Application of Laser-enhanced Ionization Spectroscopy: Effect of Dissociation Constant on the Atomization Efficiency Determination in an Acetylene-Air Flame

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By using laser-enhanced ionization (LEI) technique, we have studied atomization efficiencies of the alkali halides in an acetylene/air flame. As an aqueous solution of the metal salt was nebulized into the burner head, a flame with a high temperature of about 2500 K may cause dissociation of the ionic bond to release the free metal atoms. The ratio of the number density of free metal atoms present in the flame to the total number density of the same metal element nebulized determines the atomization efficiency. In this work, binary salt solutions including LiX, NaX, and KX (X=Cl, Br, and I) were used; each was prepared at 5 ppm (μg/mL) metal concentration. The atomization efficiency of the metal element was measured, as the accompanied halogen species was varied. We found that the ratios of atomization efficiencies of the alkali element in different halide compounds were almost equal to one. Atomization efficiency determination is dominated by the metal atom, but weakly influenced by the binding halogen species. The observation may be interpreted satisfactorily by using the Sugden-Bulewicz model. Based on this model, the metal atomization efficiency for different halide compounds depends on the number densities of the halogen atoms and the related dissociation constants. For the binary salt with a small concentration and a large dissociation constant, the atomization efficiency determination tends to be dominated by the metal atom alone.

INTRODUCTION

Laser-enhanced ionization (LEI) spectroscopy has been developed as a powerful tool to detect trace metal in flame with very high sensitivity and selectivity.[1-9] By taking advantage of the merits of preconcentration and matrix separation of the flow injection (FI), LEI combined with the FI system becomes capable of detecting the trace metal in seawater.[10-12] In addition, the capability of LEI technique may be extended to such tasks as to monitor ion lifetime,[13] to determine ion diffusion and mobility coefficients,[14,15] to resolve the spectral structures of atoms, molecules and radicals,[3] to determine the ionization yield of atoms,[16] and to measure the number density of free atoms released and in turn the atomization efficiency.[17]

The atomization efficiency of an element in flames is defined as a ratio of the number density of its free atoms present in the flame to the total number density of the same element actually nebulized. It plays one of the crucial roles which govern the limit of detection. A large atomization efficiency tends to lead to a low limit of detection. However, the atomization efficiency can be changed when some organic solvent or matrix is added to cause excess electron density released in the flame, which may suppress the efficiency of the element ionization.

Thus far, atomization efficiency has mainly been determined by the techniques such as atomic absorption spectroscopy[18-24] and atomic emission spectroscopy.[25] In addition to these optical spectroscopic methods, the LEI technique has been recently demonstrated to be a successful alternative.[26] In this work, it is further applied to determine the atomization efficiencies of the alkali elements in different halide compounds. We focus on the influence of the ionic bond energies on the atomization efficiency of the same metal element. The total free atom number density released in a flame may be estimated from the measurement of time-integrated LEI signal.[26] The resultant metal atomization efficiencies are found to be almost independent of the accompanied halogen species. To interpret the observations, we adopt the Sugden-Bulewicz model to yield theoretical estimates,[1,27] which agee with our obtained measurements. This study provides insight into the key factors which govern the atomization efficiency.

Dedicated to Professor Sheng-lieh Liu on the occasion of his ninetieth birthday.

EXPERIMENTAL

Flame System

The apparatus is depicted in Fig. 1. A commercial burner assembly (Perkin-Elmer) with a 100 mm × 0.5 mm slot burner head was coupled with an interlocked gas control system. The fuel C_2H_2 and air with flow rates of 0.5 L/min and 13 L/min, respectively, were premixed prior to reaching the burner head. The corresponding flame temperature was determined to be about 2500 K.[28,29] The uptake rate into the burner head was held at 4.5 mL/min for all the aqueous solutions of the halide compounds.

Reagents

The binary salts including LiX, NaX, and KX (X=Cl, Br, and I) were used as purchased without further purification. The aqueous solution for each salt was prepared at 5 ppm (μg/mL) of the metal concentration.

