Intensity formula for optical emission and photoelectric effect

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Abstract: *In this paper different methods supporting a new intensity formula in optical emission spectroscopy are presented. Three independent experimental and analytical methods have been developed which strongly support this new formula. Different light sources have also been used in this work. A new theory has earlier also been presented which strongly verify the new formula. Support is also given from experimental data of many old and new physical methods in the literature. Corresponding equations for ions are also presented.*

By inverting this new intensity formula a formula for the photoelectric effect is also obtained. In this way an explanation of many experimental current versus frequency observations are given. The ionization energy of many different elements has also shown to be important in the photoelectric effect in connection with this intensity formula.

Keywords: *Optical emission spectroscopy, Arc, DC, Hollow cathode excitation, Inductively coupled plasma, Analytical methods, Photoelectric effect, Electron spectroscopy , Laser experiments and Solar Cells.*

I. Introduction

During the 1980s,while working with auroral spectroscopy at the Institute of Space Physics the author found experimental evidence of the new intensity formula in optical emission spectroscopy (1,and 2). This was theoretically verified by my coworker Dr.S.Yngström at that time.

According to a new theory by S.Yngström (3) , the intensity I is given by :

$$I = C\ \lambda^{-2}(\exp(-J/kT))/(\exp(h\nu/kT)-1) \qquad (1)$$

where J is the ionization energy, and C is a factor given by transition probabilities, number densities and sample properties. λ and ν are here the wavelength and frequency of the atomic spectral line. This means that the new intensity formula consists of 4 parts : the C-factor, λ^{-2}-part, the J-dependence $\exp(-J/kT)$ and the Planck factor $1/((\exp(h\nu/kT)-1)$.

Myself and my college Dr.Sten Yngström have earlier presented many papers in the past about this formula. We have developed three methods of analyses : the fluctuation method(4 and 5),the absolute intensity method (6)(4)(7) and the detection limit method (8), all supporting the new intensity formula in equation 1. The two first methods will be presented in this paper. Similar formulas for ionic spectra will also be presented (9). Three summary papers(10)(11) and (12) over this project have been published in open access journals, which include strong evidence from the literature of this new intensity formula. References in these papers include many earlier papers from the beginning of this project. It is common in the literature to find papers and data from the past which support the new intensity formula. These literature papers come from different areas of physics, chemistry and astronomy and are summarized in paper (12).

The fundamental laws of photoelectrical effect was discovered in the beginning of the last century. Then it was discovered that the photoelectric current is directly proportional to the intensity of light. It was discovered that photons of sufficiently short wavelengths will ionize atoms and molecules when emitting a sample.

According to the photoelectric effect by Planck and Einstein , the kinetic energy of the electrons (E_{kin}) equals the difference between then photon energy (hν) of the impacting photons and the ionization energy (J) of the target ($E_{kin}= h\nu - J$). It was also discovered a heating effect by the radiation and the consequently rise of the temperature of the absorbing material.

More exact methods involve measurements of the photoelectron current density i as a function of the irradiated frequency ν. The dependence of the current i on the frequency ν can be represented by two different characteristic curves : the usual photo effect , which has an e^ν- structure a bit in on the ν-axis and the "selective" photo effect which starts in the same way as the normal one, but has a maximum in the photocurrent curve. The usual photo effect is occurring for most clean metal surfaces while the selective photo effect is working with thin films of alkali metals put on metallic backings as in photo cathodes.

There are some methods from the literature which try to explain the current versus frequency dependence. This dependence is seen and explained in different ways in the literature. Some of these are mentioned below.

The method of Fowler (13) is called the isotherm method of determining the work function from the spectral distribution curve of photo electron emission from a metal surface at a temperature T. In his investigation the photocurrent i/T^2 is measured and plotted versus hν / k T. This investigation gives for the

first time a satisfactory theory of the effect of temperature on photoelectric emission together with the theory by Sommerfield (14).

The Schottky theory (15) has been applies successfully to the problem of electron emission in accelerating fields. He has used a formula between current and the accelerating field and temperature. None of these mentioned methods gave a complete and satisfactory correlation between theory and experiment according to these authors.

On the other hand, when using methods used in this paper, based on the inverted new intensity formula, the author found excellent agreement between theory and experiments. This measurements led to a new formula for the photoelectrical effect. Measurements from the literature have been used here (16) and these measurements were first done and discovered by the author and published in (17) and in the summary paper (12).

