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Fractals: giant impurity nonlinearities in optics of fractal clusters

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A theory of nonlinear optical properties of fractals is developed. Giant enhancement of optical susceptibilities is predicted for impurities bound to a fractal. This enhancement occurs if the exciting radiation frequency lies within the absorption band of the fractal. The giant optical nonlinearities are due to existence of high local electric fields in the sites of impurity locations. Such fields are due to the inhomogeneously broadened character of a fractal spectrum, i.e. partial conservation of individuality of fractal-forming particles (monomers). The field enhancement is proportional to the Q-factor of the resonance of a monomer. The effects of coherent anti-Stokes Raman scattering (CARS) and phase conjugation (PC) of light waves are enhanced to a much greater degree than generation of higher harmonics. In a general case the susceptibility of a higher-order is enhanced in the maximum way if the process includes "substraction" of photons (at least one of the strong field frequencies enters the susceptibility with the minus sign). Alternatively, enhancement for the highest-order harmonic generation (when all the photons are "accumulated") is minimal. The predicted phenomena bear information on spectral properties of both impurity molecules and a fractal. In particular, in the CARS spectra a narrow (with the natural width) resonant structure, which is proper to an isolated monomer of a fractal, is predicted to be observed.

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1. Introduction

Fractals are known as objects of non-integer dimension immersed into a three-dimensional space [1]. In nature there is a great vareity of clusters which are the physical counterparts of fractals. Such clusters (hereafter referred to as "fractals") possess unique geometrical, statistical and kinetic properties. Among the most interesting representatives of fractal clusters are obviously metal clusters, the linear optical properties of which have been studied by Kriebig [2] and the nonlinear ones by Rautian et al. [3]. Light scattering on fractals has been studied by Berry, Percival (1986) by a mean-field approach [4]. Unlike them, in our previous work a description has been suggested which takes into account the crucial feature of the fractal, i.e. its fluctuation nature.

In this paper the technique from [5] is extended to describe the nonlinear optical properties of impurity centers bound to a fractal. The susceptibilities are calculated, responsible for coherent (parametric) phenomena such as coherent anti-Stokes light scattering (CARS), optical phase conjugation (OPC) by degenerated four-wave mixing, second- and third-harmonics generation. The effects of CARS and OPC are shown to be giantically enhanced. Third-harmonic generation has been found to be enhanced as well, though to a much smaller extent.

Optical properties of fractals are unique and different from those of gases and condensed media. This is due to the asymptotically zero integral density of the fractal. The pair interaction is, nevertheless, not weak. These properties, being mutually exclusive for a nonfractal medium, are a consequence of the power-law drop of the pair-correlation function (density-density) $g(r)$ with the intermonomer distance r and

of the scaling dependence of the number of monomers in a fractal on its radius R_c

$$g(r)=\frac{D}{4\pi}R_0^{-D}r^{D-3}, \quad N=(R_c/R_0)^D \tag{1}$$

where R_o is the length dimension parameter denoting the typical distance between monomers. Index D is called the fractal (Hausdorff) dimension. Both relations (1) directly follow from each other. Dependence $g(r)$ should be understood as an intermediate asymptotics at $R_0 \lesssim r \lesssim R_c$. A fractal is called nontrivial when $D<3$. If this is the case, the integral density $\propto R_c^{D-3}$ is asymptotically zero (at $R_c \to \infty$). Giant Raman scattering discussed earlier in [5] and giantically enhanced nonlinearities predicted in this paper are due to the existence of high local fields created near the monomers of the fractal, resonant to the exciting radiation. The local field is amplified proportionally to the quality of the monomer as of a resonator. The fractal spectrum is inhomogeneously broadened because of the dispersion of the monomers interaction; therefore in the broad band of its absorption there occur monomers for which the resonant conditions are fulfilled. The enormous enhancement of nonlinear susceptibilities follows from the fact that they are defined as the local field value raised to a higher power (e.g. to the sixth power for CARS and OPC). When $D \to 3$, i.e. when a fractal tends to become trivial, its spectra become broadened and the susceptibility is not enhanced.

Below it is also shown that the nonlinear spectra of impurities in the fractal matrix bear informtion on the properties of the impurity centers, the fractal as a whole and of the individual monomers of the fractal as well.

2. Formulation of the problem and qualitative estimations. Basic fractal properties relevant for quantitative evaluation

Consider a fractal consisting of N particles (monomers) located in the points $\{\mathbf{r}_i\}$, where the superscript (low-case Latin) indicates the number of the monomer. Coordinates $\{\mathbf{r}_i\}$ are random; a probability of finding another monomer distanced from the given one by r is determined by the correlation function $g(r)$ (1).

Monomers are dipole-polarized (at optical frequencies) particles with the nonlinear susceptibility $\chi_0(\omega)$, where ω is the frequency of the external light field. The induced dipoles of different monomers interact via the dipole-dipole forces.

Some of the monomers have the impurity centers bound to them, the number of which is considered to be small and hence the interaction between them may be ignored. The impurities are assumed to be nonlinearly polarized and characterized by the susceptibility $\chi^{(n)}$ of order n.

The reason for the giant enhancement of nonlinear susceptibilities of the impurities incorporated into a fractal is that the local field $\mathbf{E}^c$ acting on the impurity center, bound to the exciting-radiation-resonant monomer, exceeds the mean field $\mathbf{E}$. Now we turn to estimations and present some results of the theory [5] required for further discussion.

Let us consider one of the impurities bound to, say, the i-th monomer of the fractal. The radius-vector monomer-impurity will be denoted by $\mathbf{R}$, assuming $\mathbf{R}$ to be smaller than the distance between the nearest monomers R_0. Then the local electric field at the impurity $\mathbf{E}^c$ is a combination of the field $\mathbf{E}^i$ acting on the given monomer and the field of its induced dipole:

$$E_\alpha^c=\chi_0 \Pi_{\alpha\beta} E_\beta^i,$$
$$\Pi_{\alpha\beta}=(\chi_0^{-1}-R^{-3})\delta_{\alpha\beta}+3R^{-3}n_\alpha^c n_\beta^c, \quad \mathbf{n}^c \equiv \mathbf{R}/R, \tag{2}$$

where the subscripts (Greek) denote the tensor components, summation is implied to extend over the repeated indices.

The main quantitiy that we are going to estimate and calculate below is the enhancement factor $G^{(n)}$ for the n-th-order nonlinear process. $G^{(n)}$ is defined as the ratio of the radiation intensity generated at the fractal-bound impurities to the analogous intensity for the free impurity particles. Since the field amplitude generated by the n-th-order nonlinearity is proportional to the n-th power of the excited field, it is evident that

$$G^{(n)} \sim |\langle (E^c)^n \rangle / E^n|^2. \tag{3}$$

Hereafter averaging, denoted by the angular brackets, includes averaging over an ensemble of fractals.

It should be emphasized that since the phenomena under discussion are of coherent nature (i.e. leaving the state of the subsystem unchanged), it is the amplitude of the radiation that is to be averaged and not the intensity (as is the case with spontaneous Raman scattering).

In order to find E^c and to choose the averaging procedure in (3), it is necessary to know the properties (especially statistic ones) of the local field $\mathbf{E}^i$. First of all, one may try to estimate the difference between the local $\mathbf{E}^i$ and the mean (macroscopic) fields in a conventional manner by introducing the Lorentz field $\mathbf{E}^L$. The latter is determined by the familiar procedure (see e.g. [6]); it should, however, be taken into account that the density of other monomers around

the given one is not constant, but is determined by the function $g(r)$ (1). The resultant expression has the form $\mathbf{E}^L = D\mathbf{d}/3R_0^3 \times (R_L/R_0)^{D-3}$, where R_L is the radius of the cavity (Lorentz sphere) cut out around the given monomer. In contrast to the non-fractal medium ($D=3$), the Lorentz field for the nontrivial fractal ($D<3$) diverges at $R_L \to 0$.

