Correlation analysis of spectral fluctuations in inhomogeneously broadened spectra

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Abstract: It is shown that the lineshapes of inhomogeneously broadened spectra, due to the statistical nature of their formation, exhibit spectral fluctuations. Formulas are obtained that allow one, based on correlation analysis of different realizations of the inhomogeneously broadened line, to reconstruct its homogeneous lineshape and to evaluate the number of centers involved in its formation. The magnitude of these spectral fluctuations is estimated and it is shown that the proposed method can be efficiently used in practice.

OCIS codes: (300.6280) Spectroscopy, surface; (240.6490) Spectroscopy, fluorescence and luminescence

References and links

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1 Introduction

The problem of extracting the homogeneous contribution to an inhomogeneously broadened line is a classical problem of optical spectroscopy. Solving this problem allows one, in many cases, to get valuable information about the nature of broadening of spectral lines and characteristics of individual centers forming the inhomogeneously broadened line. This problem is encountered in atomic and molecular spectroscopy, in spectroscopic studies of surfaces, in spectroscopy of activated crystals and semiconductors, etc. At present, this problem has acquired a particular importance in studies of low-dimensional semiconductor structures (quantum wells and quantum dots), with the inhomogeneous broadening resulted from variance of the size quantization effects. As a rule, however, this problem cannot be solved within the framework of standard methods of linear spectroscopy. This is why, spectroscopic characteristics of individual emitters are determined, in practice, either using methods of nonlinear spectroscopy (spectroscopy of transient response, hole-burning spectroscopy, etc., see, e.g., [1]), or by realizing conditions (by

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means of near-field or far-field microscopy) when the number of emitters becomes sufficiently small and components of the inhomogeneously broadened line profile become, to some extent, resolved [2, 3, 4, 5, 6]. Note that extracting the homogeneous linewidth from the luminescence decay measurements is justified only in unique situations when the line is not broadened by dephasing processes.

In this paper, we want to call attention to the fact that information about the homogeneous broadening of an inhomogeneously broadened line can be extracted from the profile of the latter provided that this profile is recorded with a sufficiently high accuracy. We show that the inhomogeneously broadened line profile, in view of statistical nature of distribution of oscillators' frequencies, exhibits spectral fluctuations, with their correlation length (in spectral scale) being directly connected with the homogeneous linewidth and with their amplitude determined by the number of centers forming the profile in particular experimental conditions. We propose a method for measuring correlation characteristics of inhomogeneously broadened lines, estimate quantitatively the magnitude of the effect, and formulate requirements that determine the possibility of its practical observation and use.

2 Mathematical procedure

For definiteness, we will deal, in what follows, with spectra of photoluminescence (although the proposed approach can be applied to studies of other spectra of secondary emission or absorption). For this reason, individual centers forming the inhomogeneously broadened line (quantum dots, localized excitons, adsorbed atoms, impurity centers, etc.) will be further referred to as emitters.

As will be shown below, information about the homogeneous width of the spectrum can be obtained, in principle, from correlation analysis of a single realization. It is known, however, that reliability of information about a random process increases with the number of its realizations. In photoluminescence studies, the number of realization of the spectrum can be easily increased by shifting the spot of optical excitation over the sample. Each new position will give a new realization of the photoluminescence spectrum because the spectrum will be formed each time by a different combination of emitters. We assume, for simplicity, that the homogeneous spectral width does not depend in any regular way on position of the spot on the sample.

