Atomic Data Center on PC

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1 Introduction

"Atomic Data Center on PC" is a long range and large scale program of Atomic Engineering Corp. This data center provides a generic format which makes spectroscopic data uniform and usable in a PC-based format. This program consists of three functions:

(1) data collection and production,
(2) database development and
(3) evaluation and analysis.

The data center consists of two types of data:

(A) Reference laboratory data of atomic and ionic data specialized on heavy elements with Z>26.
AEDB consists of data of energy levels and lifetimes and is capable of "multi-photon Grotrian Diagram". ASDB consists of data of wavelengths, transition probabilities and intensities. The source of data are from open literatures and data archive at National Solar Observatory in Tucson, AZ.
(B) Knowledge database for laser remote sensing.
This database is designed for "new fingerprints" and related parameters for laser remote sensing. This program is in collaboration with "Laser Induced Breakdown Spectroscopic (LIBS) User Facility" at Los Alamos National Lab.

2 Database Management

Multichannel Quantum Defect Theory (MQDT) [1,2,3] is used to organize, manage and evaluate the data in the Atomic Engineering System (AES) [4]. MQDT is an unified theory comprising the Rydberg states of spectroscopy and the autoionizing states of collisional processes in atoms and small molecules [2]. It organizes atomic structures in terms of channel sets and structural parameters. A "channel set" is defined as a set of discrete and continuum states of an electron plus ion core. Each state differs in the energy of the excited electron. Subsequently, an atomic structure is characterized by three sets of quantum defect parameters:

(1) eigen-quantum defect M_a,
(2) channel mixing angle 0_a, and
(3) dipole transition matrix element d_a.

These parameters can be obtained by fitting the analytic relations to the discrete energy levels, oscillator strengths and photoionization cross sections. These parameters may also be calculated [5]. Relativistic MQDT is used to characterize high Z ions [6].

Highly efficient and powerful algorithms based on the structure parameters has been developed to organize and evaluate the data : energy levels, oscillator strengths/intensities/transition probabilities, lifetimes, photoionization cross sections and quantum defect of isoelectronic sequencies [4]. For example the whole Rydberg series and autoionizing structures as well as photoelectron angular distribution of noble gases Ne, Ar, Kr, Xe and Rn are characterized by 5 interaction channels with 5 eigen-quantum defect parameters, 5 dipole matrix elements and 10 channel mixing angle parameters [1].

3 Data Evaluation Procedures

We developed the following procedures to evaluate transition probability, intensity and lifetime. The transition probability A_{ul}, intensity I_{ul} and lifetime t_u of upper energy level E_u are related by the following expression:

$$A_{ul} = (I_{ul}/\Sigma_{l'} I_{ul'})/t_u \qquad (1)$$

where l' refers to all the lower energy levels to which the upper level u decays.

The intensity data are taken using a hollow cathode discharge and measured by high resolution Fourier Transform Spectrometer at National Solar Observatory at Kitt Peak, AZ, U.S.A. The intensity is measured by an automated AEC software MCCS system [7] that fits a line profile and the integrated area. The analysis of the spectral lines in terms of energy levels, J values and assignments is also carried out using MCCS software.

The lifetime is obtained using published data by laser-induced fluorescence from atoms and ions in a beam. We have developed an evaluation procedure for lifetime measurements based on the threshold laser induced fluorescence measurement as function of beam density and laser intensity (see the following) [8].

The transition probability is obtained from equation (1). Most of the up-to-date data on transition probabilities are obtained by this method [9].

In the absence of lifetime data, we obtain the reliable intensity by normalizing the intensity to the known data of transition probability. The normalized intensity carries the similar weight of reliability as the transition probability in terms of concentration measurement. For example, there is no reliable transition probability available for 257.601 nm line of Mn-II however it was seen in the LIBS spectrum. Following the above procedure, we determined that the normalized intensity of 257.601 nm line to be 35.

4 Knowledge Database for Laser Remote Sensing

The formation of a plasma plume and generation of emission induced by a high-power laser beam in solid material has led to the development of elemental composition analytic tools of condensed-phase specimens [10]. One high power laser beam vaporizes the sample and generates a plasma plume. Emission from the plasma is collected by a detector, e.g., a laser induced breakdown spectrometer (LIBS). This method has the advantage of being developed as a powerful in-situ and remote sensing tool which requires minimally invasive sample preparation and separation.

However, there are several challenging problems of a in-situ laser induced breakdown spectroscopy. The calibration problem is more serious because of the lack of reliable library database for environmental matrix effects, such as soil matrix, moisture and laser induced plasma. The spectral shifts, broadening and "quenching" effects generated by environmental effects make quantitative characterization difficult. Lack of computational techniques to apply the knowledge base to the correction of in-situ measurements in real-time for quantitative characterization contributes to the challenging problems.

