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Model-independent determination of the carrier multiplication time constant in CdSe nanocrystals

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The experimental determination of the carrier multiplication (CM) time constant is complicated by the fact that this process occurs within the initial few hundreds of femtoseconds after excitation and, in transient-absorption experiments, cannot be separated from the buildup time of the $1p$-state population. This work provides an accurate theoretical determination of the electron relaxation lifetime during the last stage of the p-state buildup, in CdSe nanocrystals, in the presence of a single photogenerated hole (no CM) and of a hole plus an additional electron-hole pair (following CM). From the invariance of the $1p$ buildup time observed experimentally for excitations above and below the CM threshold producing hot carriers with the same average per-exciton excess energy, and the calculated corresponding variations in the electron decay time in the two cases, an estimate is obtained for the carrier multiplication time constant. Unlike previous estimates reported in the literature so far, this result is model-independent, i.e., is obtained without making any assumption on the nature of the mechanism governing carrier multiplication. It is then compared with the time constant calculated, as a function of the excitation energy, assuming an impact-ionization-like process for carrier multiplication (DCM). The two results are in good agreement and show that carrier multiplication can occur on timescales of the order of tens of femtoseconds at energies close to the observed onset. These findings, which are compatible with the fastest lifetime estimated experimentally, confirm the suitability of the impact-ionization model to explain carrier multiplication in CdSe nanocrystals.

Keywords: carrier multiplication; nanocrystals; decay processes; pseudopotential method; CdSe.

PACS numbers: 71.15.-m, 71.55.-i

I. INTRODUCTION

Carrier multiplication (CM) in semiconductor nanocrystals (NCs) is arguably one of the most promising effects that can potentially lead to great enhancements in photovoltaic performance through an increase in the photogenerated current[1]. Although inefficient in bulk semiconductors, CM has been shown to be greatly enhanced in 0D systems where up to seven electron-hole pairs have been generated *from a single photon* in PbSe NCs[2], depending not on the pump intensity, as in conventional multiple exciton generation, but on the photon energy, yielding a non-Poissonian distribution of the excitons population. Despite similar results being reproduced in other materials[3–5], the origin and the dynamics of carrier multiplication in semiconductor nanocrystals are still a subject of debate[3,6,7]. Very recent reports of inexistent[8], or much lower than previously observed[9,10], CM yields and of the irreproducibility of some earlier results[11,12], have contributed to ignite the debate even further. One of the most controversial aspects of CM is the magnitude of its time constant, with values proposed in the literature ranging from 0 (i.e., implying an instantaneous process)[3] to several hundreds of femtoseconds[6]. The experimental determination of such constant in transient-absorption measurements is complicated by the fact that carrier multiplication occurs within the initial few hundreds of femtoseconds after NC excitation and cannot be separated from the buildup time of the $1p$-state population (which represents the electron decay time from the initially photoexcited state to the p state, see Fig. 1). The last stage of this process is represented by the electron relaxation between the $1d$ and $1p$ states, which, in CdSe NCs, are separated by energy gaps of the order of hundreds of meV, depending on the size of the dot. For some NCs therefore this may correspond to more than 10 times the typical bulk LO phonon energy, leading to the expectation of a long lifetime for the excited electron. However, as it has been observed in the case of the lifetime of the p electron[13–15], efficient inelastic scattering with the photogenerated hole (Auger cooling[16]) could provide a fast decay channel for the d electron (since in CdSe NCs p-d and s-p splittings have similar magnitudes). Indeed a fast, sub-picosecond buildup time of the $1p$ state population following excitations with energies both above and below the CM threshold was recently observed during transient-absorption measurements in CdSe NCs by Schaller and co-workers[3]. Calculating the contribution of the $1d$-to-$1p$ electron relaxation to the $1p$ buildup time could therefore lead to an estimate of the magnitude of the CM lifetime. Apart from being of great interest for device application, an accurate determination of the CM time constant would be of paramount importance to understand the origins of the process itself as it could help discriminate among the different CM models proposed in the literature (direct multi-excitons generation via virtual single-exciton states[3], impact