The divergence of the Lorentz field at small distances shows that the main contributors to the local field $\mathbf{E}^i$ are the nearest monomers. Since they are few in number, the local field $\mathbf{E}^i$ strongly fluctuates. Theories based only on the field averaged over the ensemble of systems (of the Lorentz field type) are not adequate for fractals.

In [5] a binary approximation is formulated with an exact account of the fluctuating field of the nearest neighbour. The fields of the rest monomers are treated as averaged, which results, analogously to [6], in the replacement of the external field by the mean one and addition of the Lorentz field to $\mathbf{E}^i$. However contribution of the Lorentz field appears to be small, the major contribution being given by the field of the nearest monomer. Below, an expression for $\mathbf{E}^i$ will be derived in binary approximation, and now we seek to estimate $G^{(n)}$ (3) on the basis of the above qualitative considerations. For simplicity, we ignore such unimportant factor as the influence of the Lorentz field (its account would introduce negligible quantitative corrections). Not to shadow the main physical principles, at first we shall also neglect the interaction with the generated radiation fractals. But later (see (8)) it will be taken into account.

Let us consider monomers having an isolated resonance. Their susceptibility is defined by

$$\chi_0 = -\omega_m R_m^3 (\Omega + i\Gamma)^{-1}; \tag{4}$$

where ω_m and Γ are the characteristic excitation frequency and the homogeneous width of the monomer, respectively; R_m is the characteristic geometrical size of the monomer (for a two-level system $\omega_m R_m^3 \equiv |d_{12}|^2$, where d_{12} is the transition matrix element); Ω is the frequency detuning ω from the resonance.

Interaction of the given monomer with its close neighbour leads to the resonance frequency shift (in the optical absorption) by some random amount (due to the random distribution of monomers) $\sim \Omega_f$, where we introduced a characteristic frequency

$$\Omega_f \equiv \omega_m (R_m/R_0)^3 \tag{5}$$

determining the scale of spectral broadening and shift of the fractal compared to the spectra of individual monomers. This estimate follows from (4) with the account of the dipole-dipole interaction of conventional type and the fact that the typical distance between the neighbouring monomers is of order R_0. For many of studied fractals R_0 does not substantially exceed R_m [4], therefore $\Omega_f \lesssim \omega_m$. If a monomer is a good resonator, then its quality is $Q \sim \omega_m/\Gamma \gg 1$, which we adopt for our further consideration.

Probability for the monomers to become resonant to a given pair of monomers is small in Γ/Ω_f parameter. Therefore different parts of the fractal will absorb independently. Thus we come to an idea of strongly inhomogeneously broadened (due to the dispersion of pair interactions) absorption spectrum of the fractal.

If the external radiation frequency lies in the fractal absorption band, then there should exist monomers (more exactly, pairs of monomers) which are resonant to the fractal. Their fraction is, evidently, evaluated to be $\Gamma/\Omega_f \ll 1$. The field E^c_{res} induced by the resonant monomer in its close vicinity, according to (2), (4), is defined as

$$E^c_{\text{res}} \sim \frac{\chi_0(\Omega=0)\,E}{R_m^3} \sim \frac{\omega_m}{\Gamma} E \tag{6}$$

The high local field E^c_{res}, exceeding the mean one E by a factor of $\omega_m/\Gamma \gg 1$, is responsible for the giant enhancement of the nonlinear susceptibilities (cf. (3)).

It would however be impossible to carry out averaging in (3) on the basis of the qualitative suggestions, even at an estimation level. The point is that the quantity under averaging contains an unknown phase, whose fluctuations may, in principle, suppress the enhancement effect (this suggestion is supported by the theory, see below). It is only possible to estimate $G^{(n)}$ from above and below.

The upper estimate could be obtained if one neglects the phase fluctuations in (3), i.e. with the substitution $E^c \to |E^c|$

$$G^{(n)} \lesssim (\langle |E^c|^n \rangle / E^n)^2 \sim \left(\frac{|E^c_{\text{res}}|^n}{E^n} \frac{\Gamma}{\Omega_f}\right)^2 \sim \left(\frac{\Omega_f}{\Gamma}\right)^{2(n-1)} \left(\frac{R_0}{R_m}\right)^{6n}. \tag{7}$$

If the generated frequency is little shifted from the pump frequencies, so that it also appears to be resonant to the fractal monomer, then the effect is additionally enhanced

$$G^{(n)} \lesssim \left\langle \left(\frac{|E^c_{\text{res}}|^n}{E^n} \cdot \frac{E^s_{\text{res}}}{E^s}\right)\right\rangle \sim \left(\frac{|E^c_{\text{res}}|^n}{E^n} \cdot \frac{E^s_{\text{res}}}{E^s} \cdot \frac{\Gamma}{\Omega_f}\right)^2. \tag{8}$$

Taking into account that the exceeding of the local generated field E^s_{res} over the mean one E^s is also given by (6) and making use of (5), the estimate (8) can be written as

$$G^{(n)} \gtrsim \left(\frac{\Omega_f}{\Gamma}\right)^{2n} \left(\frac{R_0}{R_m}\right)^{6(n+1)}. \tag{9}$$

On the contrary, the lower limiting value is obtained from the assumption that the influence of the phase fluctuations in (3) is strongly destructive: the large contribution to E^c proportional to ω_m/Γ, is eliminated and only the mean (nonfluctuating) value is retained. No additional enhancement of the generated field is observed as well. The resultant expression has the form

$$G^{(n)} \gtrsim |\langle E^c \rangle / E|^{2n} \sim \left(\frac{E^c_{\text{res}}}{E} \cdot \frac{\Gamma}{\Omega_f}\right)^{2n} \sim \left(\frac{R_0}{R_m}\right)^{6n}. \tag{10}$$

Thus the enhancement factor, according to (9), (10), varies within the limits

$$\left(\frac{R_0}{R_m}\right)^{6n} \lesssim G^{(n)} \lesssim \left(\frac{\Omega_f}{\Gamma}\right)^{2n} \left(\frac{R_0}{R_m}\right)^{6(n+1)}. \tag{11}$$

The appeareance in (7), (9) of the homogeneous resonance width of an isolated monomer is associated with the spatial-frequency selection characteristic of the nonlinear light interaction.

Since $R_0 \gtrsim R_m$, $\Omega_f \gg \Gamma$, the upper and lower estimates differ very much. To determine which of them approaches the value of $G^{(n)}$ for a particular effect is possible only with a complete theory (see below). Such a theory is also capable of describing the missing in (11) spectral dependence of the factor, which is largely determined by the fractal dimension.

As will be shown below, the higher-order harmonics generation (i.e. generation of a maximum attainable frequency at the given external fields and order of nonlinearity) is always described by the lower limit in (11).

The difference-frequency mixing processes with substraction of even one photon are described by (7) for coinciding exciting fields frequencies (within the limits of Γ width) and by the upper limit in (11) for the generated frequency close to the pump frequency. The same processes at frequency detunings increasing from 0 to Ω_f are characterized by the values of $G^{(n)}$ varying in order of magnitude from the upper to the lower estimate in (11).