Laser Source

The light source used for the LEI detection of Li and Na was a 10 Hz, 5-8 ns Nd:YAG laser-pumped dye laser (Quanta Ray, PDL-2), emitting at 656.5 nm and 660.5 nm with a DCM dye. The radiation was then frequency-doubled through a KDP crystal which was housed in a wavelength extender with a device of an auto-tracking controller (Quanta Ray, WEX). The Li atom was excited at the wavelength 323.3 nm in the $2^2S_{1/2} \rightarrow 3^2P_J$ transition, while the Na atom was excited at 330.2 nm in the $3^2S_{1/2} \rightarrow 4^2P_{3/2}$ transition. For the LEI detection of K, the dye laser operated with the LDS750 dye was tuned to 766 nm for the K $3^2S_{1/2} \rightarrow 4^2P_{3/2}$ absorption. The unfocused excitation beam was collimated with a pinhole of 5 mm^2 cross section and then directed longitudinally through the flame at 12 ± 0.1 mm above the burner head. The laser energy, prior to reaching the flame, was monitored continuously by a surface absorbing disk calorimeter (Scientech 36-0001).

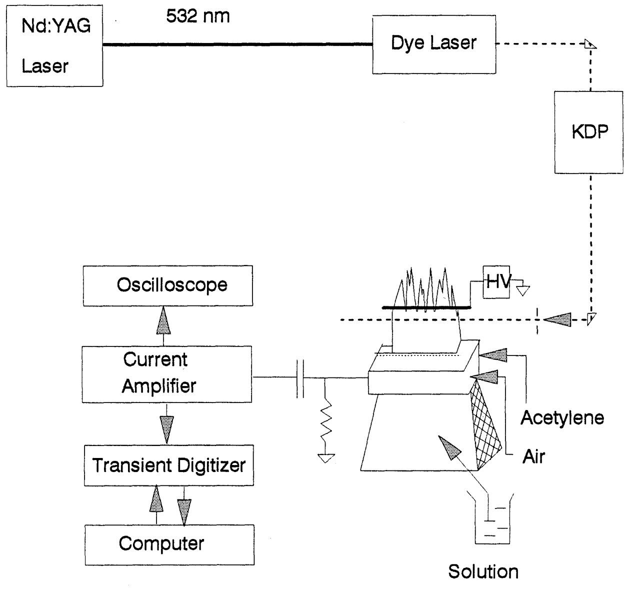

Fig. 1. Schematic diagram for the laser-enhanced ionization apparatus.

LEI Detection

A water-cooled cylinder probe along the flame axis was biased at -1000 V and suspended 2 cm above the burn head.[30] The burner served as the other electrode, from which the LEI current signal was collected and amplified with a current-to-voltage converter (Keithley, Model 428), and then fed into a transient digitizer (LeCory 9450A). The LEI waveform was averaged over 200 pulses and transferred to a PC through a GPIB interface board. The measured LEI waveform due to the Li $2^2S_{1/2} \rightarrow 3^2P_J$ transition is given as an example in Fig. 2.

Determination of the Atomization Efficiency

The atomization efficiency β is defined as

$$\beta = \frac{n_a}{n_t} \tag{1}$$

where n_a is the free atom number density of an element present in the flame, and n_t is the total number density of the same element actually nebulized. The latter can be explicitly expressed as[25]

$$n_t = 2.98x10^{21} \frac{C\phi\varepsilon}{(n_T / n_{298})Tf} \tag{2}$$

where C is the concentration of the analyte solution; ϕ the uptake (nebulization) rate (mL/min); ε the sample introduction efficiency; f the flow rate (mL/s) of unburnt gases at room temperature (298 K) and atmospheric pressure; n_{298} the number of moles of species at room temperature; and n_T the number of moles of combustion products at temperature T. The value of n_T/n_{298} was previously determined to be 1.0 for our case with an acetylene/air ratio of 1:25 and a flame temperature of 2500 K.[28,29] Therefore, substituting the experimental conditions and the measured ε values into eq. 2 may give rise to the estimate of n_t for different alkali salts. The results for the Li, Na, and K salts are listed in Table 1.

The free atom number density, n_a, for a three-level system was previously derived in relation to the time-resolved

Table 1. The Bond Energies, E_{MX}, and Dissociation Constants, K_{MX}, of Various Alkali Halides, the Number Densities of the Halogen Atoms, [X], and the Ratios of [X] to K_{MX}[a]

	n_t (cm^{-3})[b]	E_{MX} (eV)[c]	K_{MX} (cm^{-3})[d]	[X] (cm^{-3})[b]	[X]/K_{MX}
LiCl	1.57×10^{12}	4.856	5.23×10^{13}	1.57×10^{12}	0.03
LiI	1.57×10^{12}	3.643	7.49×10^{15}	1.57×10^{12}	2.0×10^{-4}
NaCl	4.74×10^{11}	4.249	8.57×10^{14}	4.74×10^{11}	5.6×10^{-4}
NaBr	4.74×10^{11}	3.838	5.43×10^{15}	4.74×10^{11}	8.7×10^{-5}
NaI	4.74×10^{11}	3.122	2.53×10^{18} [e]	4.74×10^{11}	1.9×10^{-7}
KCl	5.83×10^{10}	4.423	2.88×10^{14}	5.83×10^{10}	2.0×10^{-4}
KBr	5.83×10^{10}	3.968	1.62×10^{15}	5.83×10^{10}	3.6×10^{-5}
KI	5.83×10^{10}	3.426	2.12×10^{16}	5.83×10^{10}	2.8×10^{-6}

[a] The aqueous solution of each salt was prepared at 5 ppm of the metal concentration.

