Spectroscopic studies of Group-IIB elements and Detection of Explosive materials using LIBS

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Spectroscopy

Absorption Spectroscopy
Multi-step laser excitation of Zn, Cd and Hg

Emission Spectroscopy
Explosive Detection using LIBS
• The bound states of Cd, Zn and Hg are not extensively studied.
  (The resonance levels $^1P_1$ lie in UV and VUV region
  Ionization potentials are very high (8-10 eV))

• We have selected the inter-combination levels $^3P_1$ to
  approach the Rydberg states. The $^3P_1$ level lie at lower
  energy as compare to $^1P_1$.

• The fine structure energy difference is not very large
  therefore, the $^3P_2$ and $^3P_0$ metastable state get populated
  due to collision energy transfer.

• Consequently, one can observe the Rydberg level
  possessing larger $J$-values.
Advantages of the multi-photon excitation

- Multi-photon and multi-step excitation we can excite the atoms that can not be approached by single photon excitation.

- Transitions in the VUV region can be investigated.

- The spectral resolution depends upon the line-width of the dye laser at each step.

- Step-wise excitation provides the maximum probability of exciting the atoms in the highly excited states.
Schematic Diagram of Experimental Set-up
Two-step laser excitation Scheme of Cadmium

Cadmium, Z=48
Ground State 4d10 5s^2 1S0

\[ \lambda_1 = 30656.13 \text{ cm}^{-1} \]
\[ \lambda_2 = 41833.94 \text{ cm}^{-1} \]
or 3261.9 Å
or 2387 Å
Fig. 2

Photo-excitation spectrum of Cadmium
Photo-excitation spectrum of Cadmium

Fig. 4
Zinc Z=30
Ground State 3d^{10}4s^{2} 1S_{0}

Energy Levels Diagram of Zn

\begin{align*}
\lambda_1 &= 22097 \text{ cm}^{-1} \\
&\quad \text{or } 4525 \text{ A}^0 \\
\lambda_2 &= 21170.82 \text{ cm}^{-1} \\
&\quad \text{or } 4723.4 \text{ A}^0 \\
\lambda_3 &= 32501.39 \text{ cm}^{-1} \\
&\quad \text{or } 3076.8 \text{ A}^0
\end{align*}
Two-step laser excitation spectra of zinc excited from the fine structure components $^3P_{0,1,2}$
Two-step excitation spectrum of mercury

photoionization cross section measurements of zinc excited state.

\[ N_i = N_0 \left[ 1 - \exp\left(\frac{-\sigma U \lambda_{\text{ion}}}{2 \hbar c A}\right) \right] \]

4s4p^3P_1 \rightarrow 4s^2S_{1/2}

\( \sigma = 54 \pm 8 \text{ Mb} \)

\( \lambda_{\text{ion}} = 231 \text{ nm} \)

Oscillator strength of the Rydberg transitions of zinc

\[
f_n = \frac{4\pi \varepsilon_0 mc}{\pi e^2} \left( \frac{S_{Ryd}^*}{S^+} \right) \left( \frac{\nu_n}{\nu^+} \right) \sigma^+(\nu)
\]

\[
\frac{(n^*)^3 f_n}{2R} = \frac{df}{dE}
\]

\[
\frac{df}{dE} = 9.11 \times 10^{15} \sigma(E) \text{ cm}^{-2} \text{ (eV)}^{-1}
\]

Laser Induced Breakdown Spectroscopy (LIBS)

Laser Induced breakdown Spectroscopy is an emission spectroscopic technique with wide range of applications in different fields.
Laser Induced Breakdown Spectroscopy

Attractive Features

• Real-time sensor technology, Little or no sample preparation is required.
• Versatile technique for the analysis of solids, liquids gases, bulk and residue.
• Sensitivity to parts-per-billion and picogram levels is possible.
• It is non-invasive due to very small sampling regions.
• Simple and rapid analysis (ablation and excitation processes are carried out in a single step)
• LIBS sensors can be made rugged and field portable
Applications of Laser Induced Breakdown Spectroscopy

• Detection of explosive materials.
  LIBS is very much efficient technique for explosive detection, especially at a remote distance and at ppb level.

• Detection of landmines
  Field potable LIBS systems are vital to detect landmines, improvised explosive device (IED), unexploded ordnance etc.

