Chapter 2

Specific Design Aspects in Laser Spectroscopy Based Experimental Techniques to Explore Atomic/Molecular Structure

- *Asawari D Rath*

2.1 Introduction

The studies on structure of atoms/ions/molecules in gaseous phase are indispensable in many fundamental as well as applied areas of physics. In fundamental research, this knowledge enables one to validate the atomic/molecular or even nuclear models. In applied research e.g. trace analysis, laser ion source, elemental/isotope separation, etc., it is vital in designing experimental schemes for efficient detection or selective excitation and ionization of a particular species, be it atom, ion or molecule. This calls for precise characterization of the structure of the desired species in terms of an extensive spectroscopic database inclusive of its characteristic energy levels, level life times, angular momenta, spectral lines, their strengths, isotope shifts and hyperfine profiles, various interaction cross-sections with photons or electrons, etc. The best way to build such a comprehensive database is through probing its structure using lasers. A variety of high resolution laser spectroscopic techniques utilize different aspects of laser-matter interaction and provide us with precise information on atomic/ionic/molecular parameters.

2.2 Why Laser Spectroscopy?

As lasers are superior to the conventional sources of light in terms of their high monochromaticity, high brightness, low divergence, high degree of coherence, etc., laser spectroscopy offers many advantages over the conventional spectroscopic techniques. Some of them are listed below:

i. Higher spectral resolution - The spectral resolution is generally limited by the source line widths (Doppler broadening) or laser line widths as against the resolving power of the dispersing spectrometer in conventional techniques. With certain laser based high resolution techniques, one can obtain sub-Doppler resolution limited by the natural line width of the species under study.

ii. Improved sensitivity - The detection sensitivity improves due to higher spectral densities of lasers

iii. Improved precision - High spectral resolution and better sensitivity improve the precision of the experimental data

iv. Atoms/Molecules can be prepared in specific excited state(s) of choice

v. Multi-step, multi-colour and selective excitation of samples to higher energy states is possible.

vi. By virtue of higher brightness, better directionality, higher spectral density and coherence, lasers can be focused to obtain high intensities and nonlinear effects in laser-matter interaction can be realized.

With these intrinsic advantages laser spectroscopy offers a powerful tool in applications covering both fundamental and applied aspects of research.

2.3 Devising an Experiment

A basic laser spectroscopic experiment is based on some form of laser-matter interaction like resonant or non-resonant photon absorption, fluorescence, ionization, etc. Devising an experiment broadly involves following five steps as shown in Fig. 2.1:

1. Selection of the spectroscopic source,
2. Selection of the right kind of radiation source,
3. Selecting the laser-matter interaction event,
4. Detection of the spectroscopic event and data acquisition, and
5. Interpretation and analysis.

All these choices are mainly driven by the objective of experiment, what information/aspect is being investigated and what is the species under investigation, albeit, they are strongly interlinked. Let us discuss these steps briefly in what follows. Depending on the objective of the experiment, choice of suitable radiation – matter interaction has to be made e.g. excitation of the species, resonant absorption of radiation, emission from the species, fluorescence, ionization, etc.

2.3.1 Spectroscopic source

The spectroscopic source can be an ensemble of atoms/ions/molecules in solid, liquid, gas phase or in the form of well-collimated beam/jet of atoms, ions, molecules, aerosols or clusters. Here, the emphasis is mainly on gaseous phase atoms/ions. Typical sources of gas phase atoms are