Let the inhomogeneously broadened line be formed by N emitters, with the i-th emitter being characterized by a homogeneously broadened line $a(\omega-\omega_i)$, where ω_i ($i = 1, ..., N$) are mutually independent random quantities with the distribution function $\rho(\omega)$ ($\int \rho(\omega)d\omega = 1$). We assume, for simplicity, that $\int a(\omega)d\omega = 1$. Then, each realization of the inhomogeneously broadened line will be described by the random function $A(\omega)$:

$$A(\omega) = \sum_{i=1}^{N} a(\omega - \omega_i) \tag{1}$$

The homogeneous width of the spectral line is considered to be much smaller than the inhomogeneous width, i.e., the region where the function $\rho(\omega)$ is nonzero is much larger than that for the function $a(\omega)$. Then, for the inhomogeneously broadened line averaged over realizations $< A(\omega) >$, we have:

$$< A(\omega) >= N \int \rho(x)a(\omega - x)dx \approx N\rho(\omega)$$

Let us calculate the correlation function $< A(\omega)A(\omega') >$ (see, e.g., [7])

$$< A(\omega)A(\omega') >= N \int \rho(x)a(\omega - x)a(\omega' - x)dx + \frac{(N-1)}{N} < A(\omega) >< A(\omega') >,$$

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whence

$$\frac{< A(\omega)A(\omega') > - \frac{N-1}{N} < A(\omega) >< A(\omega') >}{N} =$$

$$\int \rho(x)a(\omega - x)a(\omega' - x)dx \approx \rho\left(\frac{\omega + \omega'}{2}\right) \int a(\omega - x)a(\omega' - x)dx$$

Let the homogeneous lineshape be a Lorentzian:

$$a(\omega) = \frac{1}{\pi}\frac{\delta}{\delta^2 + \omega^2} \tag{2}$$

Assuming that $N >> 1$ and expressing $\rho(\omega)$ through the averaged profile of the inhomogeneously broadened line, we obtain:

$$\frac{< A(\omega)A(\omega') > - < A(\omega) >< A(\omega') >}{< A\left(\frac{\omega+\omega'}{2}\right) >} = \tag{3}$$

$$\int a(\omega - x)a(\omega' - x)dx = \frac{1}{\pi}\frac{2\delta}{(\omega - \omega')^2 + 4\delta^2}$$

Thus we see that auto-convolution of the homogeneous line can be directly expressed through characteristics of the experimentally measured functions $A(\omega)$ (left-hand side of the equation). Suppose we have a set of N_R realizations of the inhomogeneously broadened line, i.e., N_R functions $A_r(\omega), r = 1, ..., N_R$. Then, the expression for auto-convolution of the homogeneously broadened line can be written in the form:

$$\frac{\sum_{r=1}^{N_R} A_r(\omega)A_r(\omega') - N_R^{-1}\sum_{rr'=1}^{N_R} A_r(\omega)A_{r'}(\omega')}{\sum_{r=1}^{N_R} A_r\left(\frac{\omega+\omega'}{2}\right)} \approx \tag{4}$$

$$\int a(\omega - x)a(\omega' - x)dx = \frac{1}{\pi}\frac{2\delta}{(\omega - \omega')^2 + 4\delta^2}$$

Formulas (3) and (4) express in a quantitative form the fact that the inhomogeneously broadened line profile is, in essence, a random function which inevitably exhibits spectral fluctuations whose correlation properties contain information about its homogeneous broadening. The result thus obtained, evidently, does not depend qualitatively on the homogeneously broadened line shape and can be formulated as follows: The left-hand side of Eq.(4) (or (3)), measured experimentally, depends only on the frequency difference $\omega - \omega'$ and represents a function with a narrow peak (right-hand side), whose width is twice as large as that of the homogeneous line.

To demonstrate efficiency of the proposed correlation method, we have made a series of computer-simulation experiments. Each realization of the inhomogeneously broadened line formed by an ensemble of N emitters was obtained using formula (1) by generating N random numbers ω_i ($i = 1, ..., N$), with the Gaussian distribution function $\rho(\omega) = \frac{1}{\Delta\sqrt{\pi}} \exp\left[-\left(\frac{\omega}{\Delta}\right)^2\right]$. The homogeneous spectral line was taken in the form of a Lorentzian (2). By repeating this procedure N_R times, we obtained N_R independent realizations of the inhomogeneously broadened line $A_r(\omega), r = 1, ..., N_R$. Then we calculated the correlation function of the inhomogeneously broadened line and checked formula (4). Note that the frequency increment used for numerical generation of the arrays $A_r(\omega)$ had to be essentially smaller than the homogeneous linewidth δ. The results thus obtained for different numbers of realizations N_R, with the number of emitters $N = 10^4$ and the inhomogeneous/homogeneous linewidth ratio $\alpha = 20$, are shown in Fig.1 The dashed line shows auto-convolution of the homogeneously broadened line. As seen from Fig.1, the results of computer simulation agree well with predictions of our analysis.