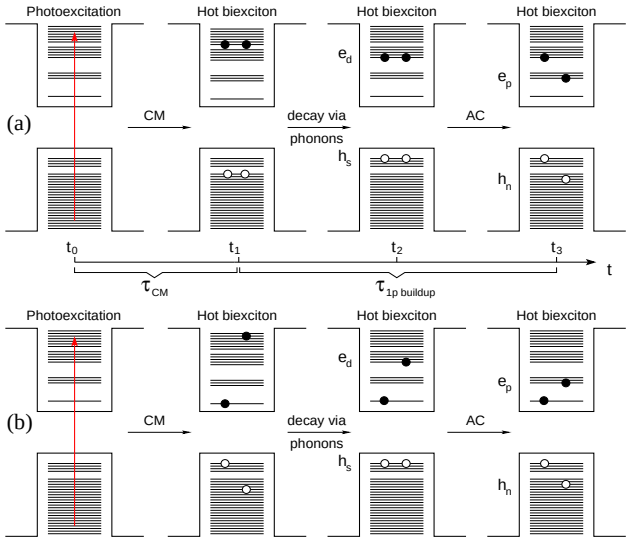

FIG. 1: Schematics of the sequence of events taking place during the high-energy-excitation/relaxation process of the NC: following the initial excitation with a high energy pump pulse, a hot biexciton is generated in a time τ_{CM}. The biexciton can, in general, be in two possible configurations [(a) two single excitons with the same energy or (b) one ground state and one hot exciton], depending on whether CM occurs, respectively, through direct photogeneration via a virtual single-exciton state[3], or through an impact-ionization-like process[19]. Regardless of the biexciton configuration, after a phonon-assisted decay through dense conduction band states, the electron reaches the lowermost $1d$ state [in case (a) it is accompanied by the other electron, whereas in case (b) it is alone], from which it relaxes to the p state via Auger cooling, by transferring its excess energy to one of the holes. The CM time constant, τ_{CM}, could therefore be obtained in principle as the difference between the total time measured experimentally from the initial excitation ($t_3 - t_0$) and the $1p$ buildup time ($t_3 - t_1$), if the latter were known.

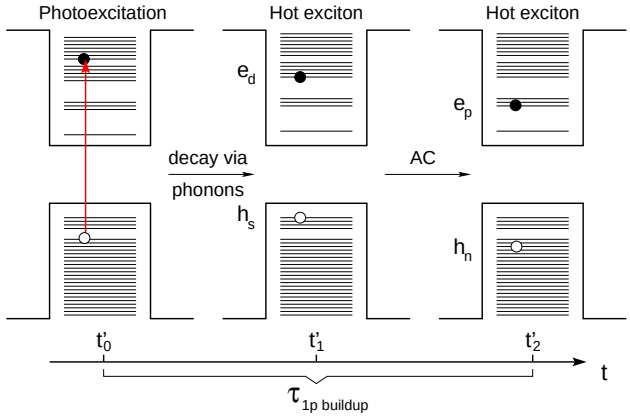

FIG. 2: Schematics of the sequence of events taking place during the low-energy-excitation/relaxation process of the NC: following the initial excitation with a low energy pump pulse, a hot exciton is generated. After a phonon-assisted decay through dense conduction band states, the electron reaches the lowermost $1d$ state, from which it relaxes to the p state via Auger cooling, by transferring its excess energy to one of the holes.

ionization[6,19], and coherent superposition of single- and multi-exciton states[7]), which predict different lifetimes for the photoexcited (possibly virtual) electron-hole pair.

In this work the atomistic semiempirical pseudopotential approach is used to provide an accurate theoretical determination of (i) the lifetime for the electron relaxation, via Auger cooling(AC), from d-like to p-like states in CdSe NCs of different sizes, in the presence of a single photogenerated hole (i.e., following low-fluence excitations below the CM threshold), and with a hole plus an additional electron-hole (e-h) pair present, (following a CM event) and (ii) the CM time constant as a function of the excitation energy for a NC with $R = 14.6$ Å, assuming an impact-ionization-like process for CM. It is important to stress that the results (i) are obtained independently of the CM mechanism (as no assumption is made on the nature of CM in their derivation) and can be used as a reference for estimating its time constant by comparing them with the $1p$ buildup time observed in the presence (Fig. 1) and in the absence (Fig. 2) of CM.