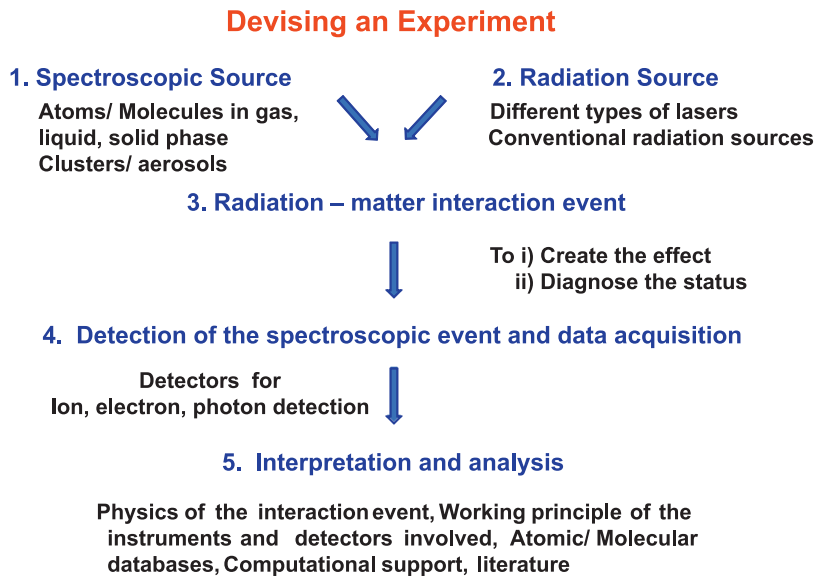

Figure 2.1: Different steps involved in devising an experiment.

- Collimated atomic beams using resistively/inductively heated ovens or electron gun bombardment;
- Hollow cathode discharge lamps (HCDL);
- Gas/Vapour cells.

Each of these sources comes with its own advantages or disadvantages. e.g. collimated atomic beams derived from resistively heated ovens offer clean environment for the species under study with most of the atoms populated in ground or lower meta-stable energy levels. However, efficient vapourization of refractory elements using resistive heating is very challenging and difficult task. Use of electron gun or induction heating may be an answer to this problem, however, their use in atomic source requires special designs to ensure external electro-magnetic field-free region in the laser (radiation)-atom interaction zone. Hollow cathode discharge lamps prove to be very simple and economic source of atoms and ions especially of refractory elements, however, there is presence of buffer gas atoms and ions along with the atoms and ions of element under study. Further, even very high lying excited energy levels are also significantly populated. On one hand it may be exploited to one's benefit in studies on emission spectra of neutrals as well as ionic spectra, while, on the other hand, it is not a "clean" system for studies such as photoionization dynamics, exploring new atomic levels connecting from a specific lower level without ambiguity where atomic population is required to be concentrated in a particular energy level - mostly ground level. For gaseous atoms like noble gases or elements with low melting point near room temperature, gas/vapour cells serve as excellent source of atoms. Fig. 2.2 depicts some popularly used atomic beam sources. For experimental techniques like emission spectroscopy, opto-galvanic spectroscopy, absorption or saturated absorption, hollow cathode discharge lamps (HCDL's) prove to be very good choice. HCDLs contain a hollow cylindrical cathode made from the refractory element under study and a ring shape anode in typically a glass enclosure which is filled with a noble gas called buffer gas at typical pressures of few torr. When appropriate voltage is applied between the anode and cathode, discharge is struck in the buffer gas forming its ions and electrons. The positive ions travel towards cathode. In doing so, they gain energy and impinge on the cathode surface (inner part of cylinder) subsequently sputtering the cathodic material in to

the discharge. Thus, the atomization of a refractory metal can be achieved at relatively low temperatures. There are three main discharge regions in this geometry: cathode dark space, negative glow and positive column. The negative glow region contains ions, electrons and neutral atoms of both the buffer gas and cathodic material. Consequently the HCDL's are a good source for emission spectroscopy. Advantages of HCDLs are as follows:

- No electric field in the negative glow region resulting in field free spectra;
- Low pressure of the order of few torr ensures no observable pressure broadening effects;
- Refractory metal atomization is achieved much below its MP;
- The Doppler broadening associated with neutrals is much narrower compared to the Doppler broadening at source for other sources of atoms.