3 Magnitude of the effect

Let us estimate the amplitude of spectral fluctuations of the inhomogeneously broadened line. Variance of a random quantity, by definition, is given by the formula:

$$D(\omega) \equiv < A^2(\omega) > - < A(\omega) >^2$$

Whence it follows, as can be easily shown, that the relative fluctuation of the line profile

$$d \equiv \sqrt{D(\omega)}/ < A(\omega) >$$

is given by the relationship:

$$d = \frac{1}{\sqrt{N}} \frac{\sqrt{\int \rho(x) a^2(\omega - x) dx - \left(\int \rho(x) a(\omega - x) dx \right)^2}}{\int \rho(x) a(\omega - x) dx} \tag{5}$$

If the homogeneous line is a Lorentzian (2), and the homogeneous linewidth δ is much smaller than the inhomogeneous linewidth, formula (5) can be approximately represented in the form

$$d \approx \frac{1}{\sqrt{2\pi N \rho(\omega) \delta}} \tag{6}$$

This formula has a simple physical meaning: the relative magnitude of spectral fluctuations of an inhomogeneously broadened line is determined by the number of emitters falling into a spectral interval equal to the homogeneous linewidth ($N\rho(\omega)\delta$), and is thus equal, within an order of magnitude, to the inverse square root of this number. Therefore, the relative magnitude of spectral fluctuations of the line increases not only with decreasing number of emitters N but also with decreasing homogeneous linewidth. In other words, the cases of smaller size of the spot of optical excitation and higher values of the inhomogeneous/homogeneous linewidth ratio (α) are, from the experimental viewpoint, more favorable (we assume, of course, that resolution of the spectrometer employed essentially exceeds the homogeneous linewidth). To give a more vivid idea about the magnitude of these fluctuations, we show in Fig.2 the inhomogeneously broadened lines (obtained by the computer simulation technique) for several values of N and α. The magnitude of the spectral fluctuations of the inhomogeneously broadened line is seen to increase with increasing α and decreasing N. Besides, as the homogeneous linewidth decreases and, correspondingly, the peak of the correlation function narrows, the Fourier spectrum of the spectral fluctuations, in conformity with the Wiener-Khinchin theorem (see, e.g., [7]), acquires higher frequencies. Note that, given the correctness of the model of formation of the inhomogeneously broadened line, the experimental value of the homogeneous linewidth thus obtained, in combination with the experimentally measured *magnitude* of the spectral fluctuations variance d, makes it possible to estimate the total number of emitters forming the inhomogeneously broadened line and to determine the mean distance between them, i.e., to obtain important physical information about the sub-optical structure of the sample. How many realizations are needed to extract the homogeneously broadened line with a sufficiently high signal/noise ratio? As a start, let us roughly estimate the achievable signal/noise ratio neglecting the noises of measurement. We can assume that one realization of the inhomogeneously broadened line, for the inhomogeneous/homogeneous linewidth ratio α, contains $\sim \alpha$ uncorrelated spectral intervals and is therefore effectively equivalent to $\sim \alpha$ realizations. In combination with N_R realizations of the whole inhomogeneous line, we have altogether an effective number of αN_R realizations. This means that uncorrelated spectral fluctuations of the inhomogeneously broadened line will be suppressed by a factor of $\sqrt{\alpha N_R}$ as compared with correlated ones. For example, the number of independent realizations needed to obtain the signal/noise ratio of the order of 10, for the inhomogeneous/homogeneous linewidth ratio $\alpha = 10$, equals 10. As was already mentioned, these independent realizations can be obtained by shifting the spot of optical excitation over the sample. Thus, in the absence of any noise of detection, the signal/noise ratio *does not depend on the number of emitters* N forming the inhomogeneously broadened line and is determined only by the effective number of realizations αN_R

