In-situ conductivity and UV-VIS absorption monitoring of iodine doping-dedoping processes in poly(3-hexylthiophene) (P3HT)

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Abstract. Poly(3-hexylthiophene) (P3HT) belongs to the family of conducting polymers whose conductivity can be controlled via doping. This paper is intended to study iodine doping-dedoping processes in P3HT films via in-situ measurements of the conductivity and light absorption. The film was spin-coated on ITO (indium tin oxide) patterned in the form of four-probe configuration. The sample was doped by iodine via exposure to iodine vapours in chamber and then de-doped by spontaneous release of the dopant under ambient conditions. The doping process was found to be several orders of magnitude faster than dedoping, which is attributed to the different mechanisms of diffusion. The theory of diffusion was applied to approximate the conductivity relaxation as measured experimentally. The best-fit parameters for the approximation were used to determine the dopant diffusivity D and β parameter of the semi-empirical relation between conductivity and dopant concentration ($\sigma \propto N_d^\beta$). Their values were found to be $(3.9±0.9) \times 10^{-13}$ cm$^2$/s and $4.28±0.04$ respectively. The latter agrees with the value know from the literature. The change of the polaron band in the absorption spectrum correlated with the conductivity changes in a complex manner and cannot be used as a measure of the concentration of free carriers contributing into the conductivity.

1. Introduction

Since the first evidence of the possibility to produce conducting polymers [1] they have become (along with organic molecular semiconductors) the basis of the fast developing field of organic electronics. Nowadays there are many applications based on conducting polymers such as photovoltaic cells [2-4], organic transistors [5,6], and light emitting diodes [7] etc.

One of the most attractive (for electronics) features of this class of materials is the ability to control their conductivity via doping as in the case of solid state electronics. The dopant molecules play the

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role of either electron donors or electron acceptors with respect to the \( \pi \)-conjugation chain of the polymer. The removal of the electron from the chain is a result of the polymer oxidation. This oxidized state is called positive polaron or polaronic cation. Sometimes it is falsely called “hole” in analogy to the electronic states formed in classical semiconductors. In contrast to a hole in solid state semiconductors, a polaron, once it is generated, induces an energy change due to the distortion of the polymer chain. Thus, the LUMO-HOMO (LUMO – lowest unoccupied molecular orbital; HOMO – highest occupied molecular orbital) gap of the chain reduces when the polaron is formed on it. The deeper oxidation with removal of the second electron from HOMO induces bipolaron formation, which further reduces the gap (figure 1). There are many evidences of doping related changes in the absorption spectrum for various types of conducting polymers and oligomers [8-11], which is indicative of the presence of polarons and bipolarons. On the other hand, when it concerns the electronics applications, it is more appropriate to distinguish the states which contribute into the net electrical conductivity. Bipolarons are associated not only to the presence of polaronic intra chain states but also and rather to interchain interactions and charge transfer processes via these localized states (hopping transport [12,13]). The comparison of light absorption spectra with electrical measurements allows one to derive quantitative characteristics of the states responsible for the conductivity.

This paper is intended to control synchronously the absorption features and the conductivity in poly(3-hexylthiophene) (P3HT) with respect to doping level changes. Our interest to this material is manifold. First, it is widely used in numerous applications [2-7]. Second, there are many experimental data on either its polaronic band behavior or its electrical characteristics. However there is a lack of the data on their correlation and quantitative estimates of the relation between polaronic features and conductivity. Third, halogens are known to be effective dopants for p-type conductivity in P3HT. In particular, iodine doping is a quite simple and straightforward process [14] and can induce a strong conductivity changes over a wide range. At the same time the doped state of P3HT in this case is rather unstable [8,9] and degrades with time via spontaneous withdrawal and evaporation of the dopant molecules, which is apparently a drawback. Nevertheless the iodine volatility is of great interest for this study, since there is a possibility to make a set of doping-dedoping cycles on the same sample in a repetitive manner. In addition, the dedoping-related time dependence of the conductivity contains some information about dopant diffusion, which is used here to derive the iodine diffusivity value. For this reason some model of the diffusion is considered and its relation to the conductivity relaxation is proposed.