To conclude this section, we present the required for further treatment results on linear fractal response, obtained in a binary approximation. The fluctuating field acting on the i-th monomer, is expressed (see below) in terms of the random response matrix M^{-1} as

$$M^{-1}_{\alpha\beta} = A\,\delta_{\alpha\beta} + (C-A)\, n^{ij}_\alpha n^{ij}_\beta,$$
$$A = (\chi_0^{-1} + \varphi)^{-1}, \quad C = (\chi_0^{-1} - 2\varphi)^{-1}, \tag{12}$$

where

$$\mathbf{n}^{ij} \equiv \mathbf{r}^{ij}/r^{ij}, \quad \mathbf{r}^{ij} \equiv \mathbf{r}^i - \mathbf{r}^j \quad \varphi = \sum_k (r^{ij})^{-3}. \tag{13}$$

In (12) the random values are the quantity φ and the orths $\mathbf{n}^{ij}$ dependent on random monomers coordinates $\mathbf{r}^{ij}$.

Averaging of the values involved in M^{-1} (12) over the fractal ensemble (i.e. over the sets $\{\mathbf{r}^i\}$) is performed [5] by proceeding to the Laplas representation with χ_0^{-1} as a variable; averaging over the distance between the monomer and its nearest neighbour is performed by means of the $g(r)$ distribution (1), yielding the result dependent on the fractal dimension D. This dependence is described by a special function $\mathbf{S}_\alpha$ of the complex variable z:

$$\mathbf{S}_\alpha(z) \equiv i \int_0^\infty \mathrm{d}t \exp\{\mathrm{i}zt - (it)^\alpha \Gamma(1-\alpha)\}, \tag{14}$$

where $\alpha \equiv D/3$ (do not confuse with the vector index), $\Gamma(\ldots)$ is the gamma-function. The integral representation in (14) is set by $\mathbf{S}_\alpha$ at $\operatorname{Im} z > 0$; in the lower semiplane the function is determined by means of the analytical expansion $\mathbf{S}_\alpha(z^*) = \mathbf{S}^*_\alpha(z)$.

The linear susceptibility of a monomer in a fractal is defined as the average

$$\chi_1 = \tfrac{1}{3} Sp\langle M^{-1} \rangle = \tfrac{1}{3} R_0^3 \{2\mathbf{S}_\alpha(X) - \tfrac{1}{2}\mathbf{S}_\alpha(-\tfrac{1}{2}X)\};$$
$$X \equiv -R_0^3 \chi_0^{-1}. \tag{15}$$

Finally, the ultimate expression for the total field acting on the i-th monomer has the form:

$$E^i_\alpha = \chi_0^{-1} M^{-1}_{\alpha\beta} k_L E_\beta, \tag{16}$$

where $\mathbf{E}$ is the mean (macroscopic) field in the fractal; $k_L = (1 - \alpha R_0^{-3} \chi_1^{-1})^{-1}$ is the factor originating from the account of the Lorentz field (the latter is not essential in the theory of interest and leads to only small corrections). With the use of (16), formula (2) describes the field on the impurity $\mathbf{E}^c$, which is the starting value for the nonlinear susceptibility calculations.

3. Nonlinear susceptibility of the impurity bound to a fractal. Giant CARS and OPC

Now we formulate a theory of nonlinear susceptibility of impurity centers in a fractal matrix. As an example we'll deal with CARS and OPC. Consider fields varying harmonically in space-time. If the fractal size is smaller than the light wavelength λ, then the waves generated by different fractal particles will always mix coherently. Otherwise (for $R_c \gg \lambda$) the phase-matching

conditions ("synchronism") (see, e.g. [7]) have to be ensured. Naturally, for $R_c > \lambda$ the validity of the theory requires that the typical distance between the nearest monomers be $R_0 \ll \lambda$. In our further consideration we assume these requirements to be satisfied. Then the oscillating components are eliminated; in what follows only their amplitudes will be considered. Because of coherence, the generated amplitude is proportional to the number of impurity molecules, and the radiation power – to the square of this value. Therefore, for short, this factor may be omitted (the amplitude recalculated per impurity center).

CARS and OPC are four-wave parametric processes during which two photons of ω_1 frequency transform into two photons with ω_2 and ω_s frequencies. Such processes are described by a third-order nonlinear susceptibility [8]

$$\chi^{(3)}_{\alpha\beta\gamma\delta}(-\omega_s; \omega_1, \omega_1, -\omega_2), \tag{17}$$

where ω_s is the generated frequency, ω_1 and ω_2 are the frequencies of the interacting waves. For CARS $\omega_s = 2\omega_1 - \omega_2$ OPC corresponds to a completely degenerate process $\omega_s = \omega_1 = \omega_2$.

For coherent effects, including the ones discussed in this paper, quantum-mechanical and statistical averaging (over random factors) is performed over the field amplitude, i.e. nonlinear susceptibility.

For isotropic (after averaging over orientations) fractals, from the familiar symmetry properties [8], it follows that the (impurity) susceptibility of the fractal $\chi^{(3F)}_{\alpha\beta\gamma\delta}$ is expressed through two independent scalar functions F_s and F_a as

$$\begin{aligned}
\langle\chi^{(3F)}_{\alpha\beta\gamma\delta}\rangle &= F_s \Delta^+_{\alpha\beta\gamma\delta} + F_a \Delta^-_{\alpha\beta\gamma\delta},\\
\Delta^+_{\alpha\beta\gamma\delta} &= \tfrac{1}{3}[\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}];\\
\Delta^-_{\alpha\beta\gamma\delta} &= \tfrac{1}{3}[\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} - 2\delta_{\alpha\delta}\delta_{\beta\gamma}].
\end{aligned} \tag{18}$$

Here the terms $F_s \Delta^+$ and $F_a \Delta^-$ are, respectively, totally and partially symmetric (turning to zero when symmetrizing in $\beta \leftrightarrow \delta$ *and* $\gamma \leftrightarrow \delta$) parts of $\chi^{(3)}$. The averaged susceptibility of an isolated impurity molecule is similarly expressed as

$$\langle\chi^{(3C)}_{\alpha\beta\gamma\delta}\rangle = f_s A^+_{\alpha\beta\gamma\delta} + f_a \Delta^-_{\alpha\beta\gamma\delta}. \tag{19}$$

The presented theory aims at describing amplitudes F_s, F_a via f_s, f_a.

Next, we take into account the nonlinear behavior of the impurity susceptibility and describe the fractal in terms of the nonlinear response theory. Then the nonlinear amplitude of the dipole moment of the impurity center (at ω_s frequency) will have the form:

$$d^{NL}_\alpha = \chi^{(3C)}_{\alpha\beta\gamma\delta} E^{(1)C}_\beta E'^{(1)C}_\gamma E^{(2)C*}_\delta, \tag{20}$$

where $\mathbf{E}^{(k)c}$ are the local (2) field amplitudes; the superscript indicates the respective field frequency.

Since in an OPC process the generated frequency coincides with the exciting one, the dipole moment (20) creates a field which self-consistently polarizes the nearest pair of monomers. It is important that the distance between them is shorter than λ, and the generated amplitudes mix coherently. Thus, radiation is actually emitted by the sum (effective) dipole $\mathbf{d}^{\text{eff}}$ which is readily found from

$$\begin{aligned}
d^{\text{eff}}_\alpha &= M^{-1}_{\alpha\beta}(\omega_s)\,\psi_{\beta\beta'}\, d^{NL}_{\beta'} + d^{NL}_\alpha,\\
\psi_{\alpha\beta} &= R^{-3}(\delta_{\alpha\beta} - 3 n^C_\alpha n^C_\beta),
\end{aligned} \tag{21}$$

where the first term in (21) corresponds to the nonlinear-impurity-induced total moment of the pair of monomers, nearest to the impurity. This term, when averaged over the fractal realizations, gives a substantially larger contribution than the second one in (21) (the dipole moment of the impurity itself), and therefore the latter will be neglected in what follows.