[b] The number densities of the halogen atoms is considered to be equivalent to the total number density, n_a, as calculated by eq. 2.

[c] Bond energies of alkali halides.

[d] The values were calculated in terms of the JANAF thermochemical tables from Ref. 31.

[e] NaI is in the liquid state.

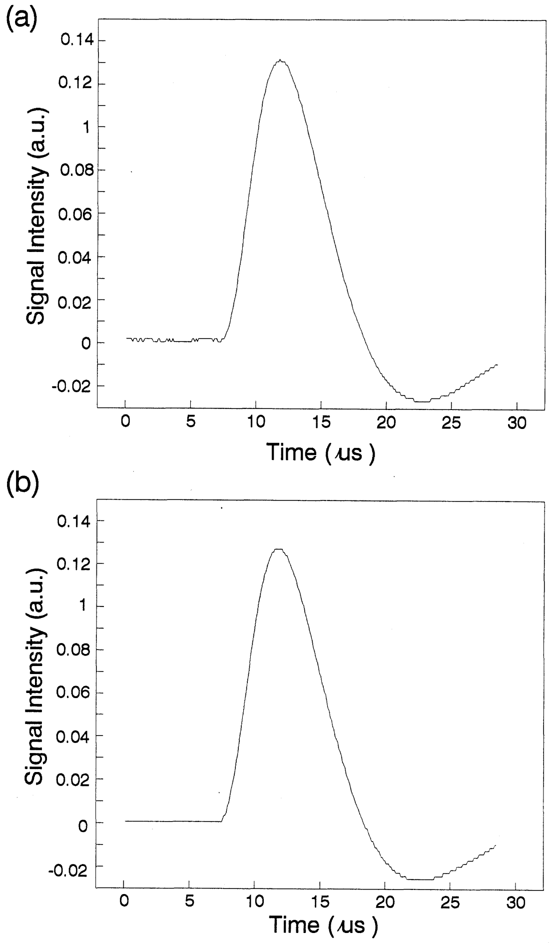

Fig. 2. The time-resolved LEI signals of Li in the $2^2S_{1/2} \rightarrow 3^2P_J$ excitation obtained from (a) LiCl and (b) LiBr.

LEI signal, as expressed by,[26]

$$n_a = \frac{k}{Ge\sigma\ell\gamma}\int_0^{\tau} V(t)dt \tag{3}$$

where G is the gain of the current amplifier; e the electron charge; σ the cross section between the laser beam and the flame; ℓ the probing length; γ the collection efficiency; $V(t)$ the amplified voltage pulse of the time-resolved LEI signal; τ the integration time interval; and k is associated with the transition rate coefficients between two levels in the system. According to eqs. 1-3, the atomization efficiencies for the Li and Na elements were successfully determined previously in terms of the LEI technique.[26] In this work, the factor of $k/Ge\sigma\ell\gamma$ turns out to be identical between the binary salts, MX and MX', with the same alkali element. Accordingly, the ratio of atomization efficiencies for these two salts can be simplified as

$$\frac{\beta_{MX}}{\beta_{MX'}} = \frac{\int_0^{\tau} V_{MX}(t)dt}{\int_0^{\tau'} V_{MX'}(t)dt} x \frac{n_{t,MX'}}{n_{t,MX}} \tag{4}$$

RESULTS AND DISCUSSION

Given the time-resolved LEI signals, $V_{MX}(t)$ and $V_{MX'}(t)$, and the total number densities of the alkali element, M, in different binary salts of MX and MX', substitution into eq. 4 may yield the ratio of metal atomization efficiencies for these salts. The results for lithium, sodium, and potassium halides are listed in Table 2. The atomization efficiencies of the alkali metals in the binary salts seem to be insignificantly affected

Table 2. The Ratios of the Atomization Efficiencies for Various Alkali Halides

	Li	Na	K
β_{MCl}/β_{MI}	1.01 ± 0.04	1.01 ± 0.03	0.98 ± 0.03
β_{MCl}/β_{MBr}	—	0.97 ± 0.04	1.03 ± 0.05
β_{MBr}/β_{MI}	—	1.00 ± 0.04	0.97 ± 0.03

by the accompanied anions, although the ionic bond dissociation energies differ between these binary salts. To interpret our observations, a theoretical estimate is given for comparison.