**Figure 1.** Illustration of gap reduction for the polaron and bipolaron states. The dot-and-dash line represents schematically Fermi level position. Inset. P3HT molecule
2. Experiment
The experimental study includes: i) the photolithographic preparation of the special drawing on the indium tin oxide (ITO) coverage; ii) electrical measurement as the dopant escapes; iii) measurement of the optical absorption spectra synchronously with electrical measurements.

2.1. Sample preparation
**ITO coated glass substrate** was patterned via standard lithographic route. The substrate was rinsed in acetone and propanol and dried in nitrogen flow. A S1805 resist was spin coated for 1 min at 1000 and dried at 115 °C for 1 min. Then it was exposed through the mask (a transparency film with the drawing made by laser printer) for 6 sec under UV radiation. The exposed fragments of the resist were removed while rinsing in a water solution of Developer 35 with a 1(developer):5(H2O) volume ratio. ITO was etched off from the open area by concentrated HCl acid for 1 min at room temperature. Then the substrate was washed in acetone to remove the residual resist and rinsed in propanol.

Before the sample preparation the patterned ITO substrate was successively washed under ultrasonication in acetone and then in 2-propanol, then in pure water followed by oxidative treatment in boiling H2O2 and dried in air. **Regioregular P3HT** (Rieke Metals) film on the freshly treated ITO was formed by spin-coating of its 2 wt % solution in chlorobenzene at 2000 rpm for 20 s followed by baking at 120 °C for 30 min under argon. The film thickness measured by atomic force microscopy was 87±5 nm.

2.2. Iodine doping-dedoping
The sample was immersed in a chamber saturated with iodine vapor. To control in-situ the process, the wires from the sample contacts were brought out and kept connected to the measurement circuit. After the doping was saturated (which was monitored by the stabilization of the conductivity value) the sample was mounted into the spectrometer for less than 10s. Two different doping/dedoping cycles were made. The first one was made after long relaxation time (more than one day), and the other one followed immediately after the 1 h relaxation of the first cycle.

2.2. Conductivity measurements
A serial connection of the power supply and the amperemeter was made to 1,4 contacts (figure 2, inset), whereas the voltmeter was connected to the 2,3 inner contacts. This is a general principle widely used to avoid the contact influence, which results in an additional voltage drop when the current flows through a contact. Since the voltmeter has a high input resistance, the current is negligible in its circuit, and the voltage between contacts 2-3 relates directly to the part of the sample length where they are connected. The geometry of the contacts is chosen so that the distances between contacts are: \( L_{1,2}:L_{2,3}:L_{3,4}=1:1:1 \) (indices indicates the numbers of the respective contacts). Thus the distance between contacts 1 and 4 is three times higher than that of \( L_{2,3} \). Prior to synchronous electrical and optical measurements, the contact resistance influence was checked at various stages of the doping level.

The experimental data relate to the reduced value of conductivity \( \sigma / \sigma_0 \) (used in further analysis) as:

\[
\frac{\sigma}{\sigma_0} = \frac{I(t)}{U_{2,3}(t)} \cdot \frac{U_{2,3}(0)}{I(0)},
\]

where \( \sigma_0, U_{2,3}(0), I(0) \) are initial values of conductivity, voltage between contacts 2,3 and current measured at the saturation of the doping process prior to the extraction of the sample from the chamber; and \( \sigma, U_{2,3}(t), I(t) \) are the corresponding values as a function of the time \( t \) after extraction from the iodine chamber (actually, \( t \) is the duration of the dedoping process).
2.3. Optical absorption

The optical absorption spectra were measured using an AvaSpec-2048 spectrometer, with the bare ITO coated glass substrate as a reference sample. The integration time to take a single spectrum was 5 ms with the final spectrum resulted from averaging over 100 scans; thus, the total time of the measurement was far less than the characteristic relaxation time of the samples which was of the order of several minutes. Normally, the spectral changes were recorded every 30-60 seconds after the sample was exposed to the iodine vapors, and the rate of the spectral changes was controlled every 0.5 s visually on a monitor.