II. METHOD

The Auger cooling lifetimes of the $1d$ electron are calculated here, using LDA-accurate pseudopotential wave functions[20], for perfectly passivated, nearly spherical wurtzite CdSe NCs with $R = 10.3$, 14.6, 19.2, and 28.0 Å, where a generic (ideal) passivation is simulated by using short-range (Gaussian) electrostatic potentials[21]. The single-particle energy levels are calculated using the plane-wave semiempirical pseudopotential method described in Ref. 20, including spin-orbit effects, and excitonic contributions are accounted for within the configuration interaction scheme[22]. The Auger rates are obtained using the formalism developed in Ref. 18 as

$$1/\tau_i = \frac{2\pi}{\hbar} \sum_f | < i|W|f > |^2 \delta(E_i - E_f), \qquad (1)$$

where $|i>$ and $|f>$ are the initial and final Auger electronic states, with energies E_i and E_f, and W is the screened Coulomb interaction. The hole is assumed to occupy its ground state at the start of the $1d$ electron relaxation (see Fig. 2), however the effect on the Auger lifetime of a different choice is also explored, for a 19-Å-radius NC[23], by placing the hole in the excited state where, according to our calculations, it would be generated, together with a d electron, by the absorption of a ~ 3.1 eV photon (the average per-exciton energy used in Ref. 3).

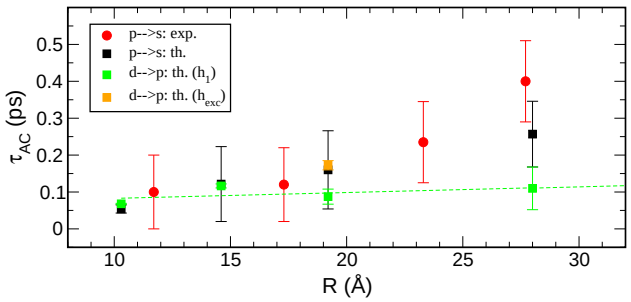

FIG. 3: Auger electron cooling lifetimes: theoretical predictions for d-to-p (green and orange squares) and p-to-s (black squares) decay and observed decay times for p-to-s transitions (red circles)[26]. The green symbols denote lifetimes calculated assuming the hole initial state to be the VBM (h_1), whereas the orange symbol is the result obtained with the hole in the initially photoexcited state (i.e., either h_{31} or h_{38} for R=19.2 Å). The error bars in the theoretical data account for a size distribution of 10% in the experimental samples as well as for some uncertainty regarding the initial state configuration. The green dashed line is the best linear fit to the green squares and extrapolates to $\tau_{AC} = 120$ fs for a $R = 32$ Å NC.

In all cases the final states for the electron are the $1p$ states, whereas the final hole states are those with energy centered around $E(h_i) - \Delta_{pd}$. This corresponds to a number of excitonic states ranging from 348 for $R =$ 10.3 Å, to a maximum of 480 for $R = 19.2$ Å (in the case of a single e-h pair). The effect of the presence of a spectator exciton (product of CM) on the Auger lifetimes is investigated by placing an additional hole in the same state as the other hole and an electron either in the $1d$ or in a different ($1s$, $1f$ or higher) state.

The delta function in Eq. (1) is broadened using a Lorentzian line shape

$$\delta(E_i - E_f) \approx \frac{1}{\pi} \frac{(\Gamma/2)}{(E_i - E_f)^2 + (\Gamma/2)^2} \qquad (2)$$

where $\hbar/\Gamma$ is the lifetime of the final states. The value $\Gamma = 10$ meV has been used here[18], as estimated from experimental energy loss rates for highly excited carriers[24]. However, the AC lifetime is found not to be very sensitive to its choice, increasing by at most a factor of three[25] for a 20-fold increase of Γ from 5 to 100 meV. A position-dependent microscopic screening function[22] is used in the calculation of the Auger integrals, instead of the "regional screening" employed for Auger multiexciton recombination calculations, as it was shown in Ref. 18 that for AC in CdSe NCs the two approaches give similar results. For $T \neq 0$ the rates are Boltzmann-averaged over the initial states.

