Experimental Verification of a New Basic Intensity Formula in Optical Emission Spectroscopy

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This is an extended version of an earlier review paper about a new intensity formula in optical emission spectroscopy and three independent experimental and analytical methods supporting it. To obtain these results, different light sources and a new theory has been used. It is shown that the data obtained from many old and new experimental methods described in the literature strongly support this formula.

1. Introduction
The origin of this work goes back to 1980s when the intensity fluctuation measurements were conducted by the author using a versatile computerized spectrometer system (IDES) suitable for simultaneous study of intensity fluctuation of a large number of spectral lines in a sample for different kind of optical sources. The formula used was given by Yngström [1], where the intensity is given by

\[ I = C \lambda^{-2} \exp(-\frac{J}{kT})/(\exp(h \nu / kT) - 1) \]  (1)

Here, \( J \) is the ionization energy and \( C \) is a factor given by transition probabilities, number densities and sample properties, and \( \lambda \) and \( \nu \) are, respectively, the wavelength and frequency of the atomic spectral line. The intensity formula consists of 4 parts: the \( C \)-factor, \( \lambda^{-2} \)-part, the \( J \)-dependence \( \exp(-\frac{J}{kT}) \), and the Planck factor \( 1/ (\exp(h \nu / kT) - 1) \).

Thelin and Yngström have developed three methods of analyses: the fluctuation analysis, the absolute intensity method and the analysis of detection limits. In a recent review paper, Thelin [2] examined different experimental methods and gave a detailed discussion using a larger set of statistical samples and a few new examples from the literature. Many areas in physics, astrophysics and analytical chemistry may utilize this intensity formula because it involves different analytical techniques for different wavelength regions (\( \gamma \), X-ray, UV, optical and IR). The intensity formula is based on calculation of the most probable photon distribution (Planck factor) and the mean value of energy levels (ionization energy factor). It is also possible to use the inverted intensity formula in breakdown and beam foil experiments.

2. The Fluctuation Method
In a hollow cathode experiment, a single-chamber, hollow, cathode spectral lamp (SCHC) was used with a water-cooled electrode. The solid metal sample was a cylinder of 4 mm inner diameter and 29 mm length. It was flushed with neon and worked at a discharge current of 0.5A. The plasma column along the sample cylinder axis was stable and intense, and the measurement conditions in the direction of this axis were favorable. The spectral lines were also sharp and the background effects were negligible. The fluctuation method deals with the study of spectral line intensity ratio fluctuations [3] and it was developed using the above method.

Taking the ratio of intensities of two simultaneously measured lines from the same sample and using the logarithmic differentiation, we obtain the following expression

\[ \frac{d(I_{a mn}/I_{b kl})}{(I_{a mn}/I_{b kl})} = \frac{d(C_{a mn}/C_{b kl})}{(C_{a mn}/C_{b kl})} + \frac{(1/kT)(dT/T)}{D(E)} \]  (2)

Where, \( D(E) = J^a - J^b + h \nu_{mn} - h \nu_{kl} \). This formula represents a straight line as shown in Fig. 1. In this figure, fluctuation data \( R \) versus \( D(E) = J^a - J^b + h \nu_{mn} - h \nu_{kl} \) (difference of ionization energy plus photon energy) were used from fifteen steel samples in hollow cathode lamp. Seventeen elements were studied giving a correlation coefficient of 0.90. Moreover, 17 elements could be identified and measured simultaneously using the IDES-system. Samples were prepared with varying concentrations of metallic elements. The SCHC lamp had the same discharge current and cooling efficiency for different steel samples. In this way,
75 intensity data values for each line were obtained.

Similar graphs were obtained in [4] and [5] with an ICP-light source (inductively coupled plasma) for liquid samples and in earlier papers by (for references, see [3]). In [3], we also surveyed the literature on the classical intensity formula and the Planck radiation law.

The fluctuation is due to ICP measurements as shown in Fig. 2, where 39 Fe I-lines were simultaneously measured 30 times with an end on ICP in combination with an IDES-system. Both Figs. 1 and 2 constitute a very strong evidence for Eqn. 1.

In the ICP analysis (Fig. 2), 39 Fe-lines were simultaneously and repeatedly measured 30 times with the IDES-system in the wavelength region 240-750 nm. In this way, it was possible to obtain ½ (39x38) = 741 intensity ratio combinations between these Fe-lines. It is very important that the spectral lines used are coming from completely different upper states in order to see the effect clearly. Therefore, the upper states of the spectral lines used originated from upper states of the energy range (3.2-7.5 eV).

