

# Laser power dependence in femtosecond ionization of fullerenes

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**Abstract.** Fullerene ionization can under some circumstances be modelled as thermal emission of electrons from a transiently hot electron gas. Application of this idea to experiments involving femtosecond lasers gave theoretical evidence for ion yields that would vary with the pulse energy of the laser to some power, identical to the behavior seen in multi-photon experiments. The reason for this behavior is investigated here. The crucial component is identified as the Poisson statistics for photon absorption and a strong variation of the ion yield with energy.

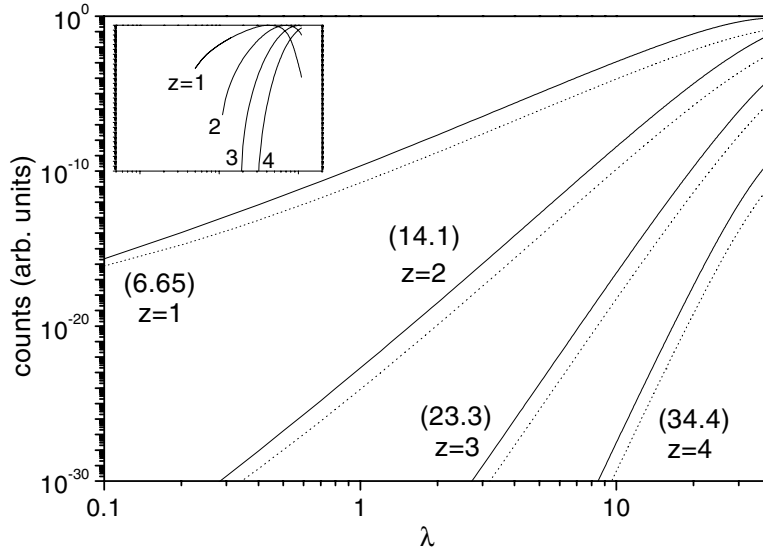
## 1. Introduction

The ionization of clusters and large molecules with photons can proceed in more ways than those open to atoms and very small molecules. A recent model for ionization of fullerenes, and potentially other large molecules, is based on the idea of a transient hot subsystem composed of the valence electrons. The ionization, which was predicted to occur on the sub-ps timescale [1], is statistical in nature. The model, designed to explain the yield in Penning ionization experiments [2], was subsequently tested in experiments where the excitation was provided by laser pulses of sub-ps duration and photon energies below the ionization energy (1.6 eV vs. 7.6 eV). A number of experimental results could be explained by the model, see [3, 4].

In order to make contact between the theory and the laser excitation experiments, it was necessary to integrate over the spatial profile of the laser beam and the Poisson statistics for photon absorption. It also included a numerical integration over the time it takes the electronic excitation to dissipate into the vibrations. One surprising result of this numerical integration was that the calculated ion yields had a power-law behavior for medium laser fluences. Interestingly, the powers were found not to be restricted to integer values, as for multi-photon ionization.

The purpose of this contribution is to elucidate the reason for the power-law behavior. To be specific we will use a photon energy of 1.6 eV and the parameters pertaining to La@C<sub>82</sub>, that is, an ionization energy (IE) of 6.2 eV for the neutral molecule, and adding 3.5 eV to the IE for each higher charge state [4]. The electronic level density, which is an important ingredient in the theory, is calculated with the levels obtained by a rescaling of the C<sub>60</sub> single particle levels to obtain the same Fermi energy. The main fit parameter in the theory, the electron-phonon coupling time, was set to the C<sub>60</sub> value of 240 fs [3].

The inset in figure 1 shows the calculated yields of charge states  $z = 1, 2, 3, 4$ , plotted vs. the excitation energy (in units of the photon energy) in a hypothetical experiment where precisely  $n$  photons are absorbed. The curves are clearly non-linear in the double-log plot.



**Figure 1.** The yields of La@C<sub>82</sub> for different charge states, integrated over a Poisson distribution (full lines) and including the Gaussian laser beam profile (dotted lines). The slope of the dotted lines are given in brackets above the charge. The inset shows the functions  $Y_n$  calculated with the parameters for La@C<sub>82</sub> given in the text. The inset abscissa is shifted upwards by a factor 5, but otherwise the scales are identical in the two plots.

