomic beam, are recorded using TOF-MS in reflectron mode. These spectra were recorded at laser intensity of the order of 10⁸ Watt/cm². As is evident from the figure 3 all isotopes of Sm as well as their oxides are well resolved. The mass resolution of ~1000 was observed for ¹⁵²Sm⁺ in our RTOF-MS. The recorded Sm spectrum is linear as shown in figure 4.

This implies that the total time of flight of different isotopes in this range can be converted to a mass spectrum for convenience.

For the purpose of simplification and comparison TOF-MS was used in the linear mode for ion density variation experiments. Figure 5 shows the typical TOF-MS spectra of Sm I and its oxides. The unwanted in-between peaks are the result of ringing effect that is normally associated with high frequency signals.

![Figure 4](image-url)  
Figure 4. Linearity of the observed Sm Time of flight spectra.

![Figure 5](image-url)  
Figure 5. Typical linear Time-of-flight spectra of Sm I and its oxides.
With the aim of identifying the optimum operating condition for operation of our mass spectrometer in this regime we have investigated the dependence of its performance on the ion density. The performance of the TOF-MS in terms of its resolution is expected to deteriorate at the production of higher ion densities in the interaction region due to the plasma effects where collective behavior starts dominating over the individual single particle. The ion density in the interaction region was varied either by changing the oven temperature, i.e., atomic number density by keeping the laser intensity constant and vice versa. During these experiments all the applied voltages were kept constant. The TOF spectra of $^{152}\text{Sm}^+$ ion signal recorded in different conditions are shown in figures 6 and 7. It is quite apparent from these figures that the TOF-MS spectra of Sm I isotopes become poorly resolved at higher ion densities from the well resolved one.

![Figure 6. Effect of change in oven temperature on $^{152}\text{Sm}$ isotope signal.](image1)

![Figure 7. Effect of change in laser intensity on $^{152}\text{Sm}$ isotope Signal.](image2)

We have estimated the ion density in the interaction region from the photoionization signal. At these number densities we calculated various plasma parameters such as Debye length ($\lambda_D$), the number density ($N_D$), frequency ($f_{pi}$), etc.

### 3. Results and Discussion

Samarium is a rare-earth element having seven stable isotopes with the following abundances: $^{144}\text{Sm}$ (3.07%), $^{147}\text{Sm}$ (14.99%), $^{148}\text{Sm}$ (11.24%), $^{149}\text{Sm}$ (13.82%), $^{150}\text{Sm}$ (7.38%), $^{152}\text{Sm}$ (26.75%) and $^{154}\text{Sm}$ (22.75%) as given in [6]. The vapour pressure of Sm at the operating temperature T K is given by the derived empirical relation as per [7]

$$\ln P(\text{atm.}) = -\frac{22572.8}{T(\text{K})} + 11.28.$$ 

The number densities of the effusing particles ‘n’ from orifice of area ‘$\sigma$’ at a later distance ‘r’ with angle ‘0’ inside the chamber is given by [8]

$$n(r,0) = \frac{n_0 \sigma \cos \theta}{4 \pi r^2},$$

where $n_0$ (or $P/ kT$) is the number density of particles inside the oven at absolute temperature T. At any working temperature T various atomic levels of Sm will be populated according to the Maxwell-Boltzmann distribution. We have calculated the atoms population as function of temperature for the ground state septet of Sm. The resultant combined population distribution for both $^7F_2$ and $^7F_4$ states
correspond to a factor ~ 0.35. Since single–colour three-photon photoionization transition at energy 17880.50 cm\(^{-1}\) used for photoionization of Sm originates from \(^7\text{F}_2\) and \(^7\text{F}_4\) states therefore atoms in these two states are only considered for the calculations of the atomic number density in the interaction region. The number densities \(n\) in the interaction region inside the chamber are calculated using the above equations. In the table 1, the \(n\) values are for \(r = 5.5\text{cm}, \theta = 0^\circ\), orifice diameter = 1.5 mm and \(\sigma = \pi (0.075)^2 \text{cm}^2\), and a factor ~0.35 for combined populations in states \(^7\text{F}_2\) and \(^7\text{F}_4\) is considered. However, these number densities are still less by a factor 0.1 as described in [9].

The ion densities in the interaction region were estimated from the integrated ion signal. The gain of the fast amplifier 100 on a 50 \(\Omega\) output, the gain of MCP detector \(\sim 2.5 \times 10^3\) at \(-1.3\text{kV}\), the transmission of 41\% (80\% each in 4 stages), the laser spot size of diameter 0.028 cm and atomic beam length of 5 mm was considered. For both isotope and the oxides only one signal was integrated and from the abundance the total ion density was estimated. The contribution of the corresponding oxide ion signals is in the process of non-selective ionization. The plot in figure 8 describes the change in total ion density with temperature and the figure 9 represents variation in total ion density with laser intensity.