• Home-land security
  Home-land security requires capability for the detection of trace elements and residues in a variety of conditions e.g., in airplane, train, ship passenger luggage, within transport container.

• Bio photonics
  Characterization of normal and malignant tissue cell.

• Other applications include the material analysis, environmental monitoring, investigation of very hard materials and simultaneous multi-elemental analysis is possible (e.g. ceramics and superconductors)
Explosive Detection:

- The detection of explosive materials and residues of explosives in real time is a challenging problem.
- Explosives are organic compounds, containing carbon, hydrogen, oxygen and nitrogen.
- The emission spectra of energetic materials contains four elements and molecular bands of CN and C₂.

<table>
<thead>
<tr>
<th>Explosive</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>RDX</td>
<td>C₃H₆N₆O₆</td>
</tr>
<tr>
<td>TNT</td>
<td>C₇H₅N₃O₆</td>
</tr>
<tr>
<td>PETN</td>
<td>C₅H₈N₄O₁₂</td>
</tr>
<tr>
<td>HMX</td>
<td>C₄H₈N₈O₈</td>
</tr>
</tbody>
</table>
Decision making strategy for Explosive detection

- By visual inspection of the emission spectrum for the presence of C₂ and CN bands.
- Intensity ratio of nitrogen, oxygen, and carbon to hydrogen ratio.

```
Are C₂ bands, H, N, O present?  No  Not explosive
Yes

Is H/C₂ = 0.5-3.0? Is O/H = 0.7-1.4?  No
Yes

Is O/N > 4?  No  Not Explosive
Yes

Is O/K > 1? Is Na/ C₂ < 2?  No  Not Explosive
Yes

Explosive
```
Standoff LIBS System

In case when the target and the LIBS system are at certain distance from each other. The O, N, C and H present in atmosphere may provide false decision.

**To over come this:**

i- Use inert gas to displace the ambient air.

ii- Use of Double pulse laser system

  Double Pulse laser-Induced Breakdown Spectroscopy ranging from collinear or orthogonal configuration.

Military has vital interest in the real-time detection of explosives residues at standoff distances.

Standoff detection is important when finding roadside bombs, and for wide area-surveillance.
(a) Collinear configuration, in which the first and second laser pulses are both focused onto or into the solid, liquid, or gaseous sample. In the orthogonal configurations, a single ablative pulse is coupled with either (b) a reheating pulse or (c) a pre-ablative air spark that is parallel to and up to several millimeters above the sample surface.
LIBS standoff system/Herschelian telescope

Standoff system developed by US Army Research Lab. (ARL) and ocean optics inc.

This system was successfully applied for the detection and characterization of energetic materials up to 45 m from the target, working under **coaxial configuration**.
Instrumentation for spacecraft must meet stringent requirements related to the harsh environment encountered on the journey as well as on the surface of the mission target. This includes radiation protection and shielding from extreme cold and heat, especially during operations on the planetary surface. In addition, size, mass, and power requirements are important engineering parameters. A compact LIBS system
Field portable LIBS System

LIBS system for the inclusion on the 2009 MARS science laboratory (MSL). Stand-off analysis range of 2-12m and can perform analysis.
Single shot LIBS spectra of DTN sample at a 45m from sample
Peak ratio analysis of O/N obtained for the DNT sample and for an aluminium foil.

LIBS Spectra of air breakdown
Thank You
Future Programs

• Development of Double pulse Laser Induced breakdown Spectroscopy experimental setup for the detection of energetic materials in close contact as well as at some distance.

• Development of telescope for LIBS standoff system

• Development of software
Salient Features / Applications of Laser Induced Breakdown Spectroscopy

**Attractive Features**

- Little or no sample preparation is required.
- Versatile technique for the analysis of solids, liquids and gases.
- Sensitivity to parts-per-billion and picogram levels is possible.
- It is non-invasive due to very small sampling regions.
- Simple and rapid analysis (ablation and excitation processes are carried out in a single step)

**Applications :**

- of explosive materials
- Study of fundamental plasma parameters i.e. electron density, electron temperature. Characterization of normal and malignant tissue cell.
- It is more versatile than conventional methods and is ideal for on-site analysis.
- Very hard materials can be investigated and simultaneous multi-elemental analysis is possible (e.g. ceramics and superconductors).
- Applications include materials analysis, environmental monitoring, forensic and biomedical studies, art restoration and more
Laser-Induced Breakdown Spectroscopy (LIBS)

- **Laser-induced plasma**
- **Pulsed laser**
- **Fiber optic**
- **Sample**
- **Emission collection**
- **Spectrometer**
- **Detector**

Atomic emission lines provide species identification.
Rydberg Atom

• A Rydberg atom is an atom with a valance electron in a state with very large principal quantum number $n$.