An intelligent software system, the Multi-spectral Chemical Characterization System (MCCS), was used to analyze the matrix effects of two of the toxic metals, Be and Pb, in soil samples measured by a LIB spectrometer [11]. MCCS can convert ASCII, binary, tape and Flexible Image Transport System (FITS) which is a standard data format for Astrophysics and Astronomy into AEC's data format. The raw data collected from LIBS are downloaded into the MCCS. The spectra are measured by the powerful and efficient algorithm which is capable of measuring 100 integrated spectra in terms of width, peak height and position in less than 15 sec. The spectra are then searched, calibrated and identified in reference to the knowledge database. The search algorithm includes a "tolerance" parameter to account for the spectral shift and broadening caused by the matrix effects. The algorithm also includes "filters" in disentangling "spectral interference". These unique softwares allow user to identify quantitatively the relative concentration ratio (ppm) of the analyte in a sample. The final decision making can be displayed in terms of tables and graphics. The results indicate that the selected fingerprints used to measure Be at 313 nm survive the matrix effects. The fingerprint of Pb, 405.9 nm, used in the calibration is quenched by the laser induced plasma. The following reports an investigation of the calibration procedure for laser induced effects. Then we use these results as guidance to search for "new fingerprints" under various environmental matrix effects.

5 The Calibration Procedure for Laser Induced Effects

We have developed a calibration procedure for non-LTE laser induced effects. The calibration procedure combines modeling with experimental measurement.

In a laser induced plasma the discrete line emission develops in the fringes (optical thin region) of the expanding plasma core where local thermodynamic equilibrium may not exist. The usual method based on local thermal dynamic equilibrium in measuring the intensities relatively and calibrating their relationship to the respective elemental composition, which has been analyzed by calibration standards, may not be sufficient.

This non-LTE model is based on the assumption that the quenching of the emission process of an element is caused by the competing ionization process of the same element. The emission rate can be derived from a rate equation analysis, which includes as many as four processes: ionization process, emission process, excitation process and stimulated process.

In order to test the model, we compare the results with a laboratory experimental investigation [8]. The experimental measurements were carried out at JilinUniversity, in a Pb atomic beam excited by a Quanta-Ray Nd:YAG dye laser system. The state 6p7s $^3P^0_1$ at 283.3 nm is excited by a uv photon (w~ 283.3 nm). The 405.9 nm radiates to level 3, 6p^2 $^3P_2$. The ionization process from level 2 can be produced by a two photon process since the two photon energy is greater than the ionization energy of Pb (=7.415 ev). The photoelectrons were collected by a channeltron. The ionization signal is processed by a boxcar and displaced on a chart recorder. The fluorescence signal was simultaneously measured by a PMT with a filter. The data shows that the fluorescence process is simultaneously present and in competition with the ionization process [8]. The result of a model calculation compared with the experimental observation shows that at lower laser intensity, the 405.9 nm emission increases with increasing laser intensity [8]. This fluorescence rate decreases as the laser intensity increased beyond 10^{16} photons/cm^2 [8]. To involve the ionization process is essential, as given in equation (1), for a correct analysis of the measured data since a computation [12] which does not include the ionization process failed in predicting the decrease of fluorescence rate. Therefore the decreasing of the fluorescence signal is caused by the increasing of the ionization signal.

We have also carried out a laser induced fluorescence measurement of Pb 405.9 nm as a function of atomic beam density [8]. The result shows that there is a flat value of fluorescence yield below beam density 10^8 atoms/cm^3. The fluorescence yield increases exponentially for beam density >10^8 atoms/cm^3 [8]. The laser power was of the order of sub-MW/cm^2. At low density the atomic beam is in thermal expansion. The mean free path among the atoms may be too large to generate laser induced effects. The flat fluorescence value is close to the atomic condition and is recommended for reference data whereas the higher beam density result may have laser induced effects. This investigation may explain the discrepancies of some of transition probabilities measured by lasers compared with non-laser methods.

The above modeling was based on laser induced ionization in atomic beams with a density ~10^8 atoms/cm^3 in vacuum. For laser induced plasmas in air with a density > 10^{12} atoms/cm^3, the ionization rate is at least two orders of magnitude larger ~10^{-16} cm^2. Consequently, the emission rate is reduced by at least two orders of magnitude. This investigation generates the key result : there is a threshold value of the laser intensity for emission process to be detected. Beyond that value, the emission process will be quenched and the relaxation process favors ionization. The low melting point and low ionization limit of Pb also contribute to the excessive generation of laser induced plasma. Consequently, the excited atom releases its energy via ionization and "quenched" the emission process. These results explain why certain "fingerprints" of metals based on laboratory results, e.g. 405.9 nm of Pb failed to show up in the field results using high power laser induced plasma method.

6 Knowledge Database for Environmental Matrix Effects

The manifestation of environmental matrix effects on the spectral lines are shifts, broadening and quenching. A knowledge database to store the calibrated data as well as the new fingerprints of matrix effects is designed. As the Pb 405.9 nm case shows, the calibration based on fingerprints from a reference database did not guarantee success. However, reliable and quantitative reference databases are necessary for the first step of any analytic science.

The spectral shifts and broadening of laser induced spectral lines in the presence of high pressure noble gas are available for Mg [13], Ba[14], Pb[8], Sn[15], Sr[16] and Stark broadening [17].

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