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Departure from local thermal equilibrium during ICP-AES and FAES: Characterization in terms of collisional radiative recombination activation energy*

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Abstract: A simplified rate model is presented showing that when analytes are determined by atomic spectroscopy first in the absence, and then in the presence, of easily ionizable elements (EIEs) as interferents, the change in collisional radiative recombination activation energy, ΔE_a , is zero when the system conforms to local thermal equilibrium (LTE). ΔE_a values of -7.462, -7.925, and -8.898 eV were obtained when Ca(II), Mg(II), and Sr(II), respectively, were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) in the absence and presence of excess Li, while ΔE_a values of -6.477 and -7.481 eV were obtained when Mg(II) and Sr(II), respectively, were determined in the absence and presence of excess K as interferent. A value of -2.223 eV for ΔE_a was obtained when Mg(I) was determined by air-acetylene flame atomic emission spectrometry (FAES) in the absence and presence of excess K. The data confirm that all the systems studied were not in LTE, and suggest pre-LTE collisional radiative recombination in the absence of the interferent in all cases, and that collisional radiative recombination involving electrons from the interferent can occur from the ambipolar diffusion state or the LTE state. Possible causes for departure from LTE, and a possible collisional radiative recombination mechanism to account for the ΔE_{a} values obtained, are discussed.

Keywords: activation energy; calcium; easily ionizable elements; inductively coupled plasma-atomic emission spectrometry (ICP-AES); interference effects; local thermal equilibrium (LTE); lithium; magnesium; optical emission spectroscopy; plasma chemistry; plasma diagnostics; radiative recombination.

INTRODUCTION

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) is one of the most widely used and extremely important tools for trace element analysis. The technique is generally superior in accuracy, precision, detection limits, dynamic range, and relative freedom from interference than other analytical instrumentation. Unfortunately, despite these proven analytical virtues, the technique still suffers from inter-element effects, in particular, matrix effects due to elements with low ionization potentials,

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known as easily ionizable elements (EIEs). Such EIEs turn up in a variety of samples where these techniques are employed, including geological samples, biological samples, environmental samples, and industrial products. The effects of EIEs on analyte line emission have been studied by several workers [1–21]. Characteristically, matrix effects observed manifest themselves as enhancements or depressions of the analyte absorption signal in flame atomic absorption spectroscopy (FAAS), and emission signal in ICP-AES and flame atomic emission spectrometry (FAES).

Current theory of atomic spectrometry assumes local thermal equilibrium (LTE) [22]. A gaseous system in complete thermal equilibrium (TE) is characterized by a number of distributions that are sensitive functions of temperature, namely, the Maxwell velocity distribution law, Boltzman population distribution law of bound states, the Saha-Eggert population distribution of ionization products, the Guldberg-Waage distribution of dissociation products, and Planck's radiation distribution law. Maxwell's distribution law defines the plasma temperature, T, while the Saha-Eggert and Gulberg-Waage distributions can be viewed as statements of the law-of-mass-action. LTE allows for spatial decoupling of temperature, and decoupling of energy and matter, while partial LTE (p-LTE) allows for decoupling of electrons and heavy particles. Because of their smaller mass, the heating of electrons in a plasma is much faster than transfer of energy from electrons to heavy particles, hence a two-tier temperature plasma is established, electrons with a higher Maxwellian distribution temperature (the electron temperature, T_{e}), and heavy particles with a lower temperature (the gas temperature, T_{o}). In addition, the assumption of LTE subsumes that, following ionization, electrons are released with kinetic energy equal to the ionization potential of the respective atom, but quickly lose this energy through thermal collisions so that at TE all the electrons will have kinetic energy equal to kT_e , where k is the Boltzmann constant. According to the LTE theory, all equilibriating processes within the plasma are due to collisional processes, and the contribution from radiative processes is negligible. All processes interfering with analyte excitation and ionization should be explainable in terms of the theory.

Techniques for studying the effect of interferents on the emission intensity of analyte atomic and ionic lines in atomic spectrometry have been reviewed by Hieftje et al. [23,24]. Three approaches are used, namely, active spectroscopic methods, passive spectroscopic methods. and kinetic modeling methods. Active spectroscopic methods involve irradiating plasma particles with electromagnetic radiation and observing the radiation they emit. Key parameters in this approach to plasma diagnostics are the electron number density (n_e) , T_e , T_g , and the Ar atom number density (n_{Ar}) . The methods employed involve a combination of Thomson scattering [25–30], Rayleigh scattering, computed emission topography [31,32], and laser-induced saturated fluorescence [33–36]. Thomson scattering enables measurement of T_e and n_e . The intensity of the Rayleigh scattering is proportional to n_{Ar} , which in turn is inversely proportional to T_g . Computed emission tomography enables the display of the full 3D structure of the plasma torch [37]. Laser-induced saturated fluorescence yields time-resolved spatial maps of ground-state analyte atoms and ions, as well as Ar excited states [38]. Passive spectroscopic methods simply observe the radiation emitted by the plasma [38], and have been used to study vertical and radial profiles of interference effects, the effects of varying the interferents, effect of varying radio frequency (rf) power, nebulizer effects, and shifts in ionization equilibria [1,8,11,20,39,40].

Kinetic modeling methods have also been used as plasma diagnostic tools [41–52]. The classical collisional-radiative rate models take into account all possible electronic states of the analyte and matrix. The difficulty encountered with this classical approach arises from the fact that the resulting models are extremely complex, such that arriving at solutions is difficult. Simplified rate models that focus on only one particular electronic level of the analyte have been proposed [53–57]. The approach employed by Zaranyika and co-workers [55–57] assumes that $I \propto n_u$, where I denotes analyte line emission intensity, and n_u denotes number density of the analyte excited state. The approach involves determining the analyte emission (I) signal ratio I'II, where the prime denotes presence of interferent, and comparing to theoretical n_u'/n_u values derived assuming steady-state kinetics in the plasma.

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Active and passive spectroscopic plasma diagnostic methods have yielded a lot of information about the spatial variation of the composition of the plasma, spatial variation of interference effects, and the effects of varying rf power. In addition, considerable success has been achieved in the determination of $n_{\rm e}$, $T_{\rm e}$, $T_{\rm g}$, and $n_{\rm Ar}$. However, the major conclusion emanating from active and passive spectroscopic studies is that the ICP is dominated by electrons from the ionization of Ar [4,6,25]. Since the LTE theory assumes that all equilibriating processes within the plasma are due to collisional processes, the appearance of interference in the presence of EIEs shows that the ICP is not in LTE [4,6,25,60,61]. To date there is no satisfactory explanation for this departure of the ICP from LTE. Zaranyika et al. [56] demonstrated the similarity between emission signal enhancement profiles in the ICP and air-acetylene flame, see Fig. 1, prompting the authors to suggest that the effects of EIEs are entirely due to the presence of the interferent, and that the differences in the temperature and composition of the ICP and those of the air-acetylene flame are not significant as far as emission signal enhancement is concerned. Further studies by Zaranyika and Chirenje [55] demonstrated that the interference effects observed could only be simulated if Ar species (atoms, ions, and electrons resulting from the ionization of Ar) are excluded from the collisional processes leading to the observed interference effects. A similar conclusion had been arrived at earlier by Lovett [49]. This non-involvement of Ar species in collisional processes leading to the observed emission signal enhancement cannot be explained fully as long as all the electrons in the plasma are regarded as being equivalent in accordance with the LTE theory.