$$S/N \approx \sqrt{\alpha N_R} \tag{7}$$

However, the magnitude proper of the spectral fluctuations d will evidently drop with increasing N and, for sufficiently large N, may 'sink' below the detected noise. It should be emphasized that the spectral noise of the inhomogeneously broadened line under study can be considered here, in the framework of this approach, as a statistical *signal*, which *should be the same* for identical realizations of the ensemble of emitters. The possibility of measuring the spectral fluctuations is determined by the ratio of their amplitude (*amplitude of signal*) to amplitude of real irreproducible noise of measurements. The latter can be associated not only with usual noise of detection (shot noise of the photocurrent, noise of electronics, etc.), but also with various kinds of spurious spectral modulation (caused, e.g., by interferometric effects on parasitic interferometers in the optical channel).

Let us make a realistic assumption that the main contribution to the noise of measurements is made by shot noise of the detector's photocurrent. Then, the magnitude of the accumulated signal n of the spectral data array (expressed in the number of photoelectrons) needed to be able to neglect the noise of detection will be given by

$$\sqrt{n} >> 1/d, \tag{8}$$

where d is the variance of spectral fluctuations of the line profile, given by Eq.(6). In other words, the method under consideration can be used when the experimental numbers of the spectral data array n essentially exceed (say by one or two orders of magnitude) the number of emitters falling into the interval equal to the homogeneous linewidth. In this case, the signal/noise ratio in the auto-convolution of the homogeneous line, obtained experimentally, will be determined, as before, by Eq. (7). Using this criterion, one can easily estimate that with the up-to-date methods of detection and accumulation of optical signals (with CCD detector arrays and automatic scanning of the optical excitation spot over the sample), this requirement can be fulfilled in a wide number of cases, which indicates feasibility of the proposed experimental approach. Note that to meet the requirement (8) one can increase the signal accumulation time and decrease the excitation spot size. As was already pointed out, spectral resolution for measurements of this kind should essentially exceed the measured homogeneous linewidth or, which is the same, the characteristic correlation interval of the spectral fluctuations.

4 Conclusion

In this paper, we have described schematically a correlation method for measuring the homogeneous linewidth of inhomogeneously broadened spectra and have shown its feasibility. The method is based on measurements of correlation characteristics of spectral fluctuations in the inhomogeneously broadened spectra. What is needed to obtain correct experimental data is essentially just to record the spectrum with sufficiently high signal/noise ratio and sufficiently high spectral resolution. In real experimental conditions, the situation may be more complicated, and the simplest model adopted here

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may need to be corrected (e.g., intensities and homogeneous linewidths may be random quantities with a finite variance or may depend in a regular way on the wavelength or spatial position on the sample, etc.). However, particular features of this kind will not affect the main results of the above treatment. The proposed approach has much in common with the hole-burning spectroscopy (which is known to be efficient not only for ensembles of identical oscillators) and allows one, in many cases, to obtain information about the homogeneous linewidth buried within a much larger inhomogeneous profile.