Spectra were modelled by the sum of four Gaussian components via mean square fit procedure. The spectra profiles can be expressed in the following forms:

\[
A(x) = \sum_{i=1}^{4} \frac{A_i}{w_i} \cdot \exp \left[ -2 \left( \frac{x-x_i}{w_i} \right)^2 \right],
\]

(2)

where \( x = h \nu \) is variable and the free parameters are (three for each component): \( x_i = h \nu_i \) (current value of the photon energy (in eV) at its i-th peak value); \( A_i \) is the integrated area of the i-th component; \( w_i \) is approximately the full width at half maximum (FWHM), i.e.:

\[
FWHM_i = \sqrt{\ln 4 \cdot w_i} = 1.177 \cdot w_i.
\]

To estimate the influence of the iodine spectrum another glass plate was immersed in the iodine chamber under the same exposition conditions, and the spectrum of the adsorbed iodine molecules was measured in the same manner as described above.

3. Results and discussions

The first and the most unexpected result was that the doping rate is much faster than the dedoping process. The conductivity rose to the saturation in about one second after the sample was immersed into the iodine vapour chamber. The reverse process (after the sample was removed from the chamber and kept under ambient) took hours. A possible interpretation of this asymmetry is presented at the end of this section. To check whether this process arises from bulk or contact phenomena, special 4-probe ITO geometry was used. Figure 2 shows that contact resistance becomes essential after 15 min of dedoping process. \( R_{1-4} \) is a drastically superlinear function of time whereas the resistance between internal contacts tends to be sublinear. After 1 h of dedoping their values differ by one order of magnitude. This means that only a high level of doping can guarantee good ITO contacts to P3HT film.

The experimental time dependence of the conductivity as calculated from (1) fits well with a linear behaviour (figure 3). The best fit parameters for curve 1 (table 1) results in a value of \( \beta = 4.28 \) (A.10) which is very close to the value \( \beta = 4.5 \) known from other experimental studies [15] and explained theoretically on the basis of the variable range hopping [13]. The repeated measurement of the conductivity relaxation (in 1 h after the first measurement) yields slightly lower values, which can be attributed to the reconstruction of the P3HT molecules, since this parameter is known to be sensitive to the dimensionality of hopping. In contrary the value of the dopant diffusivity derived from the second relaxation is a little bit higher. Probably the reason of both transformations is the same and associated with the reconstruction in the polymer film, which suppress the diffusion. To establish relations between the conductivity and polaronic states in the polymer the absorption spectra were analyzed at different time values.
The analysis of absorption spectra (figure 4) reveals that they are well described by (2). The parameters of the best mean-square fit agree with experimental results of other authors [16]. In particular the initial spectrum displays components with spectral features at $x_1=1.37$ eV, $x_2=1.64$ eV, $x_3=2.05$ eV, whereas the peaks identified in [16] as two polaronic states and interchain interaction have positions at 1.302 eV, 1.657 eV and 2.034 eV respectively. For this reason we attribute $x_1$ and $x_2$ to polaronic transitions and $x_3$ to interchain feature. Thus the sum of integrals $A_1$ and $A_2$ is taken as a measure of the polaron concentration. Since the light absorption monitors the film thickness it would be more appropriate to consider number of dopant molecules per unit area of the film, which is called in electronics as Gummel Number (GN) [17]. It is the integral characteristic of the layer which is defined as integral of the concentration over the thickness of the layer. Integrating (A.3) and taking approximation (A.4) yield:

$$GN \sim \int_0^L N_D(x,t)dx \sim t^{-3/2}.$$

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**Figure 2.** Time-dependence of the resistance on 1-4 and 2-3 contacts calculated as $R_{1-4} = U_{1-4}/I$, $R_{2-3} = U_{2-3}/I$, where $U_{1-4}$, $U_{2-3}$ are values of the potential differences between electrodes 1-4 and 2-3 respectively, $I$ is current. To normalize the resistances to the same length the value of $R_{2-3}$ is multiplied by three. **Inset.** Photolithographic drawing of the ITO coverage.

**Figure 3.** Time dependence in lg-lg plot ($\lg = \log_{10}$) of relative conductivity (1 – first measurement, 2 – second measurement) and 3 – overall integral intensity $A_1 + A_2$ ($A_1$, $A_2$ are parameters of approximation) of the polaronic band in absorption spectrum. Time is reduced to $t_0 = 1$ s (see comments to (A.9)). The solid lines are the linear mean square fit approximations (parameters are presented in table 1).
Table 1. Parameters of the linear mean square fit approximations expressed by (2) of the data presented in figure 3.

| Plot | Slope (cm²/s) | Intercept | D 10⁻¹⁵ cm²/s | β₁       |
|------|---------------|-----------|---------------|----------|
| 1    | -2.14 ± 0.02  | 3.12 ± 0.05 | 3.9 ± 0.9     | 4.28 ± 0.04 |
| 2    | -1.70 ± 0.02  | 1.72 ± 0.04 | 9.8 ± 2.4     | 3.40 ± 0.04 |
| 3    | -0.25 ± 0.04  | -0.89 ± 0.07 | -            | -        |

Figure 4. Absorption spectra (each 50 points are skipped). Solid lines are approximations calculated from (1) with parameters calculated by mean square fit and presented in table 2.