3. The Absolute Intensity Method

A second method was also developed in Yngström et al. [3] and Thelin [4] by studying absolute intensity of spectral lines. It was shown that it is possible to obtain linear relationships by studying logarithmic expression

\[ \ln(I^2) = (-\frac{h}{kT}) \left( 1 + \frac{kT}{h} \ln(1-\exp(-\frac{h}{kT})) \right) \]  

This relation was developed from Eqn. 1. The investigation was based on NBS intensity tables on arc measurements. The points in this graph represent the mean values of many spectral lines in
a small wavelength interval. The tabulated intensity data from the Striganov tables was used such that every energy range was split up into intervals of 0.2 eV in the IR region, and intervals of 0.5 eV width in the optical an UV regions. In each spectral interval, the average intensity was determined (mostly for electric dipole lines).

In these studies, the new intensity formula was used in the development of this method of analysis. In this method, $\ln(I \lambda^2)$ was plotted versus $h\nu(1+\theta/h\nu \ln(1-\exp(-h\nu/\theta)))$ eV for 17 elements. Such graphs are shown in Figs. 3 and 4, which are graphs of C(II) (ions) and C(I) atoms showing linearity over 25eV and 14 eV, respectively. This is indeed a remarkable results with correlation coefficients $r = -0.87$ for C(II) ions and corresponding result for C(I) was $r = -0.97$. The above result supports strongly Eqn. 1.

Notice that the slope shown in Fig. 3 is less than what is given in Fig. 4. According to Eqn. 3, this is probably a result of higher temperature for ions.

Each intensity value is the mean value of many individual values. Taking the maximum of the difference between $\ln I^2$ and $\ln \lambda^2$, the following formula will be the basic equation in this method of analysis.

$$
\ln (I_{\max} \lambda_{\max}^2) = \text{const.} - 1.6 J/h\nu_{\max}
$$

In Fig. 5, the graph of this equation is shown as a plot of $\ln(I_{\max} \lambda_{\max}^2)$ versus $1.6 J/h\nu_{\max} = J/\theta$ for 17 elements, where $\theta = kT_e$ (electron temperature) and J denotes the table value of ionization energy. This graph forms a good linear relationship for $h\nu_{\max} = 1.6 \theta$.

4. Detection Limit Method

A third method of analysis has been developed concerning the detection limits of ionic spectral lines in an inductively coupled plasma experiment. A table of transition probabilities of spectral lines in an arc experiment was used in Yngström [7]. Results obtained from the analysis of detection limit data are consistent with the new spectral line expression of Eqn. 1.

In the above paper, a method was developed to calculate the transition probability rates from established tables, which should be revised, however, according to the new theory of spectral line intensity. An independent method of
determining probability rates of electric dipole transitions according to this theory has been proposed in Yngström et al. [3] and Yngström [7]. Correct values of transition probability rates are important in many spectroscopic applications and in particular in astronomical spectrometry.

In this paper, an equation for ionic spectral lines has also been proposed, which is similar to Eqn. 1. Here, the second ionization energy \( J_2 \) has been added to the \( J_1 \)-term of the first ionization energy.

All this evidence apparently implies a very strong support for the new intensity formula and its extension for ions.

5. Further Evidence

The new theory in Yngström [1] is in accordance with Eqn. 1 and is based on the first principles of quantum physics, electrodynamics and statistical physics. It is possible to calculate the most probable photon distribution in this theory.

The data on new materials found by other researchers also support our intensity formula. These findings, together with our earlier works, prove to be another strong evidence of Eqn. 1. We have now found around 30 different experimental methods and observations, which support different parts of Eqn. 1 and so do many variants of each method. Some of these works are discussed here. We will now study the different parts of Eqn. 1 and correlate it other works.

6. The \( \exp(-J/kT) \) Dependence

6.1 Different gas plasmas

The term \( \exp(-J/kT) \) in Eqn. 1 is clearly shown in Dresvin [8] (Figs. 3.12, 3.13a and 3.13b, pp.100-102). In this reference, the relationships between absolute and relative line intensities versus temperature for different plasmas of \((\text{Ar, N}_2\text{, and O}_2)\) were studied. In these studies, the absolute and relative intensities were plotted versus measured temperature for a number of atomic spectral lines that were studied. These graphs go to a maximum, which is higher for elements with lower \((J + \hbar \nu)\)-values according to Eqn. 1. Similar graphs were also studied for ion spectral lines of the same gases, which gave the same results for the atomic spectral lines, i.e., higher intensity for lower \((J + \hbar \nu)\)-values. Ionic spectral lines seem to follow the similar \( J \)-dependence as the atomic spectral lines of Eqn. 1. This is examined in detail in [7].

6.2 Laser experiment

In their experiment, Meek et al. [9] (Figs. 9.7, 9.11, 9.12 and 9.13, pp.735, 744 and 745) used a neodym laser at different pulse time in combination with an Argon flash equipment. The intensity was plotted versus the Argon pressure. In this experiment, the intensity is inversely proportional to the pressure and the pressure is inversely proportional to the ionization and therefore proportional to the ionization grade, which is proportional to \( \exp(-J/kT) \) according to Saha standard equation. \( J \) is here the ionization potential. This means that the intensity is proportional to \( \exp(-J/kT) \) as given in Eqn. 1.