In CARS the generated wave frequency differs from the incident ones, though insignificantly, as a rule. That is why the effective nonlinear dipole is also described by (21).

By definition of $\chi^{(3F)}$, the emitting dipole moment is expressed through the mean (macroscopic) wave amplitudes as follows:

$$\langle d^{\text{eff}}_\alpha\rangle = \langle\chi^{(3F)}_{\alpha\beta\gamma\delta}\rangle E^{(1)}_\beta E'^{(1)}_\gamma E^{(2)*}_\delta, \tag{22}$$

where $\mathbf{E}^{(k)}$ are the mean (macroscopic) amplitudes of the exciting waves. With the use of (2), (16), (20) and (21), $\langle d^{\text{eff}}\rangle$ is obtained in form (22) with the nonlinear susceptibility

$$\begin{aligned}
&\langle\chi^{(3F)}_{\alpha\beta\gamma\delta}\rangle =\\
&-\langle M^{-1}_{\alpha\alpha''}(\omega_s)\,\psi_{\alpha''\alpha'}\,\chi^{(3C)}_{\alpha'\beta'\gamma'\delta'}\, T_{\beta'\beta}\, T_{\gamma'\gamma}\, T^*_{\delta'\delta}\rangle\, |K_L|^2 K_L,\\
&T \equiv \Pi M^{-1},
\end{aligned} \tag{23}$$

where only relevant frequency values are indicated (see below).

In (23) averaging (operation $\langle\ldots\rangle$) goes over random factors: impurity orientation (tensor $\chi^{(3C)}$), vector $\mathbf{n}^c$ angles, (materices Π), angles of the mutual orientation vector of the approached monomers $\mathbf{n}^{ij}$, and distances between them (Tmatrices).

Assuming this averaging to be independent, we rewrite (23) in the form:

$$\begin{aligned}
&\langle\chi^{(3F)}_{\alpha\beta\gamma\delta}\rangle = -\langle\chi^{(3C)}_{\alpha'\beta''\gamma''\delta''}\rangle\, |K_L|^2 K_L\\
&\cdot\langle\psi_{\alpha'\alpha''}\,\Pi_{\beta''\beta'}\,\Pi_{\gamma''\gamma'}\,\Pi^*_{\delta''\delta'}\rangle\\
&\cdot\langle M^{-1}_{\alpha\alpha''}(\omega_s)\, M^{-1}_{\beta'\beta}(\omega_1)\, M^{-1}_{\gamma'\gamma}(\omega_1)\, M^{-1*}_{\delta'\delta}(\omega_2)\rangle.
\end{aligned} \tag{24}$$

The matrices Π (2) product, involved in (24), is polynomial in R^{-1}. However the major contribution to

the enhancement of nonlinear processes is given by the highest- (12-th) order term. This term is kept in our further calculations, the terms omitted being small (smallness factor $(R/R_0)^3$).

Using (19) and the angular averaging (see above), we derive the susceptibility $\langle\chi^{(3F)}\rangle$ in the form (18) with the coefficients;

$$F_s=|K_L|^2 K_L R^{-12} f_s[\tfrac{64}{25}\langle A^2(\omega_1) A^*(\omega_2) A(\omega_s)\rangle + \tfrac{24}{25}\langle C^2(\omega_1) C^*(\omega_2) C(\omega_s)\rangle], \quad (25)$$

$$F_a=|K_L|^2 K_L R^{-12} f_a\langle A^2(\omega_1) A^*(\omega_2) A(\omega_s)\rangle. \quad (26)$$

Expressions (25) and (26) have been obtained with neglect of the interference terms, containing the products A and C which having been averaged appear to contribute little to F_s and F_a.

For $\langle\ldots\rangle$ in the main order in Ω_f/Γ, by an analogous transformation and with (12)–(15) one obtains

$$\langle A^2(\omega_1) A^*(\omega_2) A(\omega_s)\rangle = 2iA^2(\Delta\omega) A(2\Delta\omega) R_0^{12} \operatorname{Im} \mathbf{s}_\alpha(x),$$
$$\langle C^2(\omega_1) C^*(\omega_2) C(\omega_s)\rangle = iA^2(\Delta\omega) A(2\Delta\omega) R_0^{12} \operatorname{Im} \mathbf{s}_\alpha\left(-\frac{x}{2}\right), \quad (27)$$

where a resonant factor A (without random quantities) has been introduced (see below)

$$A\equiv(X_1-X_2^*)^{-1}, \qquad X_{1,2}=-R_0^3\chi_0^{-1}(\omega_{1,2}) \quad (28)$$

which at $\Omega_f \gg \Gamma$ by means of (4) is reduced to

$$A(\Delta\omega)=\Omega_f(\Delta\omega+2i\Gamma)^{-1}, \qquad \Delta\omega=\omega_1-\omega_2. \quad (29)$$

The function $\mathbf{s}_\alpha(x)$ in (27) is determined by the relation $\mathbf{s}_a(x)\equiv\mathbf{S}_\alpha(x+i0)$ where $x=-R_0^3\operatorname{Re}\chi_0^{-1}\simeq\Omega/\Omega_f$.

Ultimately, in the main order of magnitude with respect to from (25)–(27) we find

$$F_s=\tfrac{8}{25} i f_s|K_L|^2 K_L\left(\frac{R_0}{R}\right)^{12} A^2(\Delta\omega) A(2\Delta\omega) \cdot\operatorname{Im}\left[16\mathbf{s}_\alpha(x)+3\mathbf{s}_\alpha\left(-\frac{x}{2}\right)\right], \quad (30)$$

$$F_a=2if_a|K_L|^2 K_L\left(\frac{R_0}{R}\right)^{12} A^2(\Delta\omega) A(2\Delta\omega)\operatorname{Im}\mathbf{s}_a(x). \quad (31)$$

Amplitudes of nonlinear susceptibility (30), (31) together with its form (18) are the major results of the theory developed for CARS. They define susceptibility of the impurity intriduced into a fractal matrix in terms of the susceptibility of an isolated molecule. The corresponding expressions for OPC are derived from (30), (31) if $\Delta\omega$ is put equal to zero (the initial single-particle amplitudes f_s and f_a for these two effects may certainly differ).

Now we analyze in short the main expressions (30), (31). Nonlinear response amplitudes bear information on the impurity center (amplitudes f_s and f_a), the fractal absorption (functions $\mathbf{s}_\alpha$), and on the unperturbed spectrum of a particular monomer (factor A). Most exhausted information could obviously be derived from CARS (due to variability of $\Delta\omega$).

The distinctive feature of amplitudes (30), (31) is that they are proportional to the imaginary part of the fractal (cf. (15)) and hence to the fractal absorption (for a given detuning sign, only one of the values, $\operatorname{Im}\mathbf{s}_\alpha(x)$ or $\operatorname{Im}\mathbf{s}_\alpha\left(\frac{-x}{2}\right)$, is non-zero; see the properties of $\mathbf{s}_\alpha$-function [5]). Thus, the predicted giant enhancement (see below) of CARS and OPC effects on impurities is to be expected only when the frequency of exciting radiation lies within the absorption band of the fractal.