The second and final step in the comparison of theory and experiment is the integration of the energy specific yields  $Y_n$  over photon absorption statistics. First the integration over the photon absorption statistics for a specific laser fluence was made, and then the integration over the non-constant laser fluence in space. For the fluence specific absorption statistics the Poisson distribution was used. The result of this is shown in figure 1, together with the subsequent integration over the spatial variations of the laser fluence. The former is plotted vs. the average number of absorbed photons, and the latter vs. the average number of photons absorbed in the geometrical center of the Gaussian laser beam. Both are denoted by  $\lambda$ . The two curves demonstrate power-law behavior up to moderately high values of  $\lambda$ . Clearly, the spatial integration only changes the results marginally, which in hindsight is not surprising considering that the yield is a rapidly increasing function of the energy absorbed and the center of the laser beam therefore defines the bulk part of the yield [5].

Once the origin of the power law is located in the convolution of the energy-resolved yield curve with the Poisson distribution, we may inquire about the generality of the phenomenon. It is clear that if the yield vs. energy depends only weakly on energy, the convolution will produce a power law at low fluences. This is most easily seen if the total yield is written as the sum of energy resolved contributions;

$$Y = \sum_{n=5}^{\infty} Y_n \frac{\lambda^n}{n!} e^{-\lambda}. \quad (1)$$

The factors  $Y_n$  are the yields for a molecule which absorbs precisely  $n$  photons. The sum starts at  $n = 5$  because this is the minimum number of photons required to emit an electron. When  $\lambda < 6Y_5/Y_6$ , the term with  $n = 5$  will in general dominate and the yield can be approximated by  $Y \propto \lambda^5$ . Since  $Y_5/Y_6 < 1$ , this approximation is good only when  $\lambda \ll 6$ .

To explain the power-law for higher fluences we need to examine the properties of the yield curves  $Y_n$ . Irrespective of the precise physical mechanisms that determine the  $Y_n$ 's, the requirement for observing a power-law behavior with power  $c$  is that

$$\frac{d \ln(Y)}{d \ln(\lambda)} = c. \quad (2)$$

Inserting the yield from (1) into this equation gives

$$c = -\lambda + \frac{1}{Y} \sum_{n=5}^{\infty} n Y_n \frac{\lambda^n}{n!} e^{-\lambda} \approx -\lambda + \frac{1}{Y} \sum_{n=5}^{\infty} n_0 Y_n \frac{\lambda^n}{n!} e^{-\lambda} = -\lambda + n_0, \quad (3)$$

where  $n_0$  is the value of  $n$  for which the sum in (1) peaks. It is related to the functional form of  $Y_n$  and is found by equating two consecutive terms in the sum:

$$Y_n \frac{\lambda^n}{n!} e^{-\lambda} = Y_{n+1} \frac{\lambda^{n+1}}{(n+1)!} e^{-\lambda} \Rightarrow \left. \frac{d \ln(Y_n)}{dn} \right|_{n=n_0} \approx \ln(n_0) - \ln(\lambda). \quad (4)$$

Substituting  $\lambda$  from (3) we have

$$\frac{d \ln(Y_{n_0})}{dn_0} = \ln(n_0) - \ln(n_0 - c). \quad (5)$$

This can be integrated, but the solution diverges slowly, which is not consistent with a yield which cannot exceed unity. It is more fruitful to consider the second derivative;

$$\frac{d^2 \ln(Y_{n_0})}{dn_0^2} = -\frac{c}{n_0(n_0 - c)}. \quad (6)$$

We note the promising fact that the second derivative is negative, which is a feature shared with most, if not all, activated processes.

In [1]  $Y_n$  was calculated for yields not too close to unity to be approximately

$$Y_n \propto \exp\left(-\frac{\phi \sqrt{a}}{\sqrt{nh\nu - \phi/2}}\right), \quad (7)$$

where  $a$  is a parameter characterizing the level density of the Fermi-gas used to describe the electron system of the fullerene,  $\rho(E) \propto \exp(2\sqrt{aE})$ . Equation (7) is essentially the Boltzmann factor for electron emission, with the activation energy  $\phi$  and the temperature determined by the Fermi-gas level density. The term  $-\phi/2$  in the energy is a correction for the finite heat capacity of the electron system. We have left out a preexponential factor which depends on the electron phonon coupling time and constants.