Thus the slope of the lg(A₁+A₂) vs lg(t/t₀) dependence is expected to be ~ − 0.5, whereas it turns out to be half this value (table 1, 3rd row). Hence the polaronic band intensity relates to the concentration of free charges contributing to the conductivity in a complicated manner. In general, the polaronic absorption is a bad approximation for quantitative estimates of the concentration of conductivity-related charges. Similarly, it is reasonable to assume that the charges responsible for conductivity belong to bipolaron species. Since the conductivity is determined by the hopping between states near the Fermi level, this assumption seems to be rather appropriate. Indeed Fermi level must be located near the middle of the gap. Bipolaronic states locate closer to the midgap than polaronic ones (figure 1). To be accurate the only tails of the bipolaronic density of states cross the Fermi level. Probably, to study this discrepancy (between time dependences of polaron band and conductivity, figure 3) in details, one should consider polaronic/bipolaronic concentration ratio, which is out of the scope of our paper. In addition, the conductivity-related states must have one more specific peculiarity. They belong to the percolative net of current paths. The dopant diffusion along these paths can be faster (presumably) than diffusion from the rest of the film.
The presence of dopant molecules has influence on electron transitions related to both inter- and intrachain interactions. Changes of interchain interactions are expected to be analyzed from \( x_3 \) component. Indeed, \( x_3 \) position is very sensitive to the doping level. Its value changes gradually from 2.3 eV after 60 s of dedoping to 2.19 eV for 540 s monotonously approaching its initial value of 2.05 eV. But it is not properly clear whether \( x_3 \) at rather high level of doping can be assigned only to interchain interaction. An alternative suggestion requires considering at least two types of neutral P3HT chain. Prior to doping, there is only one of them with maximum at 2.37 eV (\( x_4 \)) which is consistent with the value for regioregular P3HT. Dopant molecules cause shortening of the polymer conjugation length and the intrachain peak position blue shifts. Actually, both types of polymer chains (with reduced length and pristine) are present. Thus the values 2.3 eV and 2.19 eV derived for \( x_3 \) can be the result of superposition of interchain interaction transition and band of pristine P3HT chain.

The spectrum at 10 s is deformed in a so drastic way that seeking interchain interaction feature, which is screened by more powerful component with peak at 2.77 eV, is meaningless (figure 5).

### Table 2. The best-fit values of the free parameters for the approximation of the experimental spectra presented as a sum of four Gaussians (1)

| Parameter | Initial 10s | 60s | 180s | 540s |
|-----------|------------|-----|------|------|
| \( A_1 \) | 0.006±0.0003 | 0.009±0.001 | 0.010±0.001 | 0.009±0.001 | 0.007±0.001 |
| \( x_1 \) (eV) | 1.37±0.01 | 1.35±0.001 | 1.350±0.001 | 1.35±0.001 | 1.36±0.001 |
| \( w_1 \) (eV) | 0.21±0.01 | 0.17±0.01 | 0.173±0.005 | 0.162±0.004 | 0.160±0.01 |
| \( A_2 \) | 0.006±0.0004 | 0.073±0.001 | 0.048±0.001 | 0.042±0.001 | 0.028±0.004 |
| \( x_2 \) (eV) | 1.64±0.005 | 1.51±0.003 | 1.54±0.004 | 1.557±0.003 | 1.61±0.01 |
| \( w_2 \) (eV) | 0.21±0.01 | 0.423±0.003 | 0.376±0.006 | 0.359±0.008 | 0.34±0.02 |
| \( A_3 \) | 0.005±0.0002 | 0.48±0.01 | 0.015±0.001 | 0.017±0.002 | 0.04±0.03 |
| \( x_3 \) (eV) | 2.05±0.001 | 2.77±0.001 | 2.30±0.002 | 2.25±0.004 | 2.19±0.005 |
| \( w_3 \) (eV) | 0.104±0.003 | 1.310±0.003 | 0.337±0.008 | 0.32±0.01 | 0.36±0.04 |
| \( A_4 \) | 0.297±0.001 | 0.011±0.001 | 0.380±0.001 | 0.314±0.002 | 0.23±0.03 |
| \( x_4 \) (eV) | 2.37±0.001 | 2.95±0.004 | 2.71±0.002 | 2.56±0.01 | 2.51±0.04 |
| \( w_4 \) (eV) | 0.482±0.002 | 0.32±0.01 | 1.165±0.004 | 0.886±0.009 | 0.63±0.05 |