• Rydberg atoms behave in many respects like hydrogen atom.
Emission Spectrum of Aluminum using LIBS

50 mJ/pulse

wavelength (nm)
Properties of Rydberg atoms

• Binding energy
  \[ E = \frac{R_{yd}}{n^2} \]

• Energy separation between adjacent levels
  \[ E = 2\frac{R_{yd}}{n^3} \]

• Orbital radius square of the principal quantum number
  \[ R = a_0 n^2 \]

• Radiative lifetime
  \[ \tau \propto n^3 \]

• Fine structure interval decrease as \( n^{-3} \)
Quantum Defect

• It is the measure of deviation from the hydrogen like behavior. $\ell=0,1,2,3\ldots$

• Quantum Defects are large for s electrons, decrease with increasing orbital angular momentum $\ell$.

$$E_n = IP - Ryd(n^2 - \mu)2$$
Diesel Fuel $\text{C}_{26}\text{H}_{52}\text{N}_2$  
Polyurethane $\text{C}_{11}\text{H}_{15}\text{O}_2\text{N}_2$  
Nylon $\text{C}_{12}\text{H}_{22}\text{O}_2\text{N}_2$  

Methyl-2-cyanoacrylate (adhesive)

Melamine (resins)

Oils (fatty acids) \{
CH$_3$(CH$_2$)$_2$COOH,  
CH$_3$(CH$_2$)$_{18}$COOH,  
CH$_3$(CH$_2$)$_3$CH=CH(CH$_2$)$_2$COOH
\}
Time evaluation of LIBS
Thermionic Diode Ion Detector

Buffer gas inlet

Cathode wire

Sample

Alkaline

Water cooling jackets

Laser passage

To vacuum pump
Two-step laser excitation of Zinc
Advantages/Characteristics of thermionic diode ion detector

• It is easy to set-up and operate, and low cost instrument.
• Extremely sensitive detector for highly excited Rydberg states.
• The thermionic diode ion detector works in the space charge limited mode.
• Amplification factor of the order of $10^4$-$10^6$ or even large is reported.
\[ P^2_{n,l} = r^2 R^2_{n,l}(r) \]
Selection rules (LS-coupling)

- $\Delta l = \pm 1$
  Electric dipole transitions occur only between the terms of opposite parity.

- $\Delta S = 0$

- $\Delta L = 0, \pm 1$ (L=0 $\rightarrow$ L=0 forbidden)

- $\Delta J = 0, \pm 1$ (J=0 $\rightarrow$ J=0 forbidden)
Zinc Z=30
Ground State 3d^{10}4s^{2} \, ^1S_{0}

Energy Levels Diagram of ZnI
Fine structure Splitting

\[ \Delta E = \frac{Z^4}{a_o^3 n^3 \ell(\ell + 1/2)(\ell + 1)} \]

It is due to the magnetic interaction between the orbital magnetic moment and the intrinsic moment of the electron.
The following Rydberg series have been detected from the $^3P_{0,1,2}$ intermediate level

- $4s4p \ ^3P_1 \rightarrow 4snd \ ^3D_2 \qquad (14 \leq n \leq 57)$
  $4sns \ ^3S_1 \qquad (19 \leq n \leq 35)$

- $4s4p \ ^3P_2 \rightarrow 4snd \ ^3D_3 \quad (17 \leq n \leq 50)$

- $4s4p \ ^3P_0 \rightarrow 4snd \ ^3D_1 \quad (25 \leq n \leq 40)$
• Observed series
  \[ 5sn \, d^3S_1 \ (19 \leq n \leq 38) \]
  \[ 5sn \, d^1D_2 \ (17 \leq n \leq 34) \]
  \[ 5sn \, d^3D_2 \ (12 \leq n \leq 52) \]

\[ \delta = 3.68, \delta = 2.23, \delta = 2.09 \]
• Observed series

\[ 6s nd \ ^3D_2 \ (26 \leq n \leq 48) \]

\[ 6s nd \ ^3S_1 \ (15 \leq n \leq 29) \]
Zn

3d\(^{10}\) 4s\(^2\) → 4s\(^4\)p \(^3\)P\(_1\) → 4s5s \(^3\)S\(_1\) → 4s13p \(^3\)P\(_2\) → λ\(_1\)=307.59 nm