In this very paper a comparative study is performed between all the important different basic studies with the new intensity formula.

II.   The fluctuation method

The first method which was developed supporting new intensity formula with an exponential (J + hν) term is the fluctuation method. This method concerns the study of spectral line intensity ratio fluctuations (1,2,4 and 5). By forming the ratio between the intensities of two simultaneously measured spectral lines from the same sample and by using logarithmic differentiation, we obtain the following expression :

$$ d (I^a_{mn} / I^b_{kl}) / (I^a_{mn} / I^b_{kl}) = d (C^a_{mn} / C^b_{kl}) / (C^a_{mn} / C^b_{kl}) + (1 / kT)(dT / T) D (E) \qquad (2) $$

where $D (E) = J^a - J^b + h \nu^a_{mn} - h \nu^b_{kl}$. Mathematically this formula is a straight line, which can be seen in Fig (1) from a hollow cathode experiment(4). In this figure fluctuation data R versus $D(E) = J^a - J^b + E^a_{mn} - E^b_{kl}$ (difference of ionization energy plus photon energy) were used from fifteen steel samples in a hollow cathode lamp. Seventeen elements were studied in this graph giving a correlation coefficient of 0.90 . In this paper similar graphs were obtained with an ICP –light source together with the IDES spectrometer system(1) and (5). These measurements are shown in Fig 2.
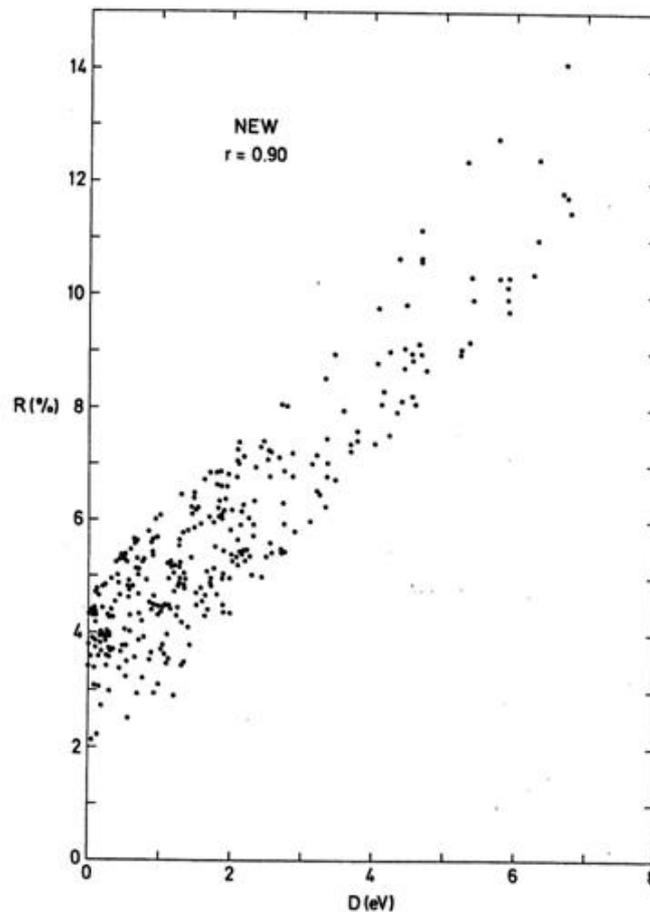