The symmetry, typical of the susceptibility of an isolated impurity (see 19) and the discussion thereafter), is reproduced, just as was expected, by the impurity susceptibility of the fractal (18). The totally symmetric part of the impurity susceptibility "generates" a totally symmetric part of the fractal susceptibility ($F_s\infty f_s$), the same goes for partially symmetric parts. It is interesting that in the longwave absorption band of the fractal (at $\Omega<0$), amplitude F_a is zero, i.e. the nonlinear response becomes totally symmetric. Note that both amplitudes F_s and F_a and hence the response symmetry can directly be measured by polarization techniques.

The enhancement coefficient $G^{(3)}$ has the form:

$$G^{(3)}=|\langle\chi^{(3F)}_{\alpha\beta\gamma\delta}\rangle e^{(1)}_\beta e'^{(1)}_\gamma e^{(2)*}_\delta/\langle X^{(3C)}_{\alpha\beta\gamma\delta}\rangle e^{(1)}_\beta e'^{(1)}_\gamma e^{(2)*}_\delta|^2, \quad (32)$$

where $e^{(1)}$, $e'^{(1)}$, $e^{(2)}$ are the polarization vectors of the incident waves. Amplitudes (30), (31) grow rapidly with the decrease of R and are maximum at an extremely small (permissible within the framework of dipole interaction model) value $R\sim R_m$. For a monomer in the form of a macroscopic sphere one may put $R=R_m$ (R_m is the sphere radius).

Assuming for definiteness identical linear wave polarizations, from (19), (30), (31) one calculates the maximum enhancement for CARS

$$G^{\mathrm{CARS}}_{\max}=G_0 L^{\mathrm{CARS}}(\Omega);$$
$$G_0=\left(\frac{R_0}{R_m}\right)^{24}|K_L|^6\left(\frac{\Omega_f}{\Gamma}\right)^6 g^2(\Delta\omega) g(2\Delta\omega);$$
$$g(\Delta\omega)=[1+(\Delta\omega/2\Gamma)^2]^{-1};$$
$$L^{\mathrm{CARS}}=(\tfrac{1}{25})^2\left\{[16\operatorname{Im}\mathbf{s}_\alpha(x)]^2+\left[3\operatorname{Im}\mathbf{s}_\alpha\left(\frac{-x}{2}\right)\right]^2\right\}. \quad (33)$$

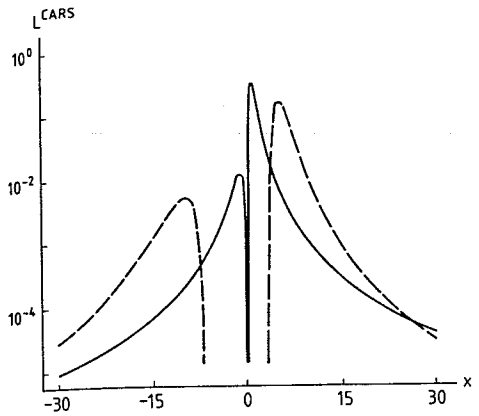

Fig. 1. The enhancement factor L^{CARS} versus the parameter $x \simeq \Omega/\Omega_f$ (Ω is the frequency detuning of the exciting radiation) for CARS and OPC

Expression for OPC is derived from (33) by putting $\Delta\omega = 0$.

The value of G_{max}^{CARS} is determined by the constant $(R_0^4\,\Omega_f/R_m^4\,\Gamma)^6 = \left(\frac{R_0}{R_m}\frac{\omega_m}{\Gamma}\right)^6 \gg 1$, and the spectral behavior of this factor depends on the smoothly varying function L^{CARS} and the resonance profile $g(\Delta\omega)$. The latter is characterized by a small spectral value, equal to 2Γ. The width Γ is typical of an isolated monomer, while the spectral width of a fractal is normally $\Omega_f \gg \Gamma$.

The factor G_0 (33), to an accuracy of the inessential factor $|K_L|^6$ (the effect of the Lorentz field) agrees with the upper estimate in (11) at $n=3$ (cf. discussion after (11)). The variable x, relating the enhancement factor G_{max}^{CARS} (33) to the frequency of the exciting radiation, with the use of (4) is equal to the relativeresonance detuning Ω/Ω_f. Figure 1 illustrates the described smooth dependence of $L^{CARS}(\Omega)$ (33). It has the form of a doublet with shortwave and longwave peaks. In the fractal absorption band, shown in Fig. 1, the enhancement factor changes by five orders of magnitude. A strong dependence on the fractal dimension is observed, e.g. for D ranging from 1.5 to 2.5 the longwave maximum is frequency-shifted by an order of magnitude.

It is worthwhile comparing (33) with the maximum enhancement attained for Raman scattering G_{max}^{RS}:

$$G_{max}^{CARS} \sim (G_{max}^{RS})^2\, g^2(\Delta\omega)\, g(2\Delta\omega). \tag{34}$$

The typical value is [9]

$$G^{RS} \sim 10^6 \tag{35}$$

which yields for CARS

$$G^{CAES} \sim 10^{12}. \tag{36}$$

Of course, these values are attainable only provided the local fields (which may be several orders of magnitude higher than the external ones) saturate neither the impurity nor the monomer susceptibilities in the fractal.

4. Enhanced harmonic generation

Let us first consider third-harmonic generation. This effect is also determined by a third-order nonlinearity. The nonlinear dipole moment of the impurity is

$$d_\alpha^{NL} = \chi_{\alpha\beta\gamma\delta}^{(3C)}(-\omega_s;\omega,\omega,\omega)\, E_\beta^{(C)}\, E_\gamma^{(C)}\, E_\delta^{(C)}; \qquad \omega_s = 3\omega, \tag{37}$$

where $\mathbf{E}^{(c)}$ is the local amplitude of the exciting field at ω frequency in the impurity location site. Nonlinear susceptibilities of the fractal-bound and isolated impurities are described, respectively, by

$$\langle\chi_{\alpha\beta\gamma\delta}^{3F)}\rangle = F\Delta_{\alpha\beta\gamma\delta}^{+}; \qquad \langle\chi_{\alpha\beta\gamma\delta}^{(3C)}\rangle = f\,\Delta_{\alpha\beta\gamma\delta}^{+}. \tag{38}$$

Note that susceptibilities (38) are totally symmetric, either of them is characterized by one amplitude $F(f)$. In the case under discussion, unlike CARS and OPC, interaction between the generated radiation (with ω_s frequency) and the fractal may be ignored, i.e. one may put $\mathbf{d}^{eff} = \mathbf{d}^{NL}$.