B. Effect of xs K on Mg I line, Flame Exp



Fig. 1 Emission signal enhancement (E/E) profile: Effect of excess K on Mg(II) and Mg(I) in the ICP and airacetylene flame (ex = excess). (Source: Zaranyika et al. [56]).

As pointed out above, the LTE theory assumes that upon ionization, electrons are released with kinetic energy equal to the ionization potential of the respective atom, but quickly lose this energy through thermal collisions so that at TE all the electrons will have kinetic energy equal to kT. If it is assumed that electronic collisions with heavy particles can occur before or after thermal equilibration, then the electron should experience different activation energies depending on whether collisions leading to the observed interference effects occurred before or after thermal equilibration. In a recent paper [57], we proposed a simplified rate model for the interference effects of EIEs in FAAS and ICP-AES, which showed that when the analyte signal is determined in the absence and presence of the interference in the conforms to LTE, and proceeded to show that when CaI, Ca(II), and Mg(II) are determined in the absence and presence of excess Li interferent, this condition was not met, while the results obtained suggested pre-LTE collisions for electrons from the ionization of the analyte and Ar. In this paper we

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report the results of a study carried out to characterize the interference effects of (a) excess K and Li on Mg(II), Sr(II), and Ca(II) line emission intensity in the ICP, and (b) excess K and Na on Mg and K atom line, respectively, in the air-acetylene flame, in terms of the activation energies involved when the determination is done in the absence and presence of the interferent, with the view to confirm our previous findings, and to assess the effect of ionization potential of both the analyte and interferent on ΔE_a . The rate model presented by Zaranyika et al. [57] was derived for FAAS conditions, then extended to ICP conditions by assuming the I'/I = A'/A, where I and A denote emission and absorbance signals, respectively. Because the composition of the plasma in the ICP differs greatly from that of flame systems, in the Theoretical section we give a generalized derivation of the rate model taking into account the composition of the plasma in the ICP.

THEORETICAL

The major processes affecting analyte ground-state and excited-state populations in the ICP are represented schematically in Fig. 2. The proposed model takes into account thermal dissociation of analyte salt (rate constant $k_{\rm D}$), atom/counter-atom collisional recombination (rate constant $k_{\rm R}$), thermal excita-



Fig. 2 Schematic representation of the proposed simplified rate model. (*n* denotes number density, the subscripts o, u, +, denote analyte ground state, analyte excited state, analyte ion; AX_2 and X denote analyte salt and counter atom, respectively; W and W⁺ denote ground-state concomitant atom and concomitant ion, respectively; k_D is the rate constant for thermal dissociation; k_{Δ} and $k_{\Delta'}$ are the rate constants for thermal excitation from ground state and excited state, respectively; $k_{c(0)}$ and $k_{c(1)}$ are the rate constants for ion-electron collisional recombination to the ground state and the first excited state, respectively; k_{CT} and k_{CT} are the rate constants for collisional constants for collisional charge transfer involving interferent species; k_R is the rate constant for collisional recombination of analyte and counter atoms).

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tion (rate constant k_{Δ}), thermal excitation from the first excited state (rate constant k_{Δ}), radiative relaxation (rate constant k_{hv}), ion/electron radiative recombination to the ground state (rate constant $k_{c(0)}$), ion/electron radiative recombination to the first excited state (rate constant $k_{c(1)}$), collisional charge transfer involving concomitant atoms (rate constant k_{CT}), and collisional charge transfer involving concomitant ions (Ar and any interferent, rate constant k_{CT}).

Assuming presence of interferent and a steady state with respect to the analyte ground state and excited state, we have

$$\frac{dn'_{o}}{dt} = k_{\rm D} n_{\rm AX_2} + k_{c(0)} n_+ N'_{\rm e} + k_{\rm CT} n_+ n_{\rm wo} + k_{h\nu} n'_{\rm u} - k_{\Delta} n'_{\rm o} - k'_{\rm CT} n'_{\rm o} n_{\rm w+} - k_{\rm R} n'_{\rm o} n'_{\rm X} = 0$$
(1)

and

$$\frac{dn'_{\rm u}}{dt} = k_{\Delta}n'_{\rm o} + k_{\rm C(1)}n_{+}N'_{\rm e} - k_{h\nu}n'_{\rm u} - k'_{\Delta}n'_{\rm u} = 0$$
⁽²⁾

where $N'_e = n_{e(Ar)} + n_e + \Delta n_e$, and $n_{e(Ar)}$, n_e , and Δn_e are the number densities of electrons from the ionization of Ar, the analyte, and interferent, respectively; $n_{wo} = n_{Ar} + n_{mo}$; $n_{w+} = n_{Ar+} + n_{m+}$. Rearranging eq. 2:

$$(k_{h\nu} + k'_{\Delta})n'_{\rm u} = k_{\Delta}n'_{\rm o} + k_{\rm c(1)}n_{+}N'_{\rm e}$$
(3)

Similarly for the absence of interferent:

$$\left(k_{h\nu} + k'_{\Delta}\right)n_{\rm u} = k_{\Delta}n_{\rm o} + k_{\rm c(1)}n_{+}N_{\rm e} \tag{4}$$

where $N_{\rm e} = n_{\rm e(Ar)} + n_{\rm e}$. Hence

$$\frac{n'_{\rm u}}{n_{\rm u}} = \frac{k_{\Delta}n'_{\rm o} + k_{\rm c(1)}n_{+}N'_{\rm e}}{k_{\Delta}n_{\rm o} + k_{\rm c(1)}n_{+}N_{\rm e}}$$
(5)

Two limiting cases can be defined for eq. 5, thus:

Limiting Case 1.0 (LC 1.0): Dominance of collisional radiative recombination to the excited state: $k_{\Delta}n_{o}' << k_{c(1)}n_{+}N'_{e}; k_{\Delta}n_{o} << k_{c(1)}n_{+}N_{e}.$ Hence

$$\frac{n'_{\rm u}}{n_{\rm u}} = \frac{k_{\rm c(1)}n_{+}N'_{\rm e}}{k_{\rm c(1)}n_{+}N_{\rm e}} = \frac{k_{\rm c(1)}\left(n_{\rm e(Ar)} + n_{\rm e} + \Delta n_{\rm e}\right)}{k_{\rm c(1)}\left(n_{\rm e(Ar)} + n_{\rm e}\right)} \tag{6}$$

$$\frac{n'_{\rm u}}{n_{\rm u}} = 1 + \frac{k_{\rm c(1)}\Delta n_{\rm e}}{k_{\rm c(1)}N_{\rm e}} = 1 + \frac{\beta_1 k_{\rm c}\Delta n_{\rm e} \exp(-E'_{\rm a} / kT)}{\beta_1 k_{\rm c} N_{\rm e} \exp(-E_{\rm a} / kT)}$$
(7)

or

$$\frac{n'_{\rm u}}{n_{\rm u}} = 1 + \left(\frac{\Delta n_{\rm e}}{N_{\rm e}}\right) \exp\left[\left(E_{\rm a} - E'_{\rm a}\right)/kT\right] = 1 + \left(\frac{\Delta n_{\rm e}}{N_{\rm e}}\right) \exp\left[\Delta E_{\rm a}/kT\right]$$
(8)

where $\beta_1 k_c = k_{c(1)}$ and β_1 is the fraction of electrons undergoing radiative recombination to the excited state, and

$$\Delta E_{\rm a} = E_{\rm a} - E_{\rm a}^{\prime} \tag{9}$$

$$k_{\rm c} = Q_{12} \left(\frac{8kT}{\pi\mu}\right)^{1/2}$$
(10)

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where Q_{12} is the collision cross-section between particles 1 and 2, and μ is their reduced mass. Since $n_{e(Ar)} >> n_e$, eq. 8 can be expressed as

$$\frac{n'_{\rm u}}{n_{\rm u}} = 1 + \left(\frac{\Delta n_{\rm e}}{n_{\rm e(Ar)}}\right) \exp\left[\Delta E_{\rm a} / kT\right]$$
(11)

i.e., n_u'/n_u will be a constant. This is contrary to the experimental curves in Fig. 1, suggesting that the electrons from the ionization of Ar do not participate in the collisional processes leading to the observed interference effects of EIEs on analyte emission signal, as observed earlier by Zaranyika and Chirenje [57]. If we make this assumption, then eq. 8 becomes

$$\frac{n'_{\rm u}}{n_{\rm u}} = 1 + \left(\frac{\Delta n_{\rm e}}{n_{\rm e}}\right) \exp\left[\Delta E_{\rm a} / kT\right]$$
(12)

Three limiting cases can be defined for eq. 12 on the basis of whether collisional radiative recombination occurs before or after thermal equilibration. These are discussed below.

Limiting Case 1A (LC 1A): Assumes LTE conditions, hence all the electrons will require the same activation, i.e.

$$E'_{a} = E_{a} \tag{13}$$

and

$$\Delta E_{\rm a} = 0 \tag{14}$$

Limiting Case 1B (LC 1B): Assumes pre-LTE collisional radiative recombination for all electrons, so that the electrons from the ionization of the interferent and the analyte would require further activation given by eqs. 14 and 15, respectively

$$E'_{a} = E_{\rm TS} - IP_{\rm m} \tag{15}$$

and

$$E_{\rm a} = E_{\rm TS} - IP_{\rm a} \tag{16}$$

Therefore

$$\Delta E_{a} = E_{a} - E_{a}' = IP_{m} - IP_{a} \tag{17}$$

where E_{TS} denotes the energy of the ionization limit transition-state complex formed by the analyte ion and the colliding electron, and IP_{a} and IP_{m} denote analyte and interferent atom ionization potentials, respectively.

Limiting Case 1C (LC 1C): Assumes pre-LTE collisional radiative recombination in the absence of the interferent, and post-LTE collisional radiative recombination in the presence of the interferent. Under these conditions, we have

$$E'_{a} = E_{TS} - E_{kT} \tag{18}$$

$$E_{\rm a} = E_{\rm TS} - IP_{\rm a} \tag{19}$$

therefore

$$\Delta E_{\rm a} = E_{kT} - IP_{\rm a} \tag{20}$$

If we assume

$$\frac{I'}{I} = \frac{n'_{\rm u}}{n_{\rm u}} \tag{21}$$

then a plot of experimental I'/I ratios vs. $\Delta n_e/n_e$ should yield a linear graph of a slope from which the activation energy can be calculated using eq. 12, and compared to theoretical values as predicted for the Limiting Cases 1A to 1C by eqs. 14, 17, and 20, respectively.

Limiting Case 2.0 (LC 2.0): Dominance of thermal excitation: $k_{\Delta}n'_{o} >> k_{c(1)}n_{+}N'_{e}$; $k_{\Delta}n_{o} >> k_{c(1)}n_{+}N_{e}$.

$$\frac{n'_{\rm u}}{n_{\rm u}} = \frac{n'_{\rm o}}{n_{\rm o}}$$
(22)

In addition, eq. 2 becomes

$$\frac{dn'_{\rm u}}{dt} = k_{\Delta}n'_{\rm o} - k_{h\nu}n'_{\rm u} - k'_{\Delta}n'_{\rm u} = 0$$
⁽²³⁾

Rearranging, we have

$$k_{h\nu}n'_{\rm u} = \left(\frac{k_{h\nu}}{k_{h\nu} + k'_{\Delta}}\right)k_{\Delta}n'_{\rm o} \tag{24}$$

Substituting into eq. 1 and rearranging:

$$n'_{0} = \frac{k_{\rm D} n_{\rm AX_2} + k_{\rm c(o)} n_{+} N'_{\rm e} + k_{\rm CT} n_{+} n_{\rm wo}}{k'_{\rm CT} n_{\rm w+} + k_{\rm R} n'_{\rm X} + k_{\Delta} \left(1 - \frac{k_{h\nu}}{k_{h\nu} + k'_{\Delta}} \right)}$$
(25)

$$n'_{\rm o} = \frac{k_{\rm D} n_{\rm AX_2} + k_{\rm c(0)} n_+ N'_{\rm e} + k_{\rm CT} n_+ n_{\rm wo}}{k'_{\rm CT} n_{\rm w+} + k_{\rm R} n'_{\rm X} + k'_{\Delta}}$$
(26)

where

$$k_{\Delta}^{\prime\prime} = k_{\Delta} \left(1 - \frac{k_{h\nu}}{k_{h\nu} + k_{\Delta}^{\prime}} \right) \tag{27}$$

In the absence of the interferent

$$n_{\rm o} = \frac{k_{\rm D} n_{\rm AX_2} + k_{\rm c(0)} n_+ N_{\rm e} + k_{\rm CT} n_+ n_{\rm Ar(0)}}{k'_{\rm CT} n_{\rm Ar(+)} + k_{\rm R} n_{\rm X} + k''_{\Delta}}$$
(28)