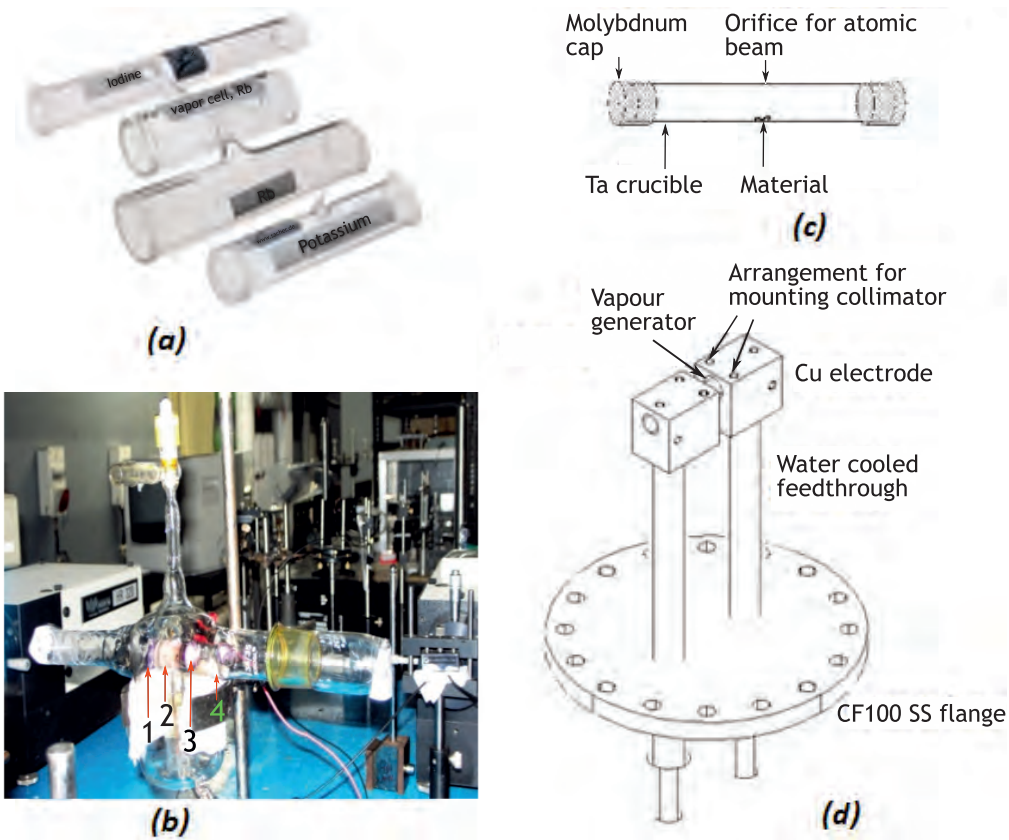

Figure 2.2: Examples of atomic sources: (a) vapour cell for atomic (molecular) gases and elements having low melting point (image source [13]), (b) glass hollow cathode discharge lamp with hollow cylindrical cathode made of material under investigation and anode in the form of tungsten ring (1 - Anode, 2 - Cathode, 3 - Discharge and 4 - Glass envelope), (c) resistively heated oven to generate collimated atomic beam, and (d) water cooled holding arrangement for the oven in (c).

2.3.2 Radiation source

Advent of lasers has revolutionized the field of high resolution spectroscopy by virtue of their distinctively superior properties over conventional incoherent light sources as described in

section 2.2 above. There are a great variety of laser sources with diverse characteristic. Synchrotron radiation and free electron lasers are next generation coherent radiation sources, which offer high intensities at higher frequencies in the regime of soft/hard UV to soft/hard X-rays, thus, making them the right choice for high-energy, high-intensity laser-matter interaction in nonlinear domain. Table 2.1 presents some radiation sources with their typical powers/energies. From the tabulated values, typical peak powers attainable with these lasers can be calculated. The lasers can operate in continuous mode (CW) or pulsed mode. They differ in various aspects like wavelength (range), average power, peak power, divergence, laser line width, pulse duration, wavelength tunability, coherence properties, etc. In some applications other aspects like portability, cost, ruggedness, ease in operation, etc., also need to be considered. Depending on the objective of the experiment, nature of investigation, and the material to be studied, the laser source with suitable parameters should be selected. For most experiments towards generation of atomic database or based on resonant laser-atom interaction, laser wavelength, tunability (so that its wavelength can be tuned in resonance with atomic transitions) and line width (the narrower, the precise data) are important criteria along with other experiment specific requirements and solid state laser pumped dye lasers offer a suitable choice.

Table 2.1: Some radiation sources with typical parameters.