The expression for $\chi^{(3F)}$ is derived quite similarly to (23):

$$\langle\chi_{\alpha\beta\gamma\delta}^{(3F)}\rangle = K_L^3\langle\chi_{\alpha\beta'\gamma'\delta'}^{(3C)}\, T_{\beta'\beta}\, T_{\gamma'\gamma}\, T_{\delta'\delta}\rangle. \tag{39}$$

Then, as it has been done when proceeding from (23) to (24), we "break" the chain of averaging and write down (39) in the form:

$$\langle\chi_{\alpha\beta\gamma\delta}^{(3F)}\rangle = K_L^3\langle\chi_{\alpha\beta'\gamma'\delta'}^{(3C)}\rangle\langle\Pi_{\beta'\beta''}\,\Pi_{\gamma'\gamma''}\,\Pi_{\delta'\delta''}\rangle \cdot\langle M_{\beta''\beta}^{-1}\, M_{\gamma''\gamma}^{-1}\, M_{\delta''\delta}^{-1}\rangle. \tag{40}$$

By angular averaging of vectors $\mathbf{n}^c$ and $\mathbf{n}^{ij}$ we make sure that the structure (38) is reproduced; the response amplitude is defined as

$$F = \tfrac{4}{75}\, f R^{-9} K_L^3 \langle 8A^3 + 3C^3 + 2AC(A+C)\rangle. \tag{41}$$

Averaging over the distance between monomers in (41) is carried out with the help of (14) similarly to the calculation of amplitudes (25), (26). One eventually obtains:

$$F=\frac{4}{75}f\left(\frac{R_0}{R}\right)^9 K_L^3\left\{\frac{d^2}{dx^2}\left[4s_\alpha(x)-\frac{3}{4}s_\alpha^*\left(-\frac{1}{2}x\right)\right]\right.$$
$$\left.-\frac{2}{3}\frac{1}{x}\left(\frac{d}{dx}-\frac{1}{x}\right)\left[s_\alpha(x)-s_\alpha^*\left(-\frac{1}{2}x\right)\right]\right\}. \quad (42)$$

Note that the singularity at $x=0$ is absent.

Maximum enhancement factor $G_{\max}^{TH}$ is found just as (33)

$$G_{\max}^{TH}=\left(\frac{R_0}{R_m}\right)^{18}|K_L|^6 L^{TH}(\Omega);$$
$$L^{TH}(\Omega)=\left(\frac{4}{75}\right)^2\left|\frac{d^2}{dx^2}\left[4s_\alpha(x)-\frac{3}{4}s_\alpha^*\left(-\frac{x}{2}\right)\right]\right.$$
$$\left.-\frac{2}{3}\frac{1}{x}\left(\frac{d}{dx}-\frac{1}{x}\right)\left[s_\alpha(x)-s_\alpha^*\left(-\frac{1}{2}x\right)\right]\right|^2. \quad (43)$$

Expression (43) differs from the analogous result (33) for CARS and OPC in mainly the following. In (43) there are no large factors (powers of the Ω_f/Γ ratio) as well as no narrow-band spectral structures. Besides, $G_{\max}^{TH}$ is determined by both the imaginary and the real parts of s_α function, which results in a slower frequency drop in the far wings of the absorption band.

Quantity $G_{\max}^{TH}$ (43) is determined by the high power of the ratio R_0/R_m, which may exceed unity. However, in a general case this is not too high (cf. [4]). For example, for a dense fractal formed, in particular, by diffusion-controlled aggregation of spherical particles, $R_0/R_m=1.11$. Ratio R_0/R_m attains large values only for the fractal in which polarized monomers are coupled by long "neutral" bonds. In any case, from comparison of (43) with (33), one may conclude that the third-harmonic generation is far less enhance than CARS and OPC effects.

In Fig. 2 the spectral behavior of the enhancement factor is shown for the third-harmonic generation. Note that the dependence on the fractal dimension is as strong as it is for CARS and OPC (cf. Fig. 1).

Second-harmonic generation is described by the second-order susceptibility of the impurity. For this process the amplitude of the nonlinear dipole moment of the impurity has the form (cf. (37)):

$$d_\alpha^{N4}=\chi_{\alpha\beta\gamma}^{(2F)}(-\omega_s;\omega,\omega)E_\beta^{(C)}E_\gamma^{(C)}, \quad \omega_s=2\omega. \quad (44)$$

The symmetry properties of susceptibilities of an isolated impurity $\chi^{(2C)}$ and a fractal $\chi^{(2F)}$ are due to noncentral symmetry of the system, and exactly due to the presence of the polar orth **m**. In virtue of these properties either of the amplitudes is expressed in terms of three independent amplitudes F_1, F_2, F_3 (f_1, f_2, f_3). Tensor structure of the susceptibility is conveniently written as

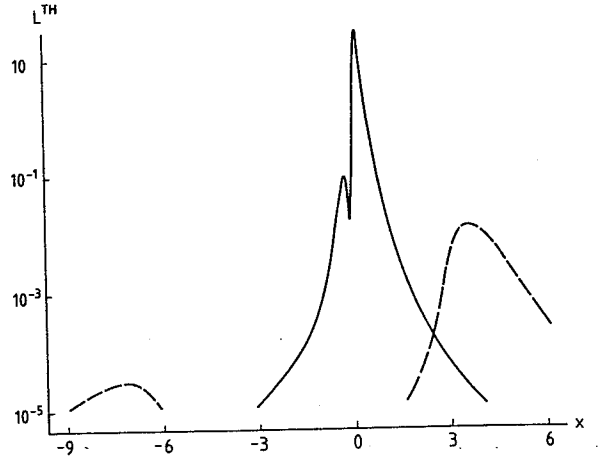

Fig. 2. x-dependence of the enhancement factor L^{TH} for third-harmonic generation

$$\langle\chi_{\alpha\beta\gamma}^{(2F)}\rangle=m_\alpha[F_1\delta_{\beta\gamma}+F_2(\delta_{\beta\gamma}-3m_\beta m_\gamma)]$$
$$+F_3(\tfrac{2}{3}m_\alpha\delta_{\beta\gamma}-m_\gamma\delta_{\alpha\beta}-m_\beta\delta_{\alpha\gamma}),$$
$$\langle\chi_{\alpha\beta\gamma}^{(2C)}\rangle=m_\alpha[f_1\delta_{\beta\gamma}+f_2(\delta_{\beta\gamma}-3m_\beta m_\gamma)]$$
$$+f_3(\tfrac{2}{3}m_\alpha\delta_{\beta\gamma}-m_\gamma\delta_{\alpha\beta}-m_\beta\delta_{\alpha\gamma}). \quad (46)$$

The direction of **m** depends, in particular, on anisotropy of the matrix (crystal) into which the fractal is inserted, or on the normal to the surface on which the fractal is located, or else on the external electric field.

Expression for $\langle\chi^{(2F)}\rangle$ is obtained by the same procedure as (40):

$$\langle\chi^{(2F)}\rangle=K_L^2\langle\chi_{\alpha\beta'\gamma'}^{(2C)}\rangle\langle\Pi_{\beta'\beta''}\Pi_{\gamma'\gamma''}\rangle\langle M_{\beta'\beta}^{-1}M_{\gamma'\gamma}^{-1}\rangle. \quad (47)$$

Keeping the terms with the maximum $(R_0/R_m)^3$ parameter and averaging over the vectors $\mathbf{n}^c$ and $\mathbf{n}^{ij}$, one can express the amplitudes F_i through $f_i(i=1\div3)$:

$$F_1=\tfrac{2}{3}R^{-6}f_1K_L^2\langle2A^2+C^2\rangle,$$
$$F_{2,3}=\tfrac{1}{75}R^{-6}f_{2,3}K_L^2\langle7A^2+2C^2+6AC\rangle. \quad (48)$$

As in the above, the fractal susceptibility reproduces the symmetry of an isolated impurity, and the tensor structures in (45), (46) appear to be the eigenfunctions of the transformation from an isolated impurity to a fractal (each of the amplitudes f_i is expressed only through the respective quantity f_i).