Therefore

$$\frac{n'_{\rm o}}{n_{\rm o}} = \left[\frac{k_{\rm D}n_{\rm AX_2} + k_{\rm c(o)}n_{+}N'_{\rm e} + k_{\rm CT}n_{+}n_{\rm wo}}{k_{\rm D}n_{\rm AX_2} + k_{\rm c(o)}n_{+}N_{\rm e} + k_{\rm CT}n_{+}n_{\rm Ar(o)}}\right] \left(\frac{k''_{\Delta} + k'_{\rm CT}n_{\rm Ar(+)} + k_{\rm R}n_{\rm X}}{k''_{\Delta} + k'_{\rm CT}n_{\rm w+} + k_{\rm R}n'_{\rm X}}\right)$$
(29)

Two further limiting cases can be defined for eq. 29, thus: Limiting Case 2.1 (LC 2.1): $k_{\rm D}n_{\rm AX_2} >> k_{\rm c(o)}n_+N'_{\rm e} + k_{\rm CT}n_+n_{\rm wo}$

$$\frac{n'_{\rm o}}{n_{\rm o}} = \frac{k''_{\Delta} + k'_{\rm CT} n_{\rm Ar(+)} + k_{\rm R} n_{\rm X}}{k''_{\Delta} + k'_{\rm CT} n_{\rm w+} + k_{\rm R} n'_{\rm X}}$$
(30)

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Since $k_R n'_X >> k_R n_X$, and $k'_{CT} n_{w+} > k'_{CT} n_{Ar(+)}$, n_u'/n_u will be less than unity, i.e., a depression of absorbance signal is expected in this case, contrary to the experimental results in Fig. 1.

Limiting Case 2.2 (LC 2.2): $k_{\rm D}n_{\rm AX_2} << k_{\rm c(o)}n_+N_{\rm e} + k_{\rm CT}n_+n_{\rm Ar(o)}$ It can be shown that

$$\frac{n'_{\rm o}}{n_{\rm o}} = \left[1 + \frac{k_{\rm c(0)}\Delta n_{\rm e} + k_{\rm CT}n_{\rm mo}}{k_{\rm c(0)}n_{\rm e(Ar)} + k_{\rm c(0)}n_{\rm e} + k_{\rm CT}n_{\rm Ar(0)}}\right] \left(\frac{k''_{\Delta} + k'_{\rm CT}n_{\rm Ar(+)} + k_{\rm R}n_{\rm X}}{k''_{\Delta} + k'_{\rm CT}n_{\rm w+} + k_{\rm R}n'_{\rm X}}\right)$$
(31)

Two further limiting cases can be defined for eq. 31, thus:

Limiting Case 2.2.1 (Dominance of charge transfer interactions): $k_{c(o)}\Delta n_e \ll k_{CT}n_{mo}$, $k_{c(o)}n_{e(Ar)} + k_{c(o)}n_e \ll k_{CT}n_{Ar(o)}$, $k'_{CT}n_{Ar(+)} \gg k_Rn_X$, and $k'_{CT}n_{w(+)} \gg k_Rn'_X$. In this case n'_o/n_o will be given by

$$\frac{n'_{\rm o}}{n_{\rm o}} = \left[1 + \frac{k_{\rm CT} n_{\rm mo}}{k_{\rm CT} n_{\rm Ar(o)}}\right] \left(\frac{k''_{\Delta} + k'_{\rm CT} n_{\rm Ar(+)}}{k''_{\Delta} + k'_{\rm CT} n_{\rm w+}}\right)$$
(32)

i.e., a constant, contrary to the experimental curves in Fig. 1, suggesting that charge transfer involving Ar and interferent species does not contribute significantly to the collisional processes leading to the observed interference effects on analyte emission signal in the presence of excess EIEs.

Limiting Case 2.2.2 (LC 2.2.2): (Dominance of collisional radiative recombination to the ground state): $k''_{\Delta} \gg k'_{CT} n_{Ar(+)} + k_R n_X$, $k_{c(o)} \Delta n_e \gg k_{CT} n_{mo}$, and $k_{c(o)} n_{e(Ar)} + k_{c(o)} n_e \gg k_{CT} n_{Ar(o)}$.

It can be shown that

$$\frac{n'_{\rm o}}{n_{\rm o}} = 1 + \frac{k_{\rm c(0)}\Delta n_{\rm e}}{k_{\rm c(0)}N_{\rm e}} = 1 + \frac{\beta_0 k_{\rm c}\Delta n_{\rm e} \exp(-E'_{\rm a} / kT)}{\beta_0 k_{\rm c} N_{\rm e} \exp(-E_{\rm a} / kT)}$$
(33)

or

$$\frac{n_{\rm o}'}{n_{\rm o}} = 1 + \left(\frac{\Delta n_{\rm e}}{N_{\rm e}}\right) \exp\left[\left(E_{\rm a} - E_{\rm a}'\right)/kT\right] = 1 + \left(\frac{\Delta n_{\rm e}}{N_{\rm e}}\right) \exp\left[\Delta E_{\rm a}/kT\right]$$
(34)

where $\beta_0 k_c = k_{CR(0)}$ and β_0 is the fraction of electrons under going radiative recombination to the ground state, and $N_e = n_{e(Ar)} + n_e$. Since $n_{e(Ar)} >> n_e$, and taking into account eq. 22, eq. 34 can be expressed as

$$\frac{n'_{\rm u}}{n_{\rm u}} = \frac{n'_{\rm o}}{n_{\rm o}} = 1 + \left(\frac{\Delta n_{\rm e}}{n_{\rm e(Ar)}}\right) \exp\left[\Delta E_{\rm a} / kT\right]$$
(35)

i.e., n'_u/n_u will be a constant. This is contrary to the experimental curves in Fig. 1, suggesting that the electrons from the ionization of Ar do not participate in the collisional processes leading to the observed interference effects of EIEs on analyte emission signal, as discussed above. If we make this assumption, then eq. 35 becomes

$$\frac{n'_{\rm u}}{n_{\rm u}} = \frac{n'_{\rm o}}{n_{\rm o}} = 1 + \left(\frac{\Delta n_{\rm e}}{n_{\rm e}}\right) \exp\left[\Delta E_{\rm a} / kT\right]$$
(36)

Equations 36 and 12 show that Limiting Cases 1A to 1C discussed above apply when the excited state is reached via thermal excitation following radiative recombination to the ground state, or via direct radiative recombination to the excited state. In addition, eq. 36 can be used to calculate ΔE_a for ICP-AES, FAES, as well as FAAS measurements.