![Figure 8. Total ion density vs. temperature.](image)

![Figure 9. Total ion density vs. laser intensity.](image)

The estimated neutral number density, interaction volume and experimental parameters are tabulated in table 1.

**Table 1. Number density of atoms, ions and oxides in the interaction region.**

| Sr. No. | Temp. (K) | Intensity \(10^4\text{W/cm}^2\) | Neutral Density \(10^{11}\text{cm}^{-3}\) | Sm I Ion Density \(10^8\text{cm}^{-3}\) | SmO Ion Density \(10^8\text{cm}^{-3}\) | Int. Volume \(10^5\text{cm}^{-3}\) | Total Ion Density \(10^8\text{cm}^{-3}\) | FWHM (ns) |
|--------|----------|-------------------------------|---------------------------------|-----------------|-----------------|-----------------|-----------------|----------|
| 1.     | 1400     | 12                            | 6.91                            | 3.14            | 2.82            | 3.079           | 5.96            | 15.3     |
| 2.     | 1500     | 12                            | 19.1                            | 7.34            | 3.72            | 3.079           | 11.1            | 28       |
| 3.     | 1650     | 12                            | 68.9                            | 21.1            | 4.16            | 3.079           | 25.3            | 93.8     |
| 4.     | 1650     | 6.1                           | 68.9                            | 4.46            | 4.68            | 3.079           | 9.14            | 14       |
| 5.     | 1650     | 8.1                           | 68.9                            | 7.9             | 6.19            | 3.079           | 14.1            | 42       |
| 6.     | 1650     | 12                            | 68.9                            | 21.1            | 3.24            | 3.079           | 24.4            | 94       |
To describe the phenomena as plasma the following three quantities were calculated as per the expressions given in [10]. The Debye length,

$$\lambda_D = 740 \left( \frac{kT}{n} \right)^{\frac{1}{2}} \text{cm};$$

the number density,

$$N_D = \frac{4}{3} \pi \left( \lambda_D \right)^3 n;$$

and the plasma oscillation time period,

$$\tau_p = \left( \frac{n}{10000} \right)^{\frac{1}{2}} \text{sec};$$

where \( kT \) is in eV and \( n \) is in cm\(^{-3}\) (m\(^{-3}\) for \( \tau_p \)). These quantities with \( \lambda_D < \text{spot size}, N_D >> 1 \), and \( \tau_p << \text{time of flight} \), result in plasma effect. The estimated experimental parameters and the plasma parameters are tabulated in table 2.

**Table 2.** Estimated experimental and plasma parameters.

| Sr. No. | Temp. (K) | Intensity (10^8 W/cm\(^2\)) | Ion No. Density (10^8 cm\(^{-3}\)) | Spot Size (cm) | \( \lambda_D \) (cm) | No. density (10^4 N_D) | \( \tau_p \) (ps) | Electron Temp. (eV) | Remarks |
|---------|-----------|------------------------------|-----------------------------------|----------------|----------------|----------------------|----------------|-------------------|---------|
| 1.      | 1400      | 12                           | 5.96                              | 0.028          | 0.026          | 3.2                  | 4.55           | 0.74              |         |
| 2.      | 1500      | 12                           | 11.1                              | 0.028          | 0.019          | 4.4                  | 3.34           | 0.74              |         |
| 3.      | 1650      | 12                           | 25.3                              | 0.028          | 0.013          | 7.3                  | 2.21           | 0.74              | Collect. Effect |
| 4.      | 1650      | 6.1                          | 9.14                              | 0.028          | 0.021          | 2.19                 | 3.67           | 0.74              |         |
| 5.      | 1650      | 8.1                          | 14.1                              | 0.028          | 0.017          | 2.88                 | 2.96           | 0.74              |         |
| 6.      | 1650      | 12                           | 24.4                              | 0.028          | 0.013          | 3.57                 | 2.25           | 0.74              | Collect. Effect |

It is quite apparent from the table 2 that with either increase in temperature or laser intensity the collective effects due to the formation of relatively dense photo-plasma becomes more dominating. Hence resulting in the broadening of the temporal width of the ion signal and thus deteriorating the resolution of the TOF-MS.

**4. Conclusion**

We have indigenously developed a reflectron TOF-MS in our laboratory. The RTOF-MS resolution \( \sim 1000 \) for \(^{155}\text{Sm}^+\) was demonstrated. The ion signal dependence on the laser intensity and oven temperature was studied. We have shown that for the ion density > 10^9/cc, the collective behavior starts dominating and thus leading to poor resolution of TOF-MS over and above the deterioration in resolution expected due to the velocity spread. Therefore, for the best performance of TOF-MS the ion density <10^9/cc is desirable.

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