Averaging over $\{\mathbf{r}^i\}$ allows one to obtain the ultimate ratios for the susceptibility amplitudes (45)

$$F_1=\frac{2}{3}f_1\left(\frac{R_0}{R}\right)^6 K_L^2\frac{d}{dx}\left[2s_\alpha(x)-\frac{1}{2}s_\alpha^*\left(-\frac{1}{2}x\right)\right], \quad (49)$$

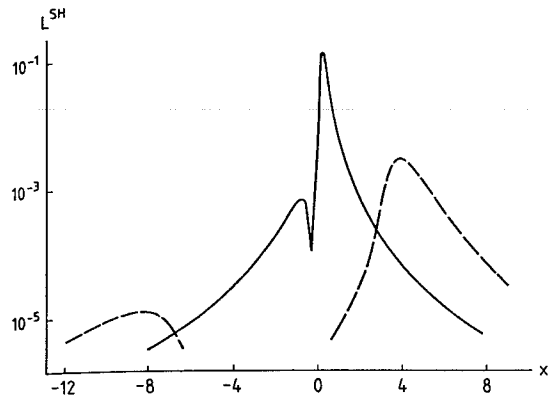

Fig. 3. x-dependence of the enhancement factor L^{SH} for second-harmonic generation

$$F_{2,3}=\frac{1}{75}f_{2,3}\left(\frac{R_0}{R}\right)^6 K_L^2\left\{\frac{\mathrm{d}}{\mathrm{d}x}\left[7\mathbf{s}_\alpha(x)-\mathbf{s}_\alpha^*\left(-\frac{x}{2}\right)\right]\right.$$
$$\left.-\frac{2}{x}\left[\mathbf{s}_\alpha(x)-\mathbf{s}_\alpha^*\left(-\frac{x}{2}\right)\right]\right\}. \tag{50}$$

For definiteness, the enhancement factor of second-harmonic generation is calculated for circular polarization. From (45), with the account of (50), we have

$$G_{\max}^{SH}=|K_L|^4\left(\frac{R_0}{R_m}\right)^{12}L^{SH}(\Omega);$$

$$L^{SH}(\Omega)=\frac{1}{75}\left|\frac{\mathrm{d}}{\mathrm{d}x}\left[7\mathbf{s}_\alpha(x)-\mathbf{s}_\alpha^*\left(-\frac{x}{2}\right)\right]\right.$$
$$\left.-\frac{2}{x}\left[\mathbf{s}_\alpha(x)-\mathbf{s}_\alpha^*\left(-\frac{x}{2}\right)\right]\right|^2. \tag{51}$$

In Fig. 3 the factor L^{SH} is plotted versus the detuning function Ω/Ω_f (parameter x). Note that the dependence on the fractal dimension is also strong, though not so strong as for the third-harmonic generation (Fig. 2). This fact is quite understandible: the higher the order of nonlinearity, the stronger the properties of the system.

As seen from (51), unlike CARS and OPC, the enhancement coefficient as well as for the third-harmonic generation bears no information on the initially narrow spectral width of the monomer; it does not involves the large coefficient (power of the Ω_f/Γ parameter). Thus one should expect a substantially smaller enhancement for harmonics generation compared with CARS and OPC effects.

5. Evaluation of the enhancement factor for arbitrary-order processes

Let us estimate the enhancement coefficient G for coherent higher-order processes. In particular, we seek to find out when G is proportional to the large factor – power of Ω_f/Γ (as is the case with CARS and OPC, and not with harmonics generation, see above).

The n-th-order susceptibility has the form:

$$\chi^{(n)}(-\omega_s;\omega_{11},\omega_{12},\dots\omega_{1p},-\omega_{21},-\omega_{22},\dots-\omega_{2m}), \tag{52}$$

where p, m are the number of absorbed and emitted (in external fields) photons; $n=p+m$; ω_s is the generated radiation frequency.

Consider first the case $m>0$, i.e. the processes with photons emission into the external fields (such as CARS and OPC). For the sake of simplicity, all absorbed photons in (52) are assumed to have equal frequencies $\omega_1=\omega_{1K}$. Then, following the result (24) and with neglect of the interference terms containing products A and C, the impurity susceptibility of the fractal is estimated as

$$\frac{\langle\chi^{(nF)}\rangle}{\langle\chi^{(nC)}\rangle}\sim K_L^p K_L^{*m} R_m^{-3(n+\delta_{p-m,1})}$$
$$\cdot\left[a_1\langle A^{\delta_{p-m,1}}(\omega_s)A^p(\omega_1)A^{*m}(\omega_2)\rangle\right.$$
$$\left.+a_2\langle C^{\delta_{p-m,1}}(\omega_s)C^p(\omega_1)C^{*m}(\omega_2)\rangle\right], \tag{53}$$

where a_1, a_2 are the numerical coefficients dependent only on m, p and the type of symmetry in the part of the susceptibility under consideration (cf., e.g. (25), (26)); $\chi^{(nC)}$ is the corresponding to $\chi^{(nF)}$ part of the susceptibility of the impurity center. Formula (53) at $p-m=1$ takes into account the additional enhancement due to the impurity-fractal interaction at the generated radiation frequency ω_s (cf. discussion of (21)). This enhancement is observed when ω_s lies within the absorption band of the cluster.

Employing A and C in the form (12), (14) for the averages and the definition of $X_{1,2}$ (28), we rewrite (53) as

$$\frac{\langle\chi^{(nF)}\rangle}{\langle\chi^{(nC)}\rangle}\sim K_L^p K_L^{*m}\left(\frac{R_0}{R_m}\right)^{3(n+\delta_{p-m,1})}$$
$$\cdot\frac{1}{(p-1)!(m-1)!}A^{\delta_{p-m,1}}(X_s,X_2)\frac{\partial^{p-1}}{\partial X_1^{p-1}}\frac{\partial^{m-1}}{\partial X_2^{*m-1}}$$
$$\cdot\Lambda(X_1,X_2)\,\mathrm{Im}\left[2a_1\,\mathbf{s}_\alpha(x)+a_2\,\mathbf{s}_\alpha\left(-\frac{x}{2}\right)\right]. \tag{54}$$

Functions $\mathbf{s}_\alpha$ in (54) vary versus $\omega_{1,2}$ frequencies typically over an interval of $\sim\Omega_f$. The strongest spectral dependence in (54) is contained in Λ factor.

Differentiating Λ in (54) gives rise to maximum powers of the large parameter Ω_f/Γ. From (54) one estimates:

$$\frac{\langle\chi^{nF)}\rangle}{\langle\chi^{nC)}\rangle}\sim K_L^p K_2^{*m}\left(\frac{R_0}{R_m}\right)^{3(n+\delta_{p-m,1})} \cdot C_{n-2}^{m-1}\Lambda^{\delta_{p-m,1}}(p\Delta\omega)\Lambda^{n-1}(\Delta\omega) \cdot \mathrm{Im}\left[2a_1 \mathbf{s}_\alpha(x)+a_2 \mathbf{s}_\alpha\left(-\frac{x}{2}\right)\right], \quad (55)$$

where C_K^e is the binomial coefficient.

As seen from the comparison with (15), the spectral dependence of the enhancement factor of the amplitude $\langle\chi^{(nF)}\rangle/\langle\chi^{(nC)}\rangle$ for the given amplitude sign reproduces the form IM χ_1, i.e. the form of the absorption index. Thus, giant impurity nonlinearities should be observed only in the absorption band of the fractal.