EXPERIMENTAL

ICP equipment

A Spectroflame Modula 90/95 Inductively Coupled Argon Plasma Echelle Spectrophotometer (supplied by SPECTRO Analytical Instruments, GmbH, Boschstrase, Germany) was used. The spectrophotometer was fitted with an aperture plate of 90×1.5 nm slits etched at 20 mm intervals, a photomultiplier tube (PMT) detector mounted on a movable frame for radial view of the ICP, a torch with three concentric tubes for outer gas, auxiliary gas, and sample transport, a 40.68 MHz rf generator with a power supply varying from 0.5 to 2 kW, a 5-channel computer controlled peristaltic pump, and an automatic Ar gas flow rate optimizer. The generator operated at 1.2 kW.

The argon (99.998 %) was supplied from a pressurised tank (Afrox Ltd., South Africa). The maximum impurities specified were: $O_2 - 3$ ppm; moisture - 3 ppm; $N_2 - 14$ ppm. The outer gas was supplied at 14 L min⁻¹, nebulizer pressure 40 psi (280 kPa) and auxiliary gas at 1 L min⁻¹. Under these conditions, the excitation temperature is between 7000 and 9000 K [58]. The instrument was optimised using a 100-mg/L solution of Mn. The strong emission of Mn line was used to find the optimum zone for analysis. The maximum temperature of 9000 K was used in the calculations for maximum effect of the interferent.

Flame equipment

Flame experiments were run using a Shimadzu AA–6701 Flame Atomic Absorption/Emission Spectrometer fitted with a high-resolution Czerny–Turner monochromator, automatic baseline drift correction using electrical double-beam signal processing, and an air-cooled premix-type 100-mm singleslot burner with a stainless steel head, Pt–Ir capillary nebulizer with Teflon orifice, glass impact bead and polypropylene chamber. The spectrometer was coupled to an ASC-6100 Shimadzu Auto Sampler. The air was supplied by an Atlas Copco air compressor (ETS SESCA, France) at 350 kPa input pressure, while the fuel gas, acetylene, was supplied from a pressurised tank (Oxyco Zimbabwe, Harare) at 1000 kPa. The spectrophotometer was fitted with an automatic fuel gas flow rate optimization for each element to be measured. Optimum air-acetylene gas flow rate for Mg was 1.8 L/min. Under these conditions, the temperature of the flame is 2300 °C (Shimadzu AA–6701 user manual). Other instrumental settings employed were as follows: wavelength 285.2 nm for Mg, and 766.5 nm for K; slit width 0.1 nm, burner height 7 mm, burner angle 0°, secondary acetylene gas pressure 90 kPa, pre-spray time 3 s, integration time 5 s, and response time 1 s.

Procedure

The experimental procedure adopted was described previously [55–57]. Two sets of standard solutions containing 0 to 30.0 mg/L analyte (Mg, Ca, Sr, and K) were prepared from freshly prepared solutions of their chloride salt. Merck GR grade reagents (Merck, Darmstadt, Germany) and de-ionized water of $0.002 \,\mu\text{Sm}^{-1}$, were used in all cases, and adjustments made to analyte concentration (or signal) for contamination from the easily ionizable interferent where necessary. One set was spiked with 1000 mg/L of interferent (Li, K, or Na) also prepared from the chloride salt. The other set was left unspiked. The interferent concentration was kept constant at a very high level (1000 mg/L) relative to that of the analyte, whilst the analyte concentration was varied, in order to minimize the effects of changes in the physical properties of the test solution in going from the interferent-free solution to the interferent-spiked solution would affect the series of interferent-spiked solutions to the same extent, and this can be compensated for by taking blank readings of a solution containing the interferent salt only. The analyte line emission intensity readings, *I* and *I'* where the prime denotes presence of the interferent, were made in triplicate. Ca, Mg, and Sr line emission signals were recorded at 393.3,

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279.6, and 407.8 nm, respectively, in the ICP. Ca and Mg ion line *I'/I* ratios were corrected for contamination from the Li and K interferents. The Mg and K atom lines were measured at 285.2 and 766.5 nm, respectively. The *I'/I* ratios obtained are shown in Table 1. Preliminary experiments were run to determine the aspiration rate and the nebulization efficiency for the type of solutions under analysis [47,48]. Mean values obtained for the aspiration rate and nebulization efficiency were 1.00 ± 0.04 g min⁻¹ (h = 8, n = 5) and 5.8 ± 0.4 % (h = 12, n = 5) at 95 % confidence level, respectively, for the ICP experiments, and 4.0 ± 0.1 g/min (h = 8, n = 20) and 5.7 ± 0.2 % (h = 12, n = 1), respectively, for the flame experiments.

Table 1 *I'/I* values^{*}: Effect of excess K and Li interferents on Mg(I) line in the air-acetylene flame and on SR(II), Mg(II), and Ca(II) lines in the ICP.

[M] (mg/L)	FAES	ICP-AES						
	Mg(I)/K**	SR(II)/K**	SR(II)/Li**	Mg(II)/K**	Mg(II)/Li**	Ca(II)/Li**		
0.1	1.75	2.326	2.261	2.635	2.431			
0.2	1.64	2.176	1.850	1.723	1.628	2.55		
0.4	1.48	1.353	1.391	1.368	1.401	2.34		
0.6	1.37	1.294	1.250		1.246	1.98		
0.8	1.23	1.217	1.182	1.135	1.150	1.53		
1.0	1.20	1.170	1.151	1.109	1.128			
2.0	1.18	1.098	1.091	1.079	1.101	1.01		
4.0	1.20	1.069	1.047	1.055	1.082	1.00		
8.0	1.17	1.057	1.037	1.069		0.93		
10.0						1.00		
12.0	1.10	1.040	1.017	1.047	1.055			
14.0						0.92		
16.0	1.07	1.032	1.025	1.051	1.052			
20.0	1.07	1.033	1.019	1.064	1.018	0.87		
30.0	1.07	1.038	1.030	1.028	1.014	0.83		

 $^*\lambda$ = 285.2 nm (Mg(I)), 407.8 nm (SR(II)), 279.6 nm (Mg(II)), 393.3 nm (Ca(II)).

** analyte/interferent system.

Theoretical calculations

Number densities were calculated assuming the aspiration rate and nebulization efficiency values above and 9000 K temperature for the ICP experiments. Number densities for M(II) assumed 93.00, 98.90, and 99.40 % degree of ionization [59], while those for M(III) assumed 0.174, 6.43, and 19.72 % degree of ionization [62]. The degree of ionization for Li and K was based on the Saha equation [63]

$$\log \frac{N_{r+1}}{N_r} N_e = \chi_{r,r+1} \Theta - \frac{3}{2} \log \Theta + 20.936 + \log \frac{2U_{r+1}}{U_r}$$
(37)

where N_r and N_{r+1} are the number densities of atoms in the *r* and *r* + 1 stages of ionization, N_e is the number density of electrons, $\chi_{r,r+1}$ is the ionization potential in *eV* from the *r* to the *r* + 1 stage of ionization, $\Theta = 5040 \ ^{\circ}$ *K/T* (*T* = plasma temperature), U_r and U_{r+1} are the partition coefficients, and the factor 2 represents the statistical weight of an electron. Number densities obtained are shown is Table 2. Figure 3 shows typical regression curves obtained for *I'/I* as a function of $\Delta n_e/n_e$.