6.3 Inductively coupled plasma

In a paper by Blades et al. [10], an ICP-temperature investigation has been done for different elements at different heights of the ICP-plasma. A straight line was obtained, where the heights of different spectral lines (peak values) from different elements were plotted versus the normal temperature. This graph showed that the \( I(\text{max}) \) is inversely proportional to the height \( h \) of the spectral lines. This graph showed (Fig. 19, p.861) that it is possible to plot the height versus \((J + \hbar \nu)\), which is linear and shows a direct proportionality between height and \((J + \hbar \nu)\) (see Fig. 6). The fact that \( I(\text{max}) \) is inversely proportional to height \( h \), means that \( I(\text{max}) \) is inversely proportional to \((J + \hbar \nu)\). This is in agreement with Eqn. 1.

In Chan et al. [11], fundamental characteristics of plasma related matrix effects were studied. The intensity from the plasma was plotted versus the first ionization energy of the elements studied. The intensity was here decreasing with increasing ionization energy according to Eqn. 1.

![Graph showing linear relationship between height in the ICP-plasma and \((J + \hbar \nu)\) for different elements studied (reproduced with permission, Thelin [2]).](image-url)
7. **The Planck Factor 1/(exp(hν/kT)-1)**

According to Penner [12] (Figs. 15-1 and 15-2, p.451), the contributions of continuous spectrum is mainly dominating in the high temperature range, while the contributions from the discrete emissions are mainly dominating in the lower temperature range.

7.1 **Astrophysics**

In Silva et al. [13], both continuous and discrete spectra of stars have the same appearance, where the hydrogen Balmer absorption lines of the stars have the same appearance as the continuous spectrum. These are the well known Planck curves with steep low wavelength side and a slow high wavelength side. The wavelength of the intensity maximum of continuous and discrete spectrum seems to be the same. This is in agreement with Eqn. 1 and the new theory. The Planck factor is a part of the new intensity formula. This is clearly seen in Fig. 7 from the spectrum of two A-stars. The normalized flux is here proportional to the emissions from the continuous and discrete spectrum. These curves constitute good examples of Planck curves, where continuous and discrete emissions seem to have the same wavelength maximum.

7.2 **Laser experiment**

In Chekhovskiy et al. [14] (Fig. 3, p.6791), an optical spectrum (power versus wavelength) from a laser experiment (laser breakdown pulses) is demonstrated over the whole visible spectrum. Laser breakdown pulses were generated in the tap water. The envelope of two peaks follows a typical Planck profile and the wavelength maxima of continuous and the discrete emissions seem to be the same and thus confirm Eqn. 1.

7.3 **LED-lamps, photoluminiscence and electroluminiscence**

The Planck factor is also supported by the intensity profile \( I = f(\lambda) \) of the LED-lamps (light emission diode). These LED lamps were kept at low temperature as in Li et al. [15] (Fig. 3, p.5087) and Choi et al. [16] (Fig. 6b, p.8267). These curves resulted from the experiment at room temperature and far below (26-200K) from FL-experiments.

![Fig.7. Plot of normalized flux versus the wavelength (Planck curve) for two different A-stars. The absorption hydrogen Balmer lines are clearly observed. The wavelength of the intensity maxima for both continuous and discrete emissions seems to be the same (reproduced with permission, Silva et al. [13]).](image-url)
In Tsuboi et al. [17] (Figs. 7 and 8, p.7431), the photoluminescence spectra for EU-doped Titania nano-particles are given at room temperature. These graphs clearly show that the intensity maximum wavelength of continuous and discrete emissions seem to be the same.

Ohshima et al. [18] (Fig. 5, p.1299) show a similar intensity-wavelength profile (Planck factor) between both electroluminescence and photoluminescence spectra. In their paper, electrons were injected into an organic field-effect transistor with Au electrodes. An electric AC-field was used to obtain electroluminescence. To obtain photoluminescence, a UV LED on tetracene thin film was used.

### 7.4 Different gas plasmas

Another evidence to support Eqn. 1 was shown for different gas plasmas, where temperature calculations in relation to absolute and relative line intensities of argon, nitrogen and oxygen were carried out. In Dresvin [8] (Figs. 3.12, 3.13a and 3.13b, pp.100-102), such an intensity versus temperature graph has the appearance of a maximum. This maximum has a higher value for higher wavelength, which is in agreement with the hv-dependent Planck factor of Eqn. 1.