Fig 1 Plot of fluctuation data R versus $D (E) = J^a - J^b + h \nu^a_{mn} - h \nu^b_{kl}$. (difference of ionization energy plus photon energy) from fifteen steel samples used in a hollow cathode lamp. Seventeen elements were studied in this graph. (Reproduction from Ref 4)
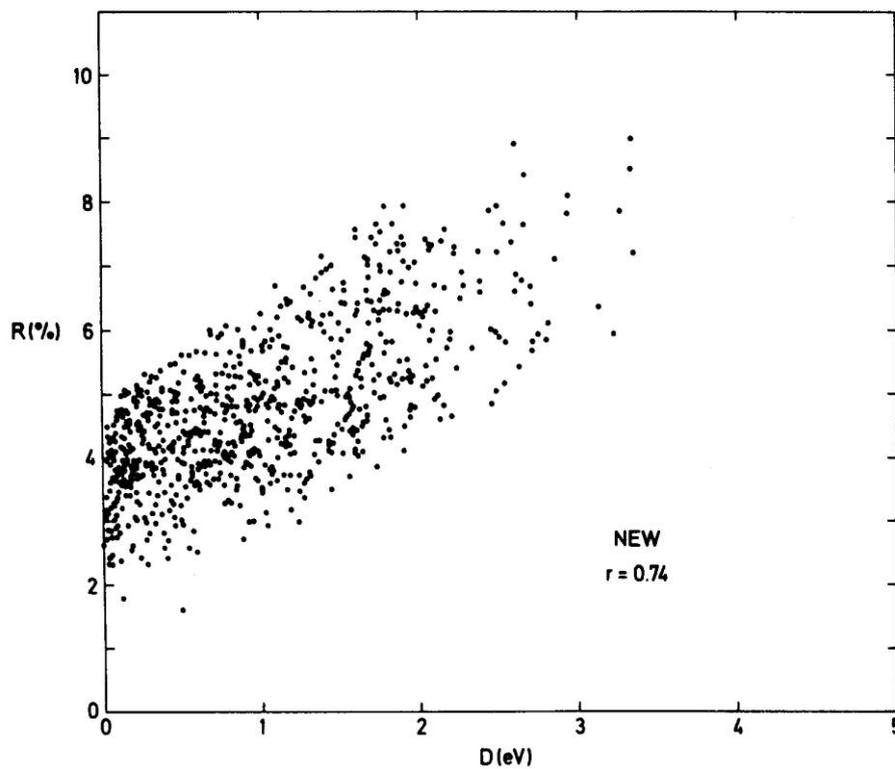
Fig 2: In the analyses of Fig 2 39 spectral iron lines in the wavelength region 240 - 750 nm were simultaneously and repeated measured 30 times with the ICP - IDES system. Reproduction from Ref (1).

These measurements gave a correlation coefficient r = 0.74 and were carried out with a computer. This is a strong evidence of the h v -term in equation 1, as D(E) = (h v_{mn}^{a} - h v_{kl}^{a}) in this case (same element).

III. The absolute intensity method

a. Atomic spectra
This method was developed for the first time in (6) and more profoundly developed in paper (4) by studying absolute intensity of spectral lines from spectral tables. According to this method it has shown to be possible to obtain linear relationships by studying the logarithmic expression :

$$\ln (I \ \lambda^2) = -(h v/kT)(1 + (kT/hv)\ln (1- \exp(-hv/kT))) \qquad (3)$$

which was developed from equation 1. This investigation was based on NBS intensity tables on arc measurements (18) and (19). The points in this graph represent the mean values of many spectral lines in a small wavelength interval. Such a graph is shown in Fig 3 ,which is a graph of C(I) data showing linearity over 14 eV. Correlation result for C(I) data was   r= -0.97. These results are a very strong evidence of equation 1.
In this method $\ln (I \lambda^2)$ was plotted versus hv (1+θ/hv ln(1-exp(-hv/θ))) eV   for 17 atomic elements. Each intensity value is the mean value of many individual values.
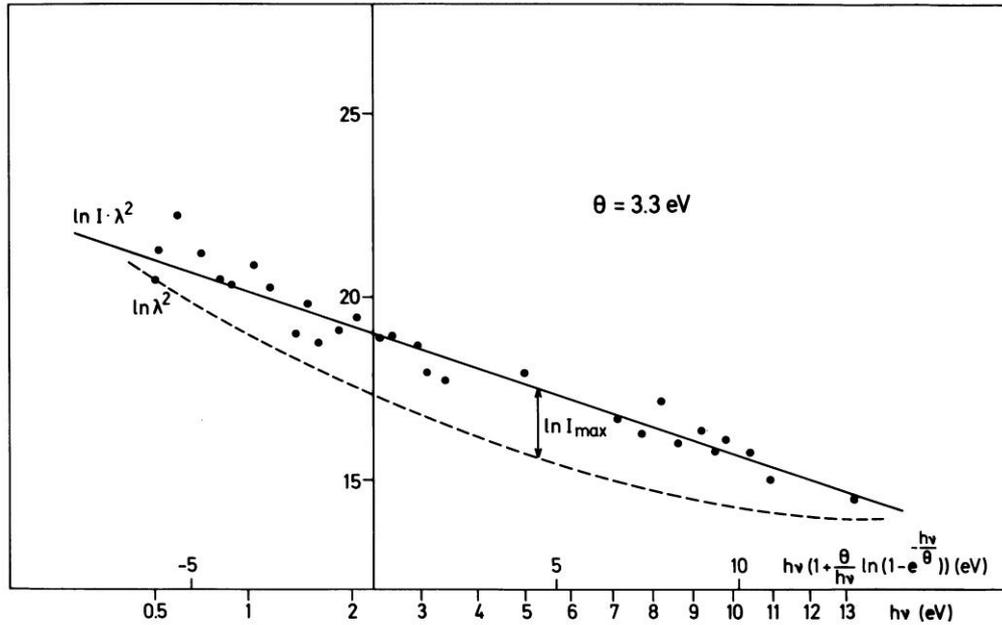
Fig 3 l n (I λ²) plotted against h ν(1 + (k T/h ν) l n(1 – exp(-h ν/k T)) e V for carbon C (I) data. Intensity data from intensity tables were used.(Reproduction from Ref 4)