M^*	FAES	ICP-AES					
	M(I)	M(II)	M(I)	M(II)	M(III)		
Ca			$2.5147 \times 10^{10} \text{ c}^{**}$	$2.46 \times 10^{10} \text{ c}$	$1.5818 \times 10^9 \text{ c}$		
Mg	$2.4058 \times 10^{11} \text{ c}$	$1.2029 \times 10^9 \text{ c}^{***}$	$4.1004 \times 10^{10} \text{ c}$	$3.8134 \times 10^{10} \text{ c}$	$2.452 \times 10^9 \text{ c}$		
K	1.7808×10^{11}	1.9589 × 10 ⁹ c					
Sr			$1.1377 \times 10^{10} \text{ c}$	$1.1309 \times 10^{10} \text{ c}$	$2.2301 \times 10^9 \text{ c}$		
Ar			2.6883×10^{19}	2.9242×10^{16}			
Li			1.4367×10^{14}	1.4367×10^{14}			
Κ	1.7808×10^{14}	$1.9589 \times 10^{12***}$	2.5495×10^{13}	2.5495×10^{13}			
Na	3.0287×10^{14}	2.8167×10^{13}					

Table 2 Flow number densities (atoms/ions $\text{cm}^{-3} \text{ s}^{-1}$).

*M = element.

c = concentration in test solution (mg/L). *Degree of ionization, $\alpha = 0.005$ (Mg), 0.011 (K), 0.093 (Na); atomization efficiency, $\beta = 84$ % (Mg) [64].



Fig. 3 I/I vs. $\Delta n_e/n_e$ regression lines: Effect of excess K and Li on Sr(II) ion line in the ICP.

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RESULTS AND DISCUSSION

Table 3 shows the regression data of I'/I vs. $\Delta n_e/n_e$, and the experimental ΔE_a values obtained when Sr(II), Mg(II), and Ca(II) line emission intensity was measured in the absence and presence of excess Li and K in the ICP. The regression data with $R^2 = 0.913 - 0.992$, and an intercept of 1.01 ± 0.04 vs. a theoretical value of 1.0, points to the validity of the kinetic model as represented by eqs. 12 or 36 that was used to calculate the activation energy for collisional radiative recombination. The regression data for the flame experiments also conforms with eqs. 12 or 36. From Table 3, it is apparent that of all the systems studied, none conforms to LTE, i.e., LC 1A, from which we conclude that collisional radiative recombination in the absence of the interferent, is always pre-LTE in the ICP as well as in FAES. Table 3b assumes equivalence of the electrons from the ionization of the M(I) and M(II) analyte. The $\Delta E_{\rm a}$ values obtained show that all the electrons from the ionization of the analyte are not in LTE, but conform closely to those expected for the pre-LTE state for electrons from the ionization of M(II) analyte. Collisional radiative recombination involving electrons from the ionization of M(I) analyte would require further activation, so that the resulting ΔE_a would be much lower than those obtained. This is confirmed in Table 3c, which assumes collisional recombination involving electrons from the ionization of M(II) analyte only, in the absence of the interferent. The ΔE_a values obtained in this case are very close to those in Table 3b.

Analyte*	M*	Slope	Intercept	\mathbb{R}^2	ΔE_{a} (Expt)	ΔE_{a} (Theoretical, eV)**		
						LC 1A	LC 1B	LC 1C
(a) FAES e	xperime	nt						
Mg(I)	K	4.43×10^{-5}	1.14648	0.851	-2.223	0	-3.306	-7.646
K(I)	Na	2.91×10^{-5}	1.21180	0.798	-2.316	0	+0.798	-4.341
(b) ICP-AE	$\text{ES:} n_{\text{e}} = n_{\text{e}}$	$n_{\mathrm{M(II)}} + n_{\mathrm{M(III)}}$ (s	ee Table 2)					
Mg(II)	Li	3.89×10^{-5}	1.0187	0.992	-7.875	0	-9.644	-14.260
Mg(II)	Κ	2.50×10^{-4}	1.00707	0.990	-6.432	0	-10.695	-14.260
Sr(II)	Li	1.25×10^{-5}	1.02964	0.979	-8.756	0	-5.638	-10.254
Sr(II)	Κ	7.78×10^{-5}	1.04770	0.913	-7.338	0	-6.690	-10.254
Ca(II)	Li	7.05×10^{-5}	0.953764	0.876	-7.414	0	-7.531	-11.096
(c) $n_{\rm e} = n_{\rm M}$	(see	Table 2)						
Mg(II)	Li	1.32×10^{-5}	1.01889	0.992	-8.713	0	-9.644	-14.260
Mg(II)	Κ	1.51×10^{-5}	1.00707	0.990	-8.609	0	-10.695	-14.260
Sr(II)	Li	1.15×10^{-5}	1.04741	0.979	-8.820	0	-5.638	-10.254
Sr(II)	Κ	1.28×10^{-5}	1.02957	0.913	-8.737	0	-6.690	-10.254
Ca(II)	Li	4.25×10^{-6}	0.95376	0.876	-9.592	0	-7.531	-11.096
Mean (<i>n</i> = 5, 95 % CL)		1.01 ± 0.04						

Table 3 Experimental and theoretical ΔE_a values: Effect of excess K on Mg(I) in the air-acetylene flame, and of K and Li on Sr(II), Mg(II), and Ca(II) ion lines in the ICP.

*Ionization potentials (eV): Mg(I) = 7.64624, Mg(II) = 15.03528, Sr(II) = 11.03013, Ca(II) = 11.87172, Li(I) = 5.39172, K(I) = 4.34066, Na(I) = 5.13908 [65].

**LC = limiting case (see text): LC 1A = LTE, LC 1B = pre-LTE, LC 1C = pre-LTE_(analyte)/LTE_(interferent); CL = confidence level.

The second conclusion arising from the non-conformance to LTE of ICP systems studied is that electrons from the ionization of Ar do not seem to participate in the collisional processes leading to the observed interference effects. As pointed out previously by Zaranyika et al. [59], the only plausible explanation for the non-involvement of electrons from the ionization of Ar in the observed interference

effects, is that collisions involving electrons from the ionization of Ar are always pre-LTE whereby the energy of the electrons at 15.755 eV (i.e., the ionization potential of Ar), is in excess of that required for radiative recombination. If we treat Ar as an interferent, the value of ΔE_a for pre-LTE collisional radiative recombination from eq. 17 will be positive, showing that the electron possesses excess energy than is required for radiative recombination, therefore the collision will be elastic. However, these electrons can participate in collisional ionization, but since the electrons from the ionization of Ar are in large excess of those from both analyte and the interferent, the extent of such collisional ionization will be virtually the same in the absence or presence of the interferent.