### 7.5 FTIR-spectra

In Huang et al. [19] (Figs. 3 and 4, p.1534), the FTIR spectra (Fourier transform infrared) was shown in the infrared region on SiO-CH films. The envelope of the molecule bands CH₃ and CH₂ show a clear Planck factor structure emanating from discrete energy levels in the molecules. Since Eqn.1 originates from atomic spectra, it is plausible to believe that this photon distribution (the most probable according to Yngström [1]) also deals with molecules. This photon distribution is the same between emission and absorption except the C-factor.

### 7.6 X-ray, γ-radiation and IR-experiments

Similar intensity wavelength profile, which is common in the optical experiments described above, has also been observed in the X-ray field as shown in Siegbahn [20] (Fig. 238, p.444 and Fig. 248, p.457). In their experiment, fast electrons were accelerated against a metal electrode and X-ray radiation was created. The X-ray emission spectral lines from this experiment follow the usual optical Planck factor profile in our formula. Planck factor profiles are also observed in the line spectrum of γ-radiation from the decay of a Ra preparation (Schaffs [21]) (Fig. 19, p.18) and in the IR-region (0.2-2µm) from a 1000W-Hg-lamp (Suits [22]) (Figs. 2-42 and 44, pp.2-51 and 52).

This means that the new intensity formula seems to be applicable to γ-radiation, X-ray, optical, and IR-regions. In these examples, the intensity maximum wavelength of discrete emission seems to be equal to the intensity maximum of the continuum, which supports the Planck factor of our formula.

### 8. The C-factor

#### 8.1 Laser experiment

In Fig. 9.9, p.737 of Meek et al. [9], the breakdown pressure is plotted versus ionization energy for some atomic and molecular gases. In this investigation the laser power was fixed. The C-factor includes the number densities of a gas (i.e., the pressure) in this experiment and the pressure is proportional to the ionization energy. This fact is in agreement with Eqn.1 because the C-factor can be expressed approximately as (inverted intensity formula)

\[
C = I \lambda^2 \exp((J + h\nu)/kT) \quad (5)
\]

#### 8.2 Beam foil experiment

Fig. 14.3 of Kaminsky [23] shows the result of a beam foil experiment, where noble gas ions were striking a Mo foil. The number of electrons (or ions) was plotted versus the kinetic energy of the incident noble gas ions. In that figure, linear plots were achieved for different ions. These graphs show higher numbers of electrons/ion for higher ionization energy. This fact supports Eqn. 1, because the number densities of electrons are included in the C-factor from Eqn. 5.

### 9. λ-dependence

#### 9.1 X-ray experiments

This dependence has been studied earlier by Comton [24] (Figs. 2-9, p.93) and Flügge [25] (Fig. 12, p.349) in the X-ray field, where

\[
I(\lambda) = \text{const} \lambda^{-2} \quad (6)
\]

for X-ray emission. In this wavelength region, the hv-value is very high making the Planck factor around 1. Eqn. 6 can be derived from Eqn. 1 when kT ≈ h\nu. This expression agrees with Eqn.1 for specific elements.
10. Discussion

The above examples show that the new intensity formula seems to be applicable to many light sources at different experimental conditions and temperatures. The present paper is an extended version of an earlier review paper concerning this formula [2]. More detailed statistical investigations are discussed in this paper.

The fluctuation analysis of spectral line intensity ratios in Yngström et al. [3], Thelin [4] and Thelin [5] is a useful method of sorting the correct formula. In this method, questions concerning the photon efficiency versus the wavelength for spectrometer systems can be eliminated. Fig. 2 and Fig.1 show, respectively, the statistical support of the ν-dependence of the formula and the (J + hν)-dependence of Eqn. 1.

In Yngström et al. [3] and Thelin [4], the absolute intensity method show linearity over 25 eV for C (II)-lines and 14 eV for C(I)-lines. This is impossible to achieve without a correct intensity formula. Deviations in the graph of photon efficiency versus wavelength for various spectrometer systems are very small. The most dominant linearity factor is a correct exponent in the intensity formula.

The height investigation of ICP-plasma supports Eqn. 1 and its J-dependence. This is clearly shown in Fig. 6, where many different elements were used, and which gives a linear relationship.

In the astrophysical field, the Planck curves of the A-stars given by Silva et al. [13] represent good evidence in support of the Planck factor in Eqn.1, because the wavelength of the intensity maximum for the continuous-and absorption lines (Balmer) seem to be the same. Many works at very low temperature are also a strong proof of this factor, because in these temperature intervals only discrete transitions are dominating. In many of these graphs, there are deep minima between the peaks. These facts verify that there are only discrete emissions here in accordance with Eqn.1. According to Yngström [1], the Planck factor originates from the most probable photon distribution. It is likely that this factor concerns both atomic and molecular spectra in all wavelength regions observed.

It has also been shown that it is possible use the inverted intensity formula in many breakdown experiments with lasers and also in beam foil experiments.

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