By forming the maximum between the difference between ln I λ² and ln λ² the following formula will be the basic equation in this method of analysis.

$$\ln (I_{max} \; \lambda^2_{max}) = \text{const.} \; - \; 1.6 \, J / h\nu_{max} \qquad\qquad (4)$$

This graph can be seen in Fig 4, where ln (I_{max} λ^2_{max}) has been plotted versus 1.6 J / $h\nu_{max}$ = J /θ for 17 elements, where θ = k T_e (electron temperature). J denotes table value of ionization energy. This graph forms a good linear relationship, where $h\nu_{max}$ = 1.6 θ. This means that this graph is a strong support of the new intensity formula, based on the new theory. It is also possible to measure the internal electron temperature(around 2eV) for different elements (Table 1 in (12)), which are supported by secondary electron temperature values from the literature (20).
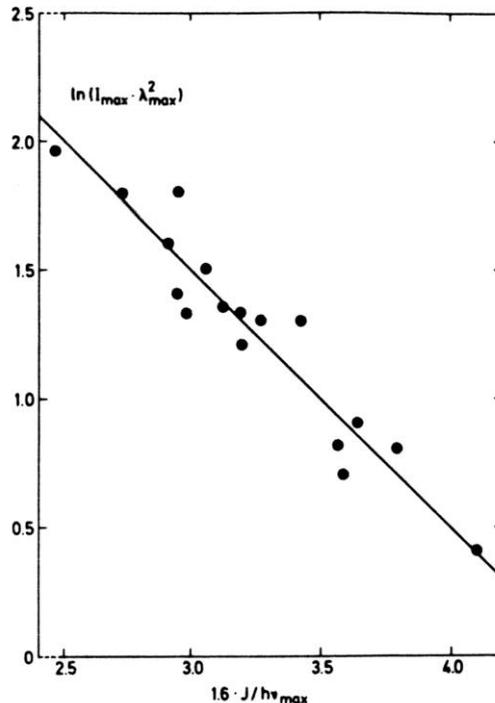

Fig 4 ln (I_{max} λ^2_{max}) plotted versus (1.6 J) / $h\nu_{max}$ for seventeen elements from the NBS tables in (18) and (19) (Reproduction from Ref 4)

b. The method of ionic spectra

The intensity formula for ions has a similar appearance as equation 1 and is shown in equation 5. This formula include ionization energies for the first and second ionization energy, which has been proposed earlier in the detection limit method (8). C is a factor given by transition probabilities, number densities and sample properties. λ and ν are here the wavelength and frequency of the ionic spectral line. The ionic intensity formula has the following appearance :

$$I = C \lambda^2 (exp (- (J_1+J_2)/ kT)) / (exp (h\nu /kT) - 1) \qquad (5)$$

To show the validity of equation 5 with this method $\ln (I \lambda^2)$ was plotted versus $h\nu$ ($1+\theta/h\nu \ln(1-\exp(-h\nu/\theta))$) eV for OI , OII and NeI, NeII in the same manner as the graph of C (I) in Fig 3. They also gave linear graphs r = -0.98 for OI and r = -0.95 for OII and r =- 0.98 for NeI and are shown in Figs 4-5 in paper (9).