III. RESULTS AND DISCUSSION

A. Auger electron cooling times

In order to demonstrate the accuracy and reliability of the method used, the p-to-s electron decay times are calculated first, for all sizes considered here, using the same procedure outlined above and assuming the hole initial state to be the VBM. The agreement with experiment is excellent, as shown in Figure 3, where the theoretical values are represented by black squares and the experimental data[26] by red circles, suggesting a high degree of accuracy to be achievable for the d-to-p decay times as well. The AC lifetimes calculated for an electron in a $1d$ state (green squares in Fig. 3) are surprisingly close to the decay times of the $1p$ electron and shorter than 200 fs for all sizes. The green dashed line in Fig. 3 represents the best linear fit to the green squares and predicts $\tau_{AC}(d \rightarrow p) \sim 120$ fs for a $R = 32$ Å NC, which is compatible with the experimental estimate of the $1p$ buildup time[3] for that size. Interestingly, it is found that the initial position of the hole affects the AC lifetime: for a 19.2-Å-radius NC the $1d$ electron decay is faster in the presence of a ground state hole (green symbols in Fig. 3), than if the hole is in the initially photoexcited state (orange symbol in Fig. 3), due to a larger wave function overlap in the former case. As shown in Fig. 3a, however, the difference in the calculated lifetimes in the two cases is a factor of about 2 for a $R = 19.2$ Å NC[27]. Assuming the same relationship to hold in the case of larger NCs, this would predict an AC decay time of about 240 fs for a $1d$ electron in the presence of an excited hole in a $R = 32$ Å NC.

B. CM time constant

The results above were obtained for the Auger decay of a *single* electron in the presence of a *single* hole (see Fig. 2). However, as it is evident from Fig. 1, following a CM event the electron relaxation occurs in the presence of a *spectator exciton*, whose presence affects the decay rates by providing additional relaxation channels. This leads to a reduction of the $1d$ electron lifetimes, the extent of which depends on the respective positions of the additional e-h pair: in the case of two excitons in the same state (Fig. 1a) the calculated reduction is of a factor of 4 (i.e., there are twice as many decaying particles with twice as many decay channels each, compared with the configurations in Fig. 2), whereas in the presence of a ground state spectator exciton (Fig. 1b) the lifetime is halved (due to the doubling of the decay channels provided by the additional hole).

These results will be now used to revisit the experimental findings reported by Schaller *et al.*[3]. In Ref. 3 the $1p$ population buildup time of 3.2-nm-radius CdSe NCs was measured using pump energies of $3.1E_g$ and $1.55E_g$, respectively above and below the CM threshold and cor-

responding to the excitation of two and one e-h pairs with the same estimated per-exciton excess energy of 1.1 eV ($E_g = 2.0$ eV). Its magnitude was found to be the same (~ 400 fs) in both cases, despite a fundamental difference in the decay dynamics of the 1S transient-absorption signal, indicative of the occurrence of CM in the former case but not in the latter. Assuming a constant value for the energy-loss rate in the two cases, equal to that estimated using a $1.55E_g$ excitation (i.e., in the absence of CM), it was therefore deduced that no additional *measurable* delay was introduced by the CM process, implying that CM occurred on shorter timescales than the experimental resolution, and suggesting that CM could be an instantaneous event. This feature was then explained in terms of a direct photogeneration of the multi-excitons via multiple virtual single-exciton states.

In the light of the theoretical results presented above a different interpretation can be attempted. Given that the decay of a $1d$ electron is two to four times faster in the presence of another electron and two holes (following CM) than in the presence of a single hole (no CM), the energy-loss rate is not constant in the two cases. As a consequence, the fact that the observed magnitude of the buildup time of the $1p$ population did not change suggests that CM occurred on timescales of the order of $\tau_{AC}(1e,1h)-\tau_{AC}(2e,2h)$, i.e., a factor of 1/2 to 3/4 of the value of $\tau_{AC}(1e,1h)$, (which corresponds to either $\sim$ 60–90 fs or $\sim$ 120–180 fs, depending on whether the hole is in its ground state or not at the start of the $1d$ electron decay), and its time constant (estimated, from the values given above, at 120 ± 60 fs) can indeed be shorter than the experimental resolution, in agreement with the conclusions reached in Ref. 3, but for a slightly different reason. It is once again important to point out that the above estimate for τ_{CM} is totally independent of the mechanism responsible for CM, as it is obtained based on the presence of the *products* of CM, two e-h pairs, regardless of their generation pathway. Another possible explanation for the invariance of the $1p$ buildup time could be that CM did not occur at all, as recent results[8] seem to suggest. However in this case the relaxation of an excess energy of the order of $(3.1-1.55)E_g = 1.55E_g = 3.1$ eV (i.e., the difference in excitation energies in the two cases) should have taken place on time scales which are shorter than the experimental resolution (50-200 fs depending on the probe wavelength[3]), implying an average electron energy-loss rate[28] larger than 9.3 eV ps^{-1}, which corresponds to more than four times the value experimentally estimated[3] for an excitation of $1.55E_g$. This result seems therefore to provide an indirect confirmation that CM indeed occurred in 32-Å-radius CdSe NCs at an excitation energy of $3.1E_g$, as reported in Ref. 3.