The spectrum measured at the highest level of doping (after 10s doping) shows many differences as compared with the other spectra (figure 5). Firstly, its \( x_3 \) and \( x_4 \) components are essentially blue shifted. As discussed above \( x_3 \) can be hardly attributed to the interchain interactions like in other spectra. It rather relates to processes similar to those associated with \( x_4 \) features on the other spectra. Instead the spectrum at the highest doping level contains its own \( x_4 \) component (figure 5, curve 4) which differs substantially from the other \( x_4 \) components. As this component is close to the spectrum of iodine (curve 5) in terms of intensity and spectral position, it is probably associated with iodine absorption. The red shift of its energetic position can be explained by a more extended localization of its exciton due to the conjugated polymer surrounding as compared to the situation when iodine molecules are separately adsorbed onto the glass surface. This behavior of the spectrum measured after a so short period of desorption is indicative of an initially very high level of dopant concentration along the whole thickness of the film. It can be assumed that just after the saturation was reached the doping level was even higher. The doping time was extremely short. How to explain such asymmetry in the doping-dedoping duration? We can propose two possible scenarios. They are complementary rather than alternative, since the first explains the enhancement of the doping process whereas the other concerns suppression of the dedoping.

**First. The doping process** is enhanced by the ambipolar diffusion. The dopant diffusivity is much lower than that of free carriers. Once dopant molecules enter the film, some number of positively charged mobile carriers is generated at the interface. They diffuse almost immediately to the rear
surface due to a huge gradient of concentration. At the same time they involve dopant molecules. Actually, both species move with a velocity which can be characterized by some averaged diffusivity which is called ambipolar diffusivity [18]. A similar increase of the rate is observed for thermal oxidation of silicon at the beginning when the oxide layer is extremely thin [19]. The reverse process is quasi steady state while no gradients are formed or at least they are not so huge.

**Second. The dedoping process** is associated with the dissociation of the charge transfer complexes formed by the dopant molecules and conjugation chains. Electrostatic forces between polaron and negative iodine ion suppress disruption of this complex. This mechanism of dedoping is described in [9].

4. **Conclusions**
P3HT can be reversibly doped-dedoped with iodine vapour. The doping process is much faster than the dedoping one, which is controlled by in-situ measurements of the conductivity. The model proposed to describe the conductivity relaxation during the dedoping process is the basis of the experimental technique measuring the dopant diffusivity and the \( \beta \) exponent corresponding to the semi empirical power law between the conductivity and doping concentration (\( \sigma \sim N_D^\beta \)). The procedure consists in the determination of the best fitting parameters for a linear approximation of the experimental \( \log(\sigma(t)/\sigma(0)) \) vs \( \log(t/t_0) \) dependence (\( t_0 =1s \)). The parameters found from (A.10) and (A.11) are \( \beta =4.28\pm0.04 \) and \( D=(3.9\pm0.9)\cdot10^{-13} \) cm\(^2\)/s.

The absorption spectrum measured at different durations of the dedoping process (synchronously with the conductivity measurements) contains two polaronic features at 1.35 → 1.37 eV and 1.51 → 1.64 eV. The ranges indicate the extent of their variation with dedoping. These values are close to those measured by other authors. The analysis of the polaron band intensity demonstrates that this parameter, although correlated with the conductivity, cannot represent a determination of the free carrier concentration contributing into the conductivity. The slope of the polaronic band intensity – time dependence in a \( \log-log \) plot is –0.25 instead of –0.5 as expected if the polaronic intensity proportionally follows the change of the free carrier concentration. It is assumed that this discrepancy is explained by the nature of the conductivity related charges which relate more to bipolaronic states.