c. This method with spectra of ions with higher ionization energies

The intensity formula for the ions with higher ionization energies follow similar linear relationships as Figs 3 in this paper and Fig (4 -10) in paper (9). These can be seen for oxygen and neon ions for OIII,OIV, OV,OVI and NeIII, NeIV, NeV, NeVI with very good correlations (Tables 3 and 4) in paper (9) The variance of the slopes of the lines depend of the difference of the electron temperatures between the graphs. The higher ionization energy the lower slope. It has also been possible to create an approximate recursion formula 6 for the ionic spectra. This recursion formula has earlier been presented in (9) and (12).

$$I_k \; \alpha \; N_1 \exp (- (\sum (J_r)_{r=1}^{r=k} + h\nu) /kT) \qquad (6)$$

IV. The photoelectric effect

As this intensity formula deals with number of emitting photons from a plasma, it has also shown to be possible to use it on the reverse process, where incoming photons emit electrons into a current. An experimental proof of that is shown below.

The fact which is important in this very paper about the photoelectric effect is a relationship between current and frequency. The usual appearance from the literature of this experimental

relationship is an $i = e^\nu$ -structure , where the current (y-axis) is an exponential function of the frequency(x-axis), and starts from the ν_0 (threshold) a bit in on the ν-axis. This experimental fact is what the different theories in the introduction have tried to fit, with some difficulties according to their own opinions.