From (55) the order magnitude of the enhancement of the effect (i.e. the output radiation intensity) is calculated for the case under discussion $m>0$:

$$G_{\max}^{(n)}\sim(C_{n-2}^{m-1})^2|K_L|^{2n}\left(\frac{R_0}{R_m}\right)^6\left(\frac{\omega_m}{2\Gamma}\right)^{2(n-1+\delta_{p-m,1})} \cdot g^{n-1}(\Delta\omega)\, g^{\delta_{p-m,1}}(p\Delta\omega)|J_\alpha(\Omega)|^2, \quad (56)$$

where $J_\alpha(\Omega)$ denotes a smooth (in the limit of the fractal absorption band) frequency dependence, described in (55) by $\mathbf{s}_\alpha$ functions.

For $m=0$, i.e. for generation at a maximum frequency (the highest-order harmonic) by means of a familiar procedure used above, one may see that the amplitude of the effect is a ploynomial in A and C to the n-th power:

$$\langle\chi^{(nF)}\rangle\sim\langle\chi^{(nC)}\rangle R_m^{-3n}K_l^n\sum_{K=0}^{n}a_K\langle A^K C^{n-K}\rangle, \quad (57)$$

where a_K are the numerical coefficients, dependent on n (cf. (41) and (48)).

Averaging in (57) is performed as described above. However, since the complex-conjugate amplitudes A^* and C^* are not involved in (57), there are no large terms $\infty\Lambda^{n-1}$ in the susceptibility. Spectral dependence of the amplitude gain $\langle\chi^{(nF)}\rangle/\langle\chi^{(nC)}\rangle$ is given by the functions $\mathbf{s}_\alpha(x)$, $\mathbf{s}_\alpha\left(-\frac{x}{2}\right)$ and their derivatives up to the n-1-th (cf. (42) and (49)); let us denote it by $J'_\alpha(\Omega)$. Function $J'_\alpha(\Omega)$ varies within a typical frequency range Ω_f; in the absorption band of the cluster this is of order unity. For the enhancement of the n-th-harmonic generation one eventually obtains a simple expression

$$G_{\max}^{(n)}\sim|\langle\chi^{(nF)}\rangle/\langle\chi^{(nC)}\rangle|^2\sim|K_L|^{2n}\left(\frac{R_0}{R_m}\right)^{6n}|J'_\alpha(\Omega)|^2. \quad (58)$$

Thus, the n-th-order nonlinear sysceptibility of the impurity in a fractal, compared to that of free impurity molecules, is enhanced by a factor of (56), proportional to the $2(n-1+\delta_{p-m,1})$-th power of the large parameter ω_m/Γ. This is always the case, except when a higher-order harmonic is generated (58), without the indicated parameter being involved.

6. Final discussion

Now we briefly summarize and discuss the main results and main principles of this work. A theory has been developed for nonlinear susceptibilities of impurity molecules bound to a fractal. To describe CARS (OPC) the respective formulas (18), (30)–(33); (38), (42), 43); (45), (49)–(51) have been derived.

The nonlinear effects are believed to be enhanced due to the existence of high local fields generated in the vicinity of the fractal monomers which appear to be essentially stronger (up to several orders of magnitude) than the mean (macroscopic) field. Large values of the local fields are, in their turn, due to the interrelated properties inherent in a nontrivial fractal: quasiresonant spectral behavior (partially concerved monomer's individuality and (mainly) inhomogeneous spectral broadening; disordered structure, strong fluctuations.).

Proceeding from the above obtained qualitative pattern, simple upper and lower estimates for the effect (11) have been calculated. These two values differ substantially: the former contains a large factor $(\Omega_f/\Gamma)^{2n}$, while in the latter it is absent. The estimates obtained are valid to an accuracy of the inessential factor, responsible for the Lorentz field effect.

Results of the complete theory (56), (58), obtained for an arbitrary-order nonlinearity, allowed us to correlate the different parametric effects with the limiting estimates (11) derived (cf. discussion after (58)). The enhancement factor $G_{\max}^{(n)}$ (58) for the higher-order harmonics generation (when the frequencies of all photons add) is always estimated by the lower limit in (11). This formally follows from the fact that all poles of the averaged susceptibility, as a complex frequency function, lie in the same (lower) semiplane (cf., e.g. analytical properties (47), (48)). Physically this implies the destructive effect of the fluctuating phase when averaged over the ensemble of fractals.

A different result (56) has been obtained for the processes with photons substraction (when susceptibility (52) contains at least one negative frequency). When excitation is nearly degenerate (the exciting

field frequencies are identical to an accuracy of Γ), $G^{(n)}_{max}$ (56) is estimated by the upper limit in (11), i.e. the susceptibility $\chi^{(nF)}$ phase fluctuations are inessential. The described nonlinear phenomena involve third-order nonlinear effects: OPC and CARS at small frequency detunings of the two exciting fields. With the detuning increasing up to the spectral width of the fractal Ω_f, the value $G^{(n)}$ decreases down to the lower limit in (11), which is described by the factor $g(\Delta\omega)$ in (33), (56). Thus at finite detunings the destructive effect of the phase fluctuations becomes important for the processes with photons substraction as well.

The described dependence of the enhancement coefficient on the nature of the process (photons substraction, frequency degeneracy) is not apparent, because in all the cases the local fields are equally enhanced (by a factor of ω_m/Γ) compared to the mean field.

Actually, for coherent effects, the field amplitude is averaged and the relative phases of the waves, generated by different impurity centers, become significant. (The earlier estimates for coherent effects have been obtained in [10] with the only account of the enhancement of the absolute local field, neglecting its phase; spectral broadening due to the disordered structure of the system was out of consideration as well).

In the processes involving photons substraction the frequency-difference dependence $\Delta\omega$ (see (33), (56)) of the enhancement coefficient is contained in factor $g(\Delta\omega)$. This dependence $g(\Delta\omega)$ has a two-photon resonance profile: it is determined by $\Delta\omega$ as compared to 2Γ (we emphasize that Γ is the natural resonance width of an isolated monomer) and is independent of the position of the system levels. The latter accounts for the fact that this resonance is not subject to inhomogeneous broadening, and hence for the resonance natural width and the resonance contribution to the enhancement. The appearance of such nonlinear resonance, in spite of the assumed linear behavior of the monomer susceptibility, is associated with the interaction of the monomer with the nonlinear impurity.

The value of the enhancement factor $G^{(n)}$ and its smooth dependence on the exciting radiation frequency depend largely on the fractal dimension. Figures 1–3 illustrate the indicated dependences for the second- and third-order effects. The value of reduces with growing fractal dimension, and its spectral profile becomes broadened. When $D=3$, the nonlinear susceptibilities are no longer enhanced (the developed theory is not adequate for this case).

All the above arguments lead us to conclude that the effects with photons substraction are enhanced to a much greater extent than higher-order harmonics generation. It is important that the value of the enhancement (56) is independent of the number of photons substracted.

In the spectral dependence of such monomers both the impurity center resonances and the nonlinear monomer resonance are observed. As far as we know, these nonlinear resonances haven't yet been considered elsewhere. Their peculiarities are due to the interaction of strong fields with a complex, consisting of the nonlinear impurity and the linear element (a monomer in a disordered fractal medium). The enhancement of the nonlinear susceptibilities strongly depends on the Hausdorff fractal dimension.

Experimental observation of the predicted effects could provide information on the properties of the monomers, forming a fractal (the question as to what is a monomer is, generally speaking, not trivial, cf. [5]) and, in particular would allow to find the spectral width from the $g(\Delta\omega)$ profile. Inserting Γ into the expression for G one can evaluate G and compare it with the independently measured value.

The most promising candidates for fractal experiments are, evidently, clusters of noble metals, e.g. particles in colloids.

Spectral properties of the impurity particles, which can be studied by CARS on fractal-bound molecules, are similar to those of free molecules. However