Inspired by this form, we will consider yields of the type

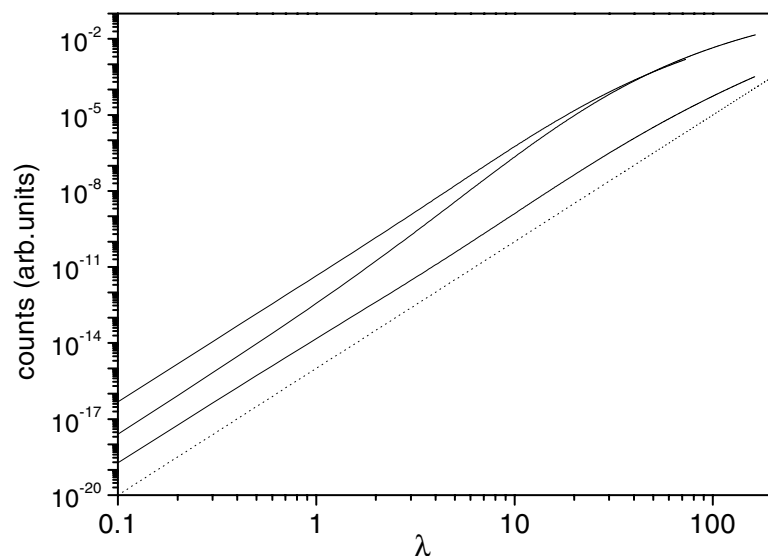
$$Y_n \propto e^{-b/n^\delta}, \quad (8)$$

with logarithmic derivatives

$$\frac{d \ln(Y_n)}{dn} = \frac{b\delta}{n^{\delta+1}}, \quad \frac{d^2 \ln(Y_n)}{dn^2} = -\frac{b\delta(\delta+1)}{n^{\delta+2}}. \quad (9)$$

The two derivatives in (9) can be equated to those in (5,6) at some fluence, or equivalently a specific value of  $n$ , denoted by  $n'$ , and then solved for the parameters  $b$  and  $\delta$ . The choice of  $n'$  or, equivalently,  $\lambda$  or  $\delta$ , is arbitrary. We have fixed  $c$  to 5, and made the three different choices  $\lambda = c$ ,  $\lambda = 2c$ , and  $\delta = 1/2$ . The last choice corresponds to the approximate energy dependence of  $Y_n$  from [1] and implicitly selects the value  $n' = 5.875\dots$  Combining (9,5,6) gives values for  $\delta$  and  $b$ , from which the yield vs. laser fluence can be calculated with (1). The results are shown in figure (2). The physically relevant parameters calculated for the curves in figure (2) are (top to bottom)  $(\delta, b) = (0.443, 43.4)$ ,  $(1/2, 54.2)$ , and  $(0.233, 49.0)$ . The larger the value of  $n'$ , i.e. the excitation energy at the expansion point, the further the power-law holds. The values of  $b$  should be compared to the one which can be derived from the approximate model calculation in [1],  $b = \phi \sqrt{a/h\nu}$ . With  $\phi = 6.2$  eV,  $h\nu = 1.6$  eV and a value of  $a = 50.9$  eV, the value becomes  $b = 35.0$ . This value is a little lower than, but of the same magnitude as the optimum values derived above, and may explain the fairly good power-law behavior at low and medium laser fluences in the simulations.

In conclusion, we have seen that ionization by a statistical mechanism can give rise to power laws in the laser fluence. The key element responsible for these power-laws is the combination of Poisson statistics with an ionization yield which increases strongly with energy. For certain values of the parameters which describe the thermal emission process the power-laws extend over more than ten orders of magnitude in ion yield.



**Figure 2.** Total yields of singly charged ions for the three energy resolved yield curves discussed in the text (full lines); from top to bottom:  $\lambda = c$ ,  $\delta = 1/2$  and  $\lambda = 2c$ . For comparison the line  $\lambda^5$  is also shown (dotted line). Note the high value of  $\lambda$  at the end points.

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