On the other hand, by using the inverse of equation 1 and express the C-factor as approximately

$$C = I \lambda^2 \exp ((J + h\nu) / kT_e) \qquad (7)$$

a very good fit could be obtained. The C-factor is here proportional to the current in the photoelectrical effect. Such a nice fit can be seen in Fig 5, from a photoelectrical experiment with potassium at different field strengths. In this fit current ratios have been calculated according to equation 7 (where the current $i \alpha C$).In this way only the ν-dependence of the C-factor(current) appeared more clearly. This data were coming from Fig 3-46 p.111 of (16) and is demonstrating the influence of electric field on the photoelectric threshold of thin layers of potassium on tungsten.

This data current ratios were calculated from the data and compared with the current from equation 7. This can be seen in equation 8.

$$i_k / i_{k-1} = (\exp (h\nu_k/kT_e) - 1)(h\nu_{k-1})^2 / (\exp (h\nu_{k-1} /kT_e) - 1) (h\nu_k)^2$$
$$\approx (\nu_{k-1}/\nu_k)^2 \exp (h/kT_e (\nu_k - \nu_{k-1})) \qquad (8)$$

Nice correlation between experimental and theoretical values were obtained at two different field strengths (A and B) in these experiments.

Similar graphs to Fig 5 can also be seen in many graphs in (16) and in photo detachment experiments in Fig 1.25 p.39 of (21) –and solar cell experiments Figs 19,25 and 27 of p.288,293 and 294 of (22) ,where photons create electrons into a current.
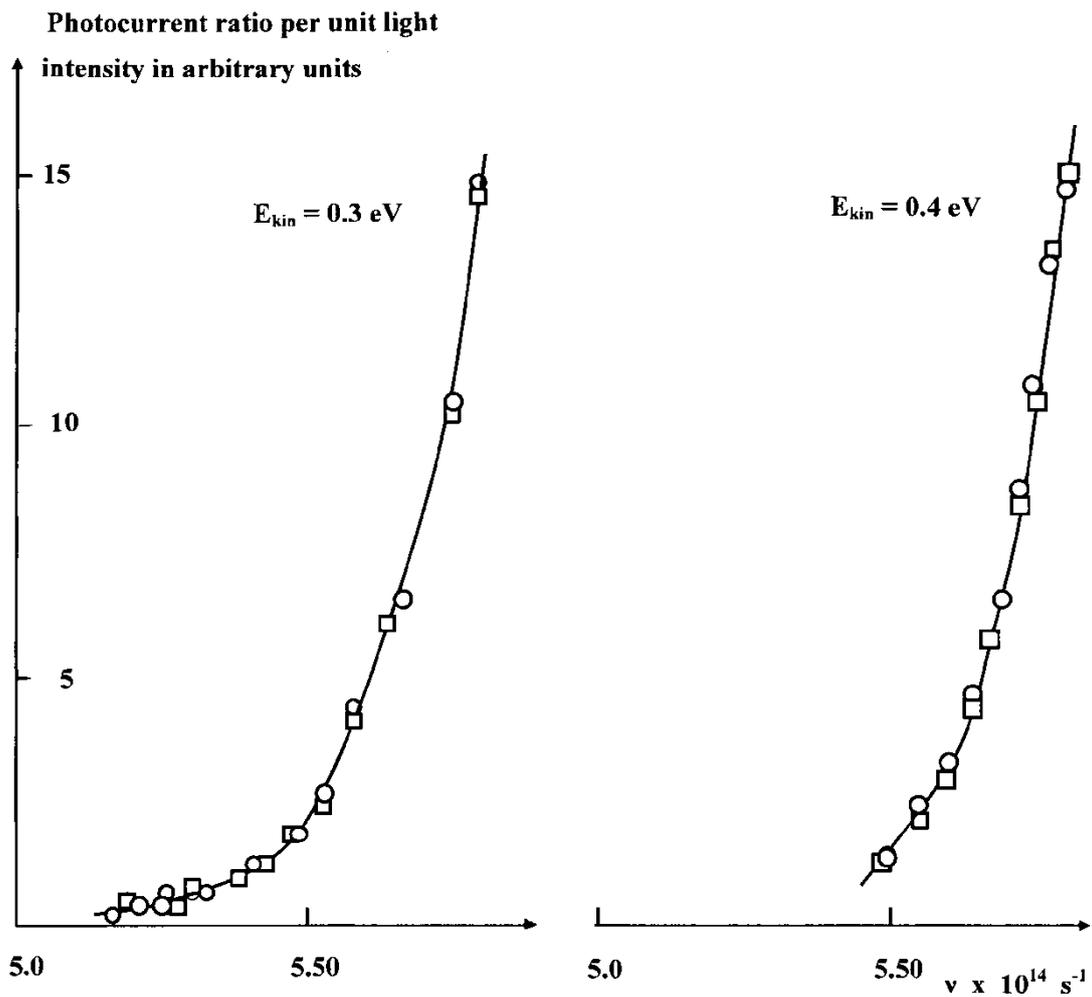
Photocurrent ratio per unit light