Experimental ΔE_a data for the effect of excess Li and K on Mg(II) line emission at -8.713 and -8.609 eV, respectively, are less than the theoretical values for the pre-LTE limiting case, LC 1B, at -9.644 and -10.695 eV, respectively. These data suggest that collisional radiative recombination involving Mg(II) ions and electrons from the ionization of Li and K, conforms to the pre-LTE limiting case. The pre-LTE limiting case involves collisions between analyte ions and interferent ion-electron ambipolar diffusion ion pair complexes. The 9.3 and 19.5 % discrepancy between the experimental and theoretical ΔE_a values falls within acceptable experimental error for the type of experiments carried out. The plasma temperature was not measured during these experimental plasma temperature from the assumed value of 9000 K. In addition, the LTE theory strictly refers to a spot in the plasma, whereas the emission measurements involve a viewing element across the plasma, hence the measurement temperature is in fact the average for the viewing element.

Experimental ΔE_a data for the effect of excess Li and K on Sr(II) and Ca(II) line emission at -8.820, -8.737, and -9.592 eV, respectively, are in excess of the corresponding pre-LTE limiting case at -5.638, -6.690, and -7.531 eV, respectively, suggesting that collisional radiative recombination involving Ca(II) ions and Sr(II) ions and electrons from the ionization of Li and K, conforms to the pre-LTE_(analyte)/LTE_(interferent) limiting case (LC IC) at -10.254 and -11.096 eV, respectively, for Sr(II) and Ca(II). The pre-LTE_(analyte)/LTE_(interferent) limiting case involves collisions between analyte ions and free electrons from the ionization of the interferent. These electrons can be expected to have some distribution of kinetic energies, so that the ΔE_a values resulting from such collisions will vary downwards from a maximum which corresponds to the difference between the ionization potential of the analyte and kT. The heating of electrons through suprathermal inelastic collisions with heavy particles in the ICP has recently been alluded to by Taylor et al. [67]. Discrepancies between experimental and theoretical ΔE_a values, amounting to 14.0, 14.8, and 13.6 %, respectively, could also be due to deviations of the plasma temperature from the assumed temperature of 9000 K. These discrepancies fall within experimental error for the type of experiments as discussed above.

Although departure from LTE is often discussed with reference to interference effects due to easily ionizable interferents, interference effects due to high ionization potential elements (relative to the analyte) have also been reported [4]. Equation 17 predicts that ΔE_a for high ionization potential interferents will be positive, signifying that the interferent electron possesses energy in excess of that required for collisional radiative recombination, so that such collisions will be elastic. Thus interference effects due to high ionization potential interferents can only be explained on the basis of Limiting Case 1C: pre-LTE in absence of interferent, and post-LTE in presence of interferent. From Table 3a, it is apparent that ΔE_a data obtained for the effect of excess Na on K line emission, at -2.316 eV vs. theoretical values of +0.798 and -4.34066 eV for Limiting Cases 1B and 1C, respectively, conform with Limiting Case 1C. The discrepancy between the experimental value and the theoretical Limiting Case 1C value is probably due to deviation of the flame temperature from the assumed value of 2573 K, or due to the fact that the free electrons involved in the collisional recombination are expected to have some distribution of kinetic energies, so that the ΔE_a values resulting from such collisions will vary downwards from a maximum which corresponds to the difference between the ionization potential of the analyte and kT as discussed above.

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From the preceding discussion we conclude that electrons from the ionization of the analyte and Ar maintain their ionization energies in the ICP. Similarly electrons from the ionization of the analyte and easily ionizable interferent maintain their ionization energies in the air-acetylene flame. Similar conclusions were arrived at following a similar study of the interference effects of Li on Ca(I) and Ca(II) line emission [59]. This behavior of electrons from the ionization of the analyte and Ar in the ICP, and from the ionization of the analyte and EIE interferent in the air-acetylene flame, was attributed to ambipolar diffusion. Ambipolar diffusion is common in plasmas [1,64,68], and occurs in a gas containing an appreciable quantity of ions and electrons. Because of their small mass, electrons tend to diffuse faster than ions. The resultant charge separation produces an electric field that retards the diffusion velocity of electrons, and increases that of ions, until a state of balance is reached in which ions and electrons diffuse with the same velocity. In this state, the ion and electron behave as an ion pair, and the electron is not completely free and therefore not capable of random motion. The number density of electrons in the ambipolar diffusion layer will depend on the ionization potential of the ion and temperature of the plasma. Collisions involving ambipolar diffusion layer ion-electron pairs are possible when the lifetime of the electron in the ambipolar diffusion layer is longer than its collisional lifetime. The collisional lifetime is determined by the density or pressure of the system. From Table 3, ΔE_a data for the flame experiment show that collisional radiative recombination is clearly pre-LTE in the absence and presence of the interferent. Data in Table 3 show that whereas collisions involving electrons from the ionization of the analyte and Ar appear to occur from the ambipolar diffusion state, it appears that collisions involving electrons from the ionization of the EIE interferent can occur from the ambipolar diffusion state or from the LTE state. It would appear from these results that the number density of electrons in the ambipolar diffusion layer bears an inverse relationship to both ionization potential of the parent atom or ion and plasma temperature.

Implications with respect to the Boltzmann distribution law for bound states

The Boltzmann distribution law for bound states is defined for thermal excitation from the ground state. Equation 12, which forms the basis for calculating the activation energy for collisional radiative recombination, was arrived at by assuming Limiting Cases 1.0, 2.0, and 2.2.2. As discussed above, Limiting Cases 2.0 and 2.2.2 show that thermal excitation is dominant only when the ground state is reached via ion/electron collisional radiative recombination to the ground state, while Limiting Case 1.0 refers to radiative recombination directly to the excited state. If we assume that the distribution of recombining electrons into the various levels is such that the Boltzmann law for bound states is maintained, we can safely assume that k_{s0} and k_{s1} , the rate constants for radiative relaxation to the s_0 and s_1 electronic states, have values equal to the inverse of the Boltzmann factors for the corresponding ionization processes as shown in Table 4.