According to the Sugden-Bulewicz model, the metal atomization efficiency for the halide compounds in flame can be expressed as[1,27]

$$\beta(M) = \frac{[M]}{[M]+[M^+]+[MO]+[MX]+.....} \tag{5}$$

where $[M]$, $[M^+]$, $[MO]$, and $[MX]$ denote the number densities of metal atoms, metal ions, metal oxides, and metal halides, respectively. This model considers the total number density of the metal element nebulized as the sum of the number densities of the metal element present in various forms. Assuming that the number density of monohalide, $[MX]$, dominates over the other polyhalides in the flame, eq. 5 becomes

$$\begin{aligned}\frac{1}{\beta(M)} &= \frac{[M]+[M+]+[MO]+[MX]+...}{[M]}\\ &= 1+\frac{ki}{[e]}+\frac{[O]}{K_{MO}}+\frac{[X]}{K_{MX}}...\end{aligned} \tag{6}$$

where k_i is the ionization constant of M; K_{MO} and K_{MX} are the dissociation constants of MO and MX, respectively. The value, $1+\frac{ki}{[e]}+\frac{[O]}{K_{MO}}+...=K''$, remains invariant for the same metal element. Thus the $\beta(M)$ values for different halides depend mainly on the term of $[X]/K_{MX}$.

Eq. 2 is adopted to estimate the number density of the halogen atom, $[X]$, yielding the n_t value as its upper limit. The dissociation constants of metal halides, K_{MX}, may be evaluated by using the JANAF thermochemical tables.[31] The values of $[X]/K_{MX}$ are accordingly calculated and listed in Table 1. Given the case of 5 ppm LiCl solution as an example, the dissociation constant is 5.23×10^{13} cm^{-3} and the number density of Cl is estimated to be 1.5×10^{12} cm^{-3} as the upper limit. Thus $[X]/K_{MX}$ yields a value of 0.03. This value is much smaller than K'' ($K''>1$) and may be negligible in the estimate of $\beta(M)$ (eq. 6) within 5% experimental error. Similarly, the $[X]/K_{MX}$ values for other metal halides can be estimated. Their results (Table 1) appear to be smaller than 0.03. Since the upper limit of $[X]$ is used, the $[X]/K_{MX}$ values are actually smaller than the results in Table 1. Therefore, the calculated atomization efficiencies of the metal element in binary salts are independent of the accompanied halogen species. This fact explains why our measurements of $\beta_{MX}/\beta_{MX'}$ ratios are close to 1. Unless the metal halide solution is under a concentrated condition which gives rise to a large number density of X, the atomization efficiency determination may depend on the metal element alone.

The dissociation constant of metal halide is associated with the dissociation energy. Based on the statistical model, the dissociation constant of MX can be expressed as[22,32]

$$K_{MX} = K_{MX}^{0}\exp(-5040\,E_{MX}/T) \tag{7}$$

where K_{MX}^{0} is a temperature-dependent pre-exponential factor; E_{MX} the dissociation energy of MX in units of eV; and T the flame temperature in K. If the dissociation energy is fixed, then the dissociation constant increases with temperature. The acetylene/air flame with temperature as high as 2500 K may enhance the dissociation of MX and thus lead to a small value of $[X]/K_{MX}$. As a result, determination of the metal atomization efficiencies in flames may not be significantly affected by variation of the complex species, if the corresponding dissociation energies do not differ markedly from each other.

CONCLUSION

The LEI technique has been applied to determine the atomization efficiencies of the metal elements in flames. We have studied the dependence of atomization efficiencies of the alkali elements on the accompanied halogen species in an acetylene/air flame. The atomization efficiencies appear to be insignificantly affected by the binding halogen atoms. These observations may be interpreted in terms of the Sugden-Bulewicz model. Based on this model, determination of the metal atomization efficiencies for different halide compounds depends on the number density of halogen atoms and the related dissociation constants. Under the conditions of a small metal salt concentration and a large dissociation constant, the atomization efficiency determination may be solely governed by the metal element.

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Key Words

Laser-enhanced ionization (LEI); Atomization efficiency.

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