intensity in arbitrary units

$E_{kin} = 0.3\ eV$

$E_{kin} = 0.4\ eV$

$v\ x\ 10^{14}\ s^{-1}$

Fig 1

Fig 5: The v- dependence of the photocurrent ratios between literature experiment(circles) and the new theory (squares)(inversed intensity formula) Results at different electron energies are shown. (Reproduction from Ref 17)

This e^x – structure is very common in many graphs of (16) where the low frequency side goes up to a maximum. The high frequency side represents an $e^{1/x}$ – structure. This can be seen in Fig 3-6 p.46 in (16) .This $e^{1/x}$ –structure is probably caused by the heating effects of the sample. Therefore the kT_e – part of equation 7 will be dominating the structure of the high frequency part and show a $e^{1/x}$ –structure.

These e^x and $e^{1/x}$ – structures are very common in (16) and in the literature of electron spectroscopy.
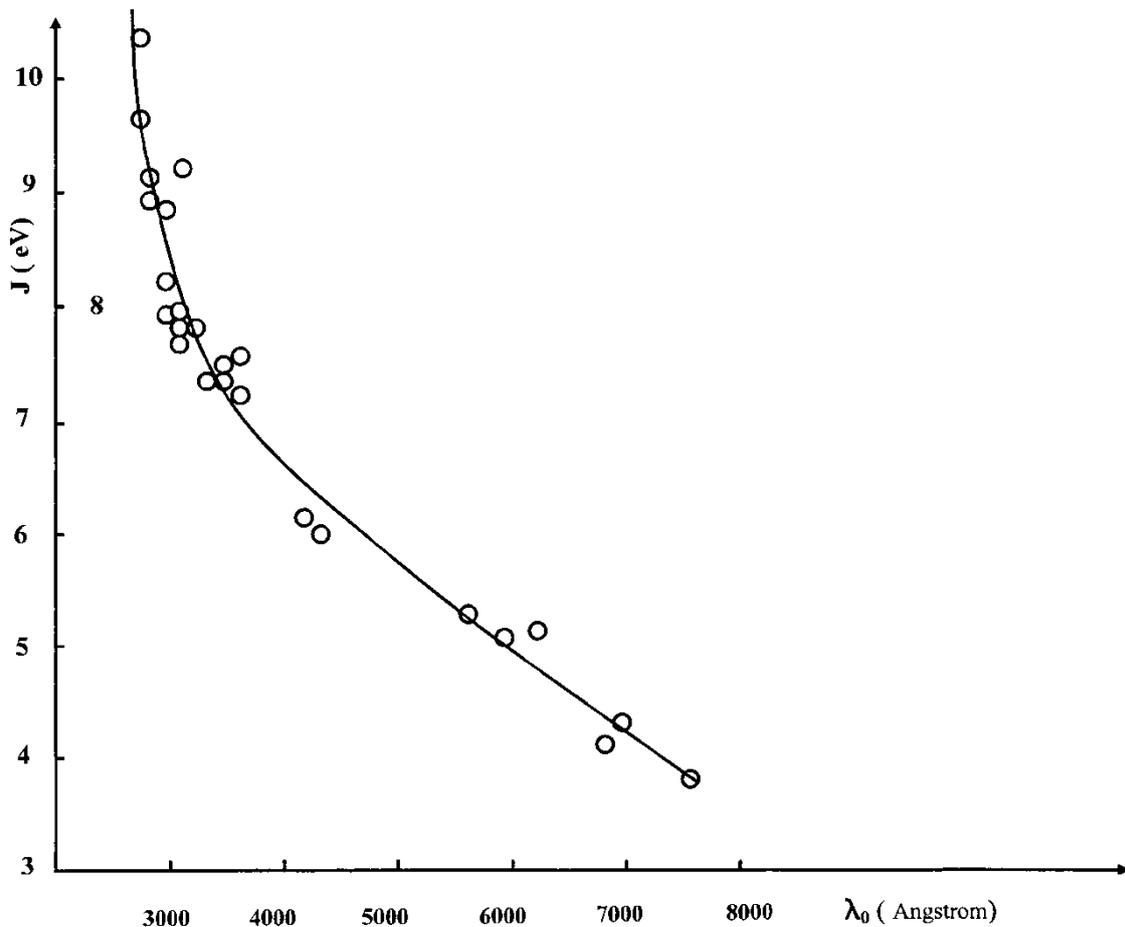
Fig 2

Fig 6: The influence of the ionization energy J versus the threshold wavelengths of the photoelectric effect. 22 different elements(metals) have been studied. (Reproduction from Ref 17)

The influence of the J-term of equation 7 on the photoelectric effect, has also been seen in several ways. In Table 3-2 p.75-76 of (16) photoelectric and thermionic work functions of different elements(metals) have been studied. This table has been used in Fig 6, where the ionization energies(J) have been plotted versus the threshold wavelengths of that table. Here is it possible to study the photoelectric effect of different elements. Fig 6 is similar to Fig 5 as

J α i α C α v α 1/ λ according to equation 7 and includes information from 22 different metal elements. Fig 6 is a clear evidence of J-dependence of the photoelectric effect, where the slope of the curve increases with higher (J + h v)- values (5.5 – 16 eV) according to equation 7.

If we express J as a function of λ from equation 7 we obtain :

$$\mathbf{J = f\ (\lambda_0) = k\ T_e \ln (C/I\ \lambda^2)\ -\ hc\ /\lambda} \qquad (9)$$

The influence of kT_e will increase for lower wavelengths of Table 3-2 in (16) Therefore the slope of the low wavelength side is much higher than the high wavelength side of the curve. This is also seen by derivating this expression.

The derivative of equation 9 is :