A direct calculation of the CM time constant can, however, only be performed within the framework of a specific theoretical description of the CM process, i.e., by making some assumptions on how CM works. In this work the impact-ionization-like model (direct carrier multiplication, DCM) suggested in Ref. 19 will be used. According to the DCM model, the absorption of a high energy photon with $\hbar\omega > 2E_g$ creates a highly excited e-h pair. If the excess energy of one of the carriers (due to its lighter effective mass, usually the electron) exceeds E_g then, upon relaxation of the carrier to its band edge, such energy can be transferred efficiently, via a Coulomb-mediated transition, to a valence electron, promoting it across the band gap and creating an additional e-h pair. DCM is therefore the inverse process of Auger multiexciton recombination (AR), where the recombination energy of an e-h pair is not emitted as a photon but, due to a confinement-enhanced Coulomb interaction, is efficiently transferred non radiatively to one of the remaining carriers which is promoted to a highly excited state. As a consequence the matrix elements involved in the calculation of the CM lifetime are the same that are used for calculating the AR time, the only *crucial* difference being the inversion between initial and final states in the two processes:

$$\frac{1}{\tau_{\mathrm{DCM}}} = \frac{2\pi}{\hbar}\sum_f |\langle X_i|W|XX_f\rangle|^2\delta(E_i-E_f) \tag{3a}$$

$$\frac{1}{\tau_{\mathrm{AR}}} = \frac{2\pi}{\hbar}\sum_f |\langle XX_i|W|X_f\rangle|^2\delta(E_i-E_f). \tag{3b}$$

After the pioneering calculations of AR[18] and DCM[19] rates in CdSe NCs were published, such identity between the matrix elements of AR and DCM was used to dismiss[3,4] the impact-ionization model as a possible explanation for CM based on the perceived incompatibility between the $\sim$ 10 ps AR lifetimes and the observed $<$ 400 fs CM decay. Franceschetti *et al.*[6], however, showed that the DCM rates in PbSe NCs could be consistent with experiment, since the difference, mentioned above, between excitonic and biexcitonic density of states (which represent, respectively, the final states of AR and DCM) could account for the difference of about 3 orders of magnitude in the observed AR and CM time constants. To obtain this result the theorists[6] exploited the property, recently confirmed by Delerue *et al.*[29] for the case of PbSe, InAs and Si, that the matrix elements are almost constant over a wide range of energies of the initial DCM states. The same property is exploited here in the case of a CdSe NC with $R = 14.6$ Å (this size was chosen as it was small enough to allow the direct calculation of all bound states without resorting to any approximation[30]): the CM time constant is evaluated, as a function of the excitation energy, using the matrix elements employed in the calculation of the DCM lifetime (3a) at a specific excitation energy E_0[31] and the density of states calculated for negative trions ($\rho_{\mathrm{X^-}}(E) = \delta(E - E_f^{X^-})$) and biexcitons ($\rho_{\mathrm{XX}}(E) = \delta(E - E_f^{XX})$) according to

$$\tau_{\mathrm{DCM_1}}(E) = \tau^e_{\mathrm{DCM}}(E_0)\frac{\rho_{\mathrm{X^-}}(E_0)}{\rho_{\mathrm{XX}}(E)} \tag{4}$$

(the density of states of a negative trion appears in the numerator of (4) since $\tau^e_{\mathrm{DCM}}(E_0)$ was calculated[19] con-