53672.241 cm\(^{-1}\) → 32501.390 cm\(^{-1}\)
Zn

Term Energy cm$^{-1}$

Ionization Signal (arb.units)

12p $^{3}P_{2}$
13p $^{3}P_{2}$
13p $^{3}P_{2}$
4s5s $^{3}S_{1}$
14p $^{3}P_{2}$
Ionization Single

Laser energy cm$^{-1}$

$^{18p}_{1}P_{1}$

$^{21p}_{1}P_{1}$

$^{21p}_{3}P_{2}$

$^{26p}_{3}P_{2}$
Conclusion

- The even-parity $^3D_{1,2,3}$, $^3S_1$ and $^1D_2$ Rydberg series in Zn, Cd and Hg were explored for the first time using two frequency doubled dye lasers.

- Comparison of the experimental results of Zn, Cd, Hg and assignment of J-values of the highly excited states.
• Transition Probability

\[ P_{if} = \frac{\pi \rho(\omega_{if})}{3\varepsilon\hbar^2} |\langle f | e r | i \rangle|^2 \]

Since in electromagnetic fields with wavelengths much larger than atomic dimension. We therefore approximate the electric field by a constant over the dimensions of the dipole. This is called dipole approximation.
\[ V_{\text{eff}} = V(r) + \frac{l(l+1)}{2r^2} \]

Diagram:
- Energy axis
- Curves labeled as effective potential, centrifugal potential, and \(-\frac{1}{r}\) Coulomb potential.
Table 2.2 Radial hydrogen wave functions $R_{n,l}$

(1s) $R_{1,0} = \left( \frac{Z}{a_0} \right)^{3/2} 2 e^{-Zr/a_0}$

(2s) $R_{2,0} = \left( \frac{Z}{2a_0} \right)^{3/2} 2 \left( 1 - \frac{Zr}{2a_0} \right) e^{-Zr/2a_0}$

(2p) $R_{2,1} = \left( \frac{Z}{2a_0} \right)^{3/2} \frac{2}{\sqrt{3}} \left( \frac{Zr}{2a_0} \right) e^{-Zr/2a_0}$

(3s) $R_{3,0} = \left( \frac{Z}{3a_0} \right)^{3/2} 2 \left[ 1 - 2 \frac{Zr}{3a_0} + \frac{2}{3} \left( \frac{Zr}{3a_0} \right)^2 \right] e^{-Zr/3a_0}$

(3p) $R_{3,1} = \left( \frac{Z}{3a_0} \right)^{3/2} \frac{4\sqrt{2}}{3} \left( \frac{Zr}{3a_0} \right) \left( 1 - \frac{1}{2} \frac{Zr}{3a_0} \right) e^{-Zr/3a_0}$

(3d) $R_{3,2} = \left( \frac{Z}{3a_0} \right)^{3/2} \frac{2\sqrt{2}}{3\sqrt{5}} \left( \frac{Zr}{3a_0} \right)^2 e^{-Zr/3a_0}$

normalized to make $\int_0^\infty r^2 \text{d}r R^*R = 1$

\[
\left( a_0 = \text{1st Bohr radius} = \frac{4\pi\varepsilon_0 \hbar^2}{me^2} = 5.29 \times 10^{-11} \text{ m} \right)
\]
Two-step excitation scheme for Cd

$\lambda_1 = 326\text{ nm}$

$\lambda_{\text{scan}} = 247-239\text{ nm}$

$5s^2 \, ^1S_0$

$5s5p \, ^3P_1$

$72540.07 \text{ cm}^{-1}$

$30656.09 \text{ cm}^{-1}$
Penetrating and non-penetrating orbits
Dye laser cavity

Diagram:
- Pump laser
- Cylindrical lens
- Dye cell
- Mirror
- Prism
- Rotation stage
- Grating
- Output beam
Experimental Set-up
A Narrow-band Multiple-Prism Dye Laser Cavity

Multi-Prisms are used for the beam expansion
Thermionic Diode Ion Detector/ Atomic Beam Set up

National Institute of lasers & Optronics (NILOP)
Standoff system developed by US Army Research Lab. (ARL) and ocean optics inc.

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