These results are expected to contribute not only to a better understanding of the electronic processes in P3HT material but also to the general knowledge about conductivity formation in conjugated polymers. The volatility of the iodine dopant in P3HT makes this system to be a very suitable and flexible model object to study electronic processes responsible for the conductivity.

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5. **Appendix (model of diffusion and its relation to the conductivity change while dedoping)**

One-dimensional concentration distribution of a diffusing species is described by Fick’s law:

\[
\frac{\partial N_D(x,t)}{\partial t} = D \cdot \frac{\partial^2 N_D(x,t)}{\partial x^2}, \tag{A.1}
\]

where \( D \) is the dopant diffusivity (the unknown quantity in our study); \( x \) is coordinate along the diffusion flow direction, \( t \) is time. The boundary conditions corresponding to the experiment are based on the following assumptions: i) initial distribution is uniform since the doping reaches the saturation value; ii) once the sample is extracted from the iodine chamber, the dopant concentration at the surface relaxes till zero very quickly (it is evidenced experimentally for halogen dopants [20]). Hence, the boundary conditions are:
\[ N_D(x,t) = N_{D0} = \text{const}, \quad t < 0 \]
\[ N_D(0,t) = 0, \quad t > 0 \]  
(A.2)

The solution of (A.1), (A.2) is [21]:
\[ N_D(x,t) = N_{D0} \cdot \text{erf} \left( \frac{x}{2\sqrt{D \cdot t}} \right), \]
(A.3)

where the abbreviation \( \text{erf} \) means the error function defined as:
\[ \text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-t^2} dt = \frac{2}{\sqrt{\pi}} z. \]  
(A.4)

The conductivity analysis based on the hopping model and evidenced experimentally demonstrated power law dependence of the conductivity on the dopant concentration [13]:
\[ \sigma \sim N_D^\beta. \]  
(A.5)

If \( N_D \) is a function of coordinate at any instant \( t \), then contribution of some layer \( dx \) into the net conductivity can be presented as:
\[ d\sigma(x,t) \sim \frac{1}{L} N_D^\beta(x,t) dx, \]  
(A.6)

and the integral value reduced to the initial conductivity \( \sigma \sim N_{D0}^\beta \) is
\[ \frac{\sigma}{\sigma_0} = \frac{2}{L \sqrt{\pi}} \int_0^L \left( \frac{x}{2\sqrt{D \cdot t}} \right)^\beta dx, \]  
(A.7)

where approximate value of the error function is used (A.4). Taking the logarithms of both sides one yields:
\[ \log \frac{\sigma}{\sigma_0} = \log \frac{L^\beta}{(\beta+1) \cdot (\pi t_0)^{\beta/2}}, \]  
(A.7)

which allows one to present the experimental data as linear dependence:
\[ \log \frac{\sigma}{\sigma_0} = a \left( \log \frac{t}{t_0} \right) + b, \]  
(A.8)

where slope and intercept are:
\[ a = -\frac{\beta}{2}, \quad b = \log \left( \frac{L^\beta}{(\beta+1) \cdot (\pi t_0)^{\beta/2}} \right), \]  
(A.9)

and \( t_0 = 1s \). Thus the best fit parameters of the linear approximation for the experimental data presented as \( \log(\sigma(t)/\sigma_0) \) vs \( \log(t/t_0) \) dependence relates to the desired quantities.
\[ \beta = -2a, \quad \text{(A.10)} \]

\[ D = \frac{L^2}{\pi \cdot t_0} \left( \frac{10^{-b}}{\beta + 1} \right)^{2/\beta}. \quad \text{(A.11)} \]

The estimate of the relative error is derived by differentiating (A.11):

\[ \delta D = 2 \cdot \delta L + \frac{2}{\beta} \ln 10 \cdot (\Delta b + b \cdot \delta \beta) + 2 \left( \frac{1}{1 + \beta} + \frac{\ln(1 + \beta)}{\beta} \right) \delta \beta, \quad \text{(A.12)} \]

where \( \delta D = \frac{\Delta D}{D}, \delta \beta = \frac{\Delta \beta}{\beta}, \delta L = \frac{\Delta L}{L} \) are relative errors, \( \Delta D, \Delta \beta, \Delta L, \Delta b \) are absolute errors.

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