$$\mathbf{J' = kT_e\ (I\ /C)(-\ 2\ /\lambda) + hc\ /\lambda^2} \qquad (10)$$

It is obvious here that kT_e is very important for the slope of the curve. At lower wavelengths the kT_e is higher which increases the slope of the curve.
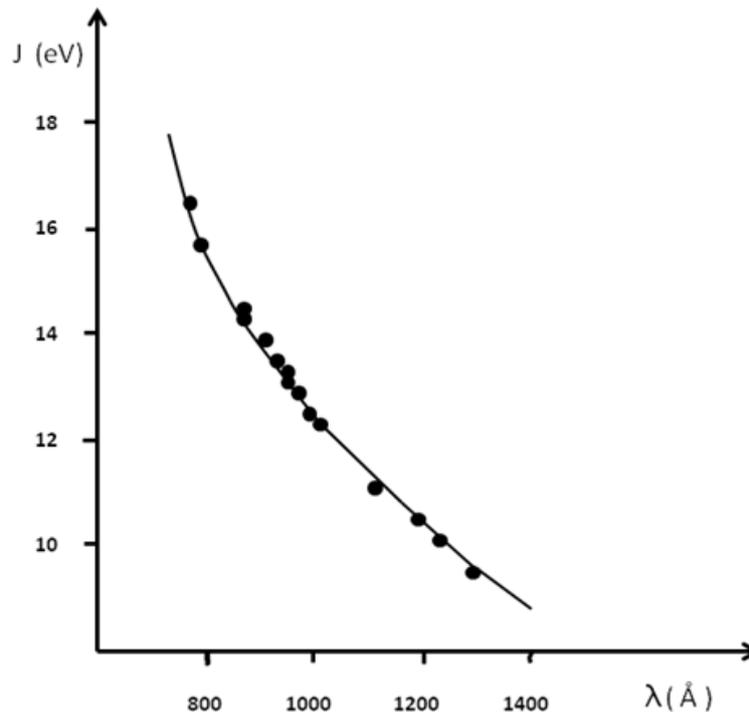
Fig 7: The influence of the ionization energy J versus the threshold wavelengths of the photoelectric effect. 19 different gases have been studied. (Reproduction from Ref 17)

A similar graph to Fig 6 have also been seen for 19 different gases and is shown in Fig 7 from data of Table7 -5 p. 274 (16). The curve profile is similar to Fig 6, but does not show any "knee" like Fig 6. This is probably because of the fact that the heating effect is not so strong in the gas phase here.

The J – term of equation 7 can also be shown when comparing the big difference in ionization energy between A (15.76 eV) and He (24.58 eV). This is also illustrated in the breakdown experiments with lasers and also in Fig 9.10, p.739 and Fig 9.13, p.745 in (21) In these experiments a big separation between the A and He – curves is shown, where the He-curve is situated at much higher pressure. This is in accordance to equation 7. This J – dependence is also illustrated in the laser experiments as the curve is situated at much higher pressure. This is in accordance to equation 7. This J – dependence is also illustrated in the laser experiments in Fig 9.9, p.737 in (21) , where the elements with higher ionization energy are situated at higher pressure according to equation 7.

V.   Discussion

The new intensity formula has shown to be applicable to many light sources at different experimental conditions and temperatures. The spectral line intensity ratio fluctuation analysis of in Figs 1 and 2 is a very sophisticated method of sorting the correct formula, where questions concerning photon efficiency versus wavelength for spectrometer systems, can be eliminated.

In Fig 3 the absolute intensity method show linearity over 14 eV for C (I) – lines. This is impossible to achieve without a correct intensity formula. Deviations caused by photon efficiency versus wavelength for spectrometer systems are here very small in these graphs. The most dominant linearity factor is a correct exponent in the intensity formula.

This investigation shows that it is easy to find articles in the literature with data supporting equation 1. On the other hand we have not found any data which disagree with our formula. Therefore it is surprising that such a formula for the discrete emissions has been so hard to find.

The results in this paper explain the general appearance of the shape of the current versus frequency expression in the photoelectrical effect. On the low frequency side of the curve, an e^x –structure is appeared, and on the high frequency side an $e^{1/x}$ – structure is appeared. This appearance is general for all kinds of current measurements from old and newer papers in the literature. These observations have also been seen in the electron spectroscopy field where the photo ionization cross section has been calculated versus photon energy. These graphs have also the same e^x and $e^{1/x}$ – structure as is described above. One explanation of this e^x – structure is the photon energy hv of equation 7 and the $e^{1/x}$ –structure depends on the heating effect kT_e which raises with increasing photon energy. Fig 5 is a strong evidence of the frequency depending part of equation 7.

Fig 6 is a strong evidence of the J-term of equation 7. From this graph it is possible to study the J-dependence of 22 different elements(metals). The "knee" of this curve depends of the heating effect at higher frequencies, which is also clearly demonstrated by the derivative

in equation 10. The J - dependence is also demonstrated in Fig 7 for 16 different gases. The threshold wavelengths here are much shorter compared to Fig 6 and the heating effect is lower.

A similar graph to Fig 6 is seen in Fig 7, where the metals were heated to high temperatures. This graph also demonstrates a clear "knee" at high temperatures with more spread in the experimental points.

According to theoretical physics and mathematics, a condition of a correct formula in physics is that it is invariant. This means that its inverse should also be applicable in the nature. This is the case for the new intensity formula in optical emission spectroscopy and its inverse in the photoelectric effect, which this paper has shown.

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