Reaction	Rate constant*	Eq. number	
(a) $M^+_{(\text{KE}=k\text{Tg})} + e^*_{(\text{KE}=\text{IP})} \rightarrow (M^+ - e^*)_{(\text{KE}=\text{IP})}$	$k_{\rm c} = Q_{12} \left(\frac{8kT}{\pi\mu}\right)^{1/2} e^{-\mathrm{IP}/kT}$	38	
(b) $(M^+e^-)^* \rightarrow M + hv_{(s0)}$	$k_{s0} = (g_{s0}/g_{TS})e^{+(IP - \Delta E_{s0})/kT}$	39	
(c) $(M^+e^-)^* \rightarrow M + hv_{(s1)}^{(s0)}$	$k_{s1} = (g_{s1}/g_{TS})e^{+(IP-\Delta E_{s1})/kT}$	40	
(d) $(M^+e^-)^* \rightarrow M + hv_{(si)}^{(S1)}$	$k_{si}^{\rm SI} = (g_{si}^{\rm SI}/g_{\rm TS})e^{+({\rm IP}-\Delta E_{si})/kT}$	41	

 Table 4 Rate constants for steps involved in collisional radiative recombination.

 $*k_{s_0}$ and k_{s_1} are the rate constants for radiative relaxation to the s_0 and s_1 electronic states, IP = ionization potential of M, and ΔE_{s_0} , ΔE_{s_1} and ΔE_{s_i} are the energy differences between the s_0 , s_1 , and s_i electronic states with the ground state, s_0 , and g_{s_i} and g_{TS} are the statistical weights of the S_i state and ambipolar diffusion ion-electron transition state, respectively.

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From (b), we have

$$\int dn_{s_0} = \int_0^1 k_{S_0} n_{(M^+ e^-)^*} dt \tag{42}$$

$$n_{s_0} = k_{s_0} n_{(M^+ e^-)^*} \tag{43}$$

Assuming a steady state with respect to the ionization limit ion pair complex

$$\frac{dn_{(M^+,e^{-*})}}{dt} = k_c n_{M^+} n_{e^*} - k_{s_0} n_{(M^+e^-)^*} - k_{s_1} n_{(M^+e^-)^*} - k_{s_i} n_{(M^+e^-)^*} = 0$$
(44)

$$n_{s_1} = k_{s_1} n_{\left(M^+ e^-\right)^*} = \left(\frac{k_{s_1}}{k_{s0} + k_{s_1} + k_{s_i}}\right) k_c n_{M^+} n_{e^*}$$
(45)

or

$$n_{s_1} = \left(\frac{k_{s_1}}{\Sigma k_{s_i}}\right) Q_{12} \left(\frac{8kT}{\pi\mu}\right)^{1/2} n_{M^+} n_e e^{-IP/kT} = \beta_1 Q_{12} \left(\frac{8kT}{\pi\mu}\right)^{1/2} n_{M^+} n_e e^{-IP/kT}$$
(46)

Similarly

$$n_{s_0} = \beta_0 Q_{12} \left(\frac{8kT}{\pi\mu}\right)^{1/2} n_{M^+} n_{\rm e} e^{-IP/kT}$$
(47)

where β_0 and β_1 are the fractions of electrons undergoing radiative relaxation to the ground state and excited state, respectively, and k_c is the rate constant for thermal activation of the free electron from the LTE state to the ionization limit state of the atom M. Therefore

$$\frac{n_{s_1}}{n_{s_0}} = \frac{\beta_1}{\beta_0} = \frac{k_{s_1}}{k_{s_0}} = \frac{g_{S_1}e^{+(IP - \Delta E_{s_1})/kT}}{g_{S_0}e^{+(IP - \Delta E_{s_0})/kT}} = \left(\frac{g_{S_1}}{g_{S_0}}\right)e^{-\Delta E_{s_1}/kT}$$
(48)

in agreement with the Boltzmann law ($\Delta E_{s0} = 0$). Our interpretation of this is that the Boltzmann law for bound states is obeyed even though the plasma is not in LTE.

Effect of ionization potential and temperature on free electron number density

1

The steps involved in ion-electron radiative recombination can be summarized as shown in Fig. 4. Steps 1 to 5 relate to ionization, while steps 6 to 9 relate to collisional radiative recombination. *Ionization:* thermal excitation of the atom to the ionization limit excited state (step 1), followed by transfer of the internalized energy of excitation to the electron to give the ambipolar diffusion ion pair (step 2), then ejection of the activated electron (step 3), and simultaneous return of the ion to the LTE state (step 4), and finally thermal de-activation of the electron and its relaxation to the LTE state (step 5); *Collisional radiative recombination*: thermal activation of the electron (step 6), followed by collision with the ion to give the ambipolar diffusion ion pair (step 7), internalization of the activation energy of the electron to give the ionization limit excited state (step 8), release of the potential energy of the electron as a photon, and relaxation of the atom to the LTE state (step 9).



Fig. 4 Proposed detailed mechanism of thermal ionization and radiative recombination (E = energy, k = Boltzmann constant, $T_g = \text{gas temperature}$, $T_e = \text{electron temperature}$, IP = ionization potential, $k_I = \text{ionization rate constant}$, $k_{s0} = \text{rate constant}$ for radiative relaxation to the ground state, $k_c = \text{ion/electron collisional rate constant}$, $k_e = \text{rate constant}$ for release of free electrons).

If the ionization limit transition state, $(M^+e^-)^*$, and the ambipolar diffusion ion pair, (M^+-e^*) , in Fig. 4 are regarded as resonance structures, it can be shown that

$$\frac{d[e^*]}{dt} = \left(\frac{k_e}{k_{s0} + k_e}\right) k_I[M]$$
(49)

where $k_I =$ ionization rate constant, $k_{s0} =$ rate constant for radiative relaxation to the ground state, $k_e =$ rate constant for release of free electrons. From Table 4, the rate constant for radiative relaxation, k_{s0} , increases with increase in ionization potential, leading to reduced rate of generation of free electrons. Similarly, k_I increases with temperature, leading to an increase of step 3 in Fig. 4. This would explain why the ambipolar diffusion Ar ion/electron transition state would be expected to have a longer lifetime than that of EIEs, which have much lower ionization potentials, and why an increase in temperature tends to reduce the lifetime of EIE ambipolar diffusion ion/electron transition state.

CONCLUSIONS

From the foregoing discussion, we conclude that the major excited-state populating processes during ICP-AES and FAES are direct collisional radiative recombination to the excited state or thermal excitation following collisional radiative recombination to the ground state. The experimental ΔE_a values reported in this paper confirm the now accepted position that the ICP and flame plasmas are not in LTE. The departure from LTE derives from the finding that, whereas current theory of atomic spectrometry assumes that all collisional processes occur after thermal equilibration, data presented in this paper suggest that ion/electron collisions can occur before or after thermal equilibration depending on plasma temperature and ionization potential of the parent atom or ion. Pre-LTE collisional radiative recombination predominates in the absence of interferents both in flame and ICP systems. In ICP systems, col-

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lisions involving electrons from the ionization of Ar are either elastic or do not lead to recombination because of the high energy of the electrons (equal to the ionization potential of Ar), whereas collisions involving electrons from the ionization of EIE interferents can occur before or after thermal equilibration, leading to the observed interference effects.

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