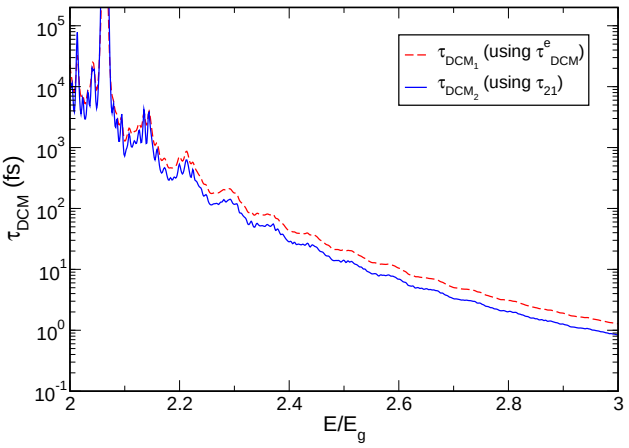

FIG. 4: (Color online): Excitation-energy dependence of the DCM time constant for a $R = 14.6$ Å CdSe NC estimated using (dashed line) the DCM lifetime calculated at a specific excitation energy E_0, and (solid line) the calculated AR lifetime (for details see text). In both cases the value of $\tau_{\rm DCM}$ at the CM threshold observed for such small NCs ($E/E_g \gtrsim 2.5$[3]) is of the order of 20 fs. The large oscillations near the energy conservation threshold $E/E_g = 2$, also found in previous theoretical studies[29], are due to the low density of biexcitonic states at that energy. This effect is particularly pronounced in CdSe, compared, e.g, with PbSe, as the CBM is non-degenerate in this semiconductor.

sidering an electron-initiated process with final density of states $\rho_{\rm X^-}(E_0)$).

Following an alternative route, based on the equivalence of the matrix elements in (3), a second estimate for the DCM lifetime is obtained using the calculated[18] AR lifetime (3b) according to

$$\tau_{\rm DCM_2}(E) = \tau_{\rm AR}\frac{\rho_{\rm X}(2Eg)}{\rho_{\rm XX}(E)}. \qquad (5)$$

The results are within a factor of less than 1.5 (see Fig. 4), confirming the equivalence of the two approaches and the validity of the nearly-constant-matrix-element assumption. What is more, the predicted CM time constant at the observed energy onset ($\sim 2.5E_g$) is of the order of 20 fs, consistent with both the model-independent theoretical estimate obtained above and the experimental upper limit of $\sim$ 50-200 fs estimated for CdSe and PbSe NCs[3]. This result confirms the accuracy of the DCM calculations performed in Ref. 19 and the compatibility of the DCM model with the observed fast CM decay times.

IV. CONCLUSIONS

In summary, the Auger cooling lifetimes for the electron $1d$-to-$1p$ relaxation, occurring during the last stage of the $1p$-state population buildup, were calculated, using semiempirical pseudopotential wave functions, in different excitonic configurations, consistent with the experimental conditions reported in Ref. 3. Based on (i) the *invariance* of the $1p$ buildup time observed experimentally in the presence and in the absence of a CM event and (ii) the *variation* of the calculated Auger lifetimes in the two cases, but crucially (iii) without making any assumption on the specific nature of the CM mechanism, the carrier multiplication time constant for a 32-Å-radius CdSe NC was estimated to be of the order of 120 ± 60 fs, consistent with experimental estimates. The same quantity was then calculated, for a 14-Å-radius NC, assuming an impact-ionization-like process, yielding good agreement with both estimates. Finally it was speculated that these results could provide an indirect confirmation of the occurrence of CM in CdSe NCs, as an unlikely high electron energy-loss rate would have been required for the observed invariance of the $1p$ buildup time to be possible at an excitation energy of $3.1E_g$ in the absence of CM.

V. ACKNOWLEDGEMENTS

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[27] This result indicates that even if the hole initial Auger state h_i used in Eq. (1) were not the ground state (as it is assumed in the calculations), the calculated 1p-to-1s decay times presented in Fig. 3a would still be within the experimental error and therefore in excellent agreement with the observed values.

[28] This value was obtained assuming the electron to receive 60% of the excitation energy, according to the results of our simulations of the absorption of a 3.1 eV photon by 19-Å-radius NC.

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[31] The DCM lifetime calculated for an electron with the lowest possible excess energy compatible with energy conservation $\Delta E_e = E_g + \delta E$[19].