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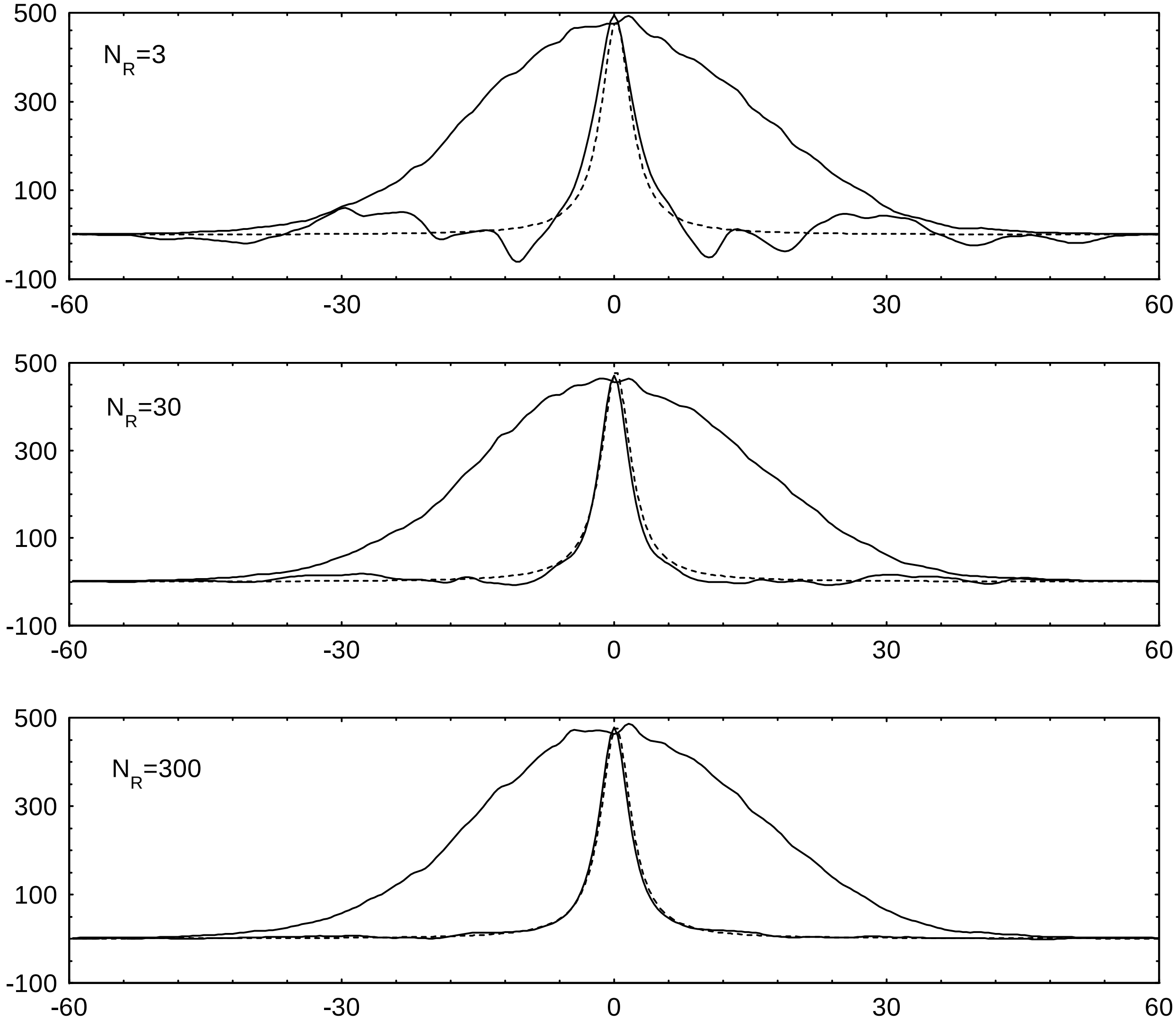

Fig. 1. Results of correlation analysis of an inhomogeneously broadened line obtained by computer simulation. Correlation functions of the line profile (narrow peak, solid curve) are compared with auto-convolution of the homogeneously broadened line (dashed curve) for several numbers of realizations N_R ($N_R = 3$, 30 and 300). The inhomogeneous/homogeneous linewidth ratio $\alpha = 20$. Broad spectrum in each figure is a realization of the inhomogeneously broadened line.