Light Sources	**Power/pulse energy**	**Pulse duration**	**Linewidth**
CW Diode laser	50 mW	—	Sub-MHz
Nd: YAG pumped dye laser	50 mJ	10 nsec	1-6 GHz
Nd: YAG laser/DPSSL	500 mJ	10 nsec	Tens of GHz
Picosecond solid state laser	3 mJ	10 ps	Few nm
Femtosecond solid state laser	1 mJ	50 fs	Tens of nm
Synchrotron	200 μJ	nsec	Sub-nm
Free electron laser	50 μJ	30 fs	Tens of nm

2.3.3 Laser-atom interaction event

This is the most vital part of the laser spectroscopic experiment. A certain laser-atom interaction phenomena is employed to create certain effect like change in physical property or change in atomic state consequent to emission/absorption of photons, ionization, etc. Thus, an 'event' is triggered by laser-atom interaction. The effect of this interaction is detected. Various high resolution spectroscopic techniques, diverse in nature depending on what is detected and how (methodology used for measurement of the effect of the event), can be used to probe the structure of matter. Table 2.2 summarizes various techniques commonly used in high resolution laser spectroscopic experiments.

2.3.4 Detection of the spectroscopic event

The nature of detection decides the detector to be used and the subsequent electronics required for data acquisition. The detection can be in continuous mode, pulsed mode after a delay or in gated mode. For photon detection photo-multiplier tubes and photodiodes are commonly used. For ion detection Faraday cups, electron multipliers (Channeltron, MCP -micro channel plates), photo-multiplier conversion dynodes are used. In opto-galvanic spectroscopy using HCDLs, change in the discharge current consequent to change in discharge impedance is detected. Even though primary detection may be of photons, ions or other

parameters like impedance, often, this is converted into a voltage signal by suitable electronics. The sensitivity, response time and dynamic range of a detector are additional important criteria in their selection.

Table 2.2: High resolution laser spectroscopic techniques.

Technique	**Spectroscopic Event**
Laser absorption spectroscopy • Saturated absorption spectroscopy (SAS)	Absorption of photons resonant to atomic spectral line SAS is a high resolution technique giving sub-Doppler resolution. It is based on intense pump laser and weak probe laser used for achieving sub-Doppler resolution
Fluorescence spectroscopy	The atoms are prepared in specific state under study by resonant laser excitation and consequent fluorescence is studied
Opto-galvanic spectroscopy (OGS)	The change in discharge characteristics like impedance is measured when laser resonant to spectral line of discharge species irradiates the discharge
Photoionization spectroscopy • Photo ionization (PI) OGS • RIMS (Resonance ionization mass spectroscopy)	Resonant or non-resonant multi-step, multi-colour photoionization ✓ In photoionization OGS, the ionization event takes place in cathode dark space of hollow cathode. ✓ In RIMS, resonance ionization is combined with mass spectrometers to achieve two-fold advantage of elemental/isotopic selectivity combined with elimination of isobaric effect usually seen in mass spectrometers
Laser polarization spectroscopy	Effect of laser polarizations on photon absorption or ionization is employed
Time resolved spectroscopy	This is a method of detection employed in above high resolution techniques. Event (absorption, fluorescence, ionizataion, etc) is triggered and detection is delayed and gated in time. Time evolution of the interaction process can be studied using measurements at varying delays.
Pump-probe spectroscopy e.g. saturated absorption spectroscopy	The effect is created by pump laser and quantified/measured using the probe laser
Laser induced breakdown spectroscopy (LIBS)	High intensity laser pulse converts part of the sample into nanoplasma after irradiation. The emissions from this plasma at various time scales owing to recombination of ions/neutrals or de-excitation of excited species to lower energy levels are measured.

2.3.5 Interpretation and analysis

Any experiment is incomplete without appropriate analysis and interpretation of results. Before the experiment is performed, assessment of what to expect based on theoretical understanding is very important in improving overall quality of the work. Often, to extract required spectroscopic parameters from the recorded data, one needs to model the interaction event theoretically. Theoretical simulations of the process when fitted with experimental results provide required parameters under investigation.

2.4 Summary

Physics of the interaction event, good knowledge of working principle of the instruments and detectors involved, atomic/molecular databases, computational tools, etc. is requisite in designing and executing a high quality spectroscopic experiment. In BTDG, many applications like separation of medical isotopes based on selective photoionization of desired isotopes in gaseous phase have been realized which stand on the strong foundation of extensive high resolution spectroscopy studies of these elements.

Suggestions For Further Reading:

a) [14–16]