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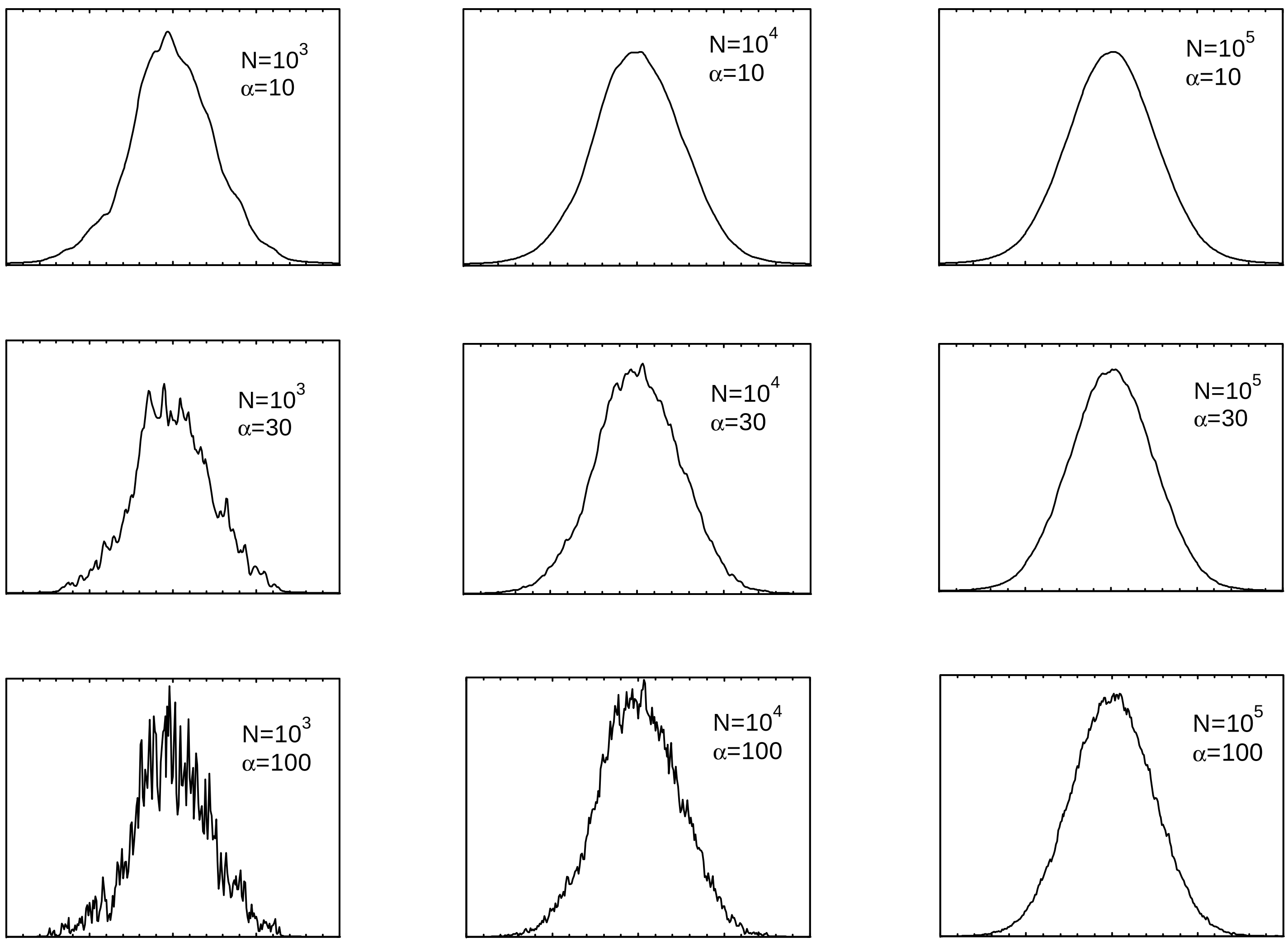

Fig. 2. Computer-simulated realizations of an inhomogeneously broadened line for total number of emitters $N = 10^3$, 10^4, and 10^5 and for the inhomogeneous/homogeneous linewidth ratio $\alpha = 10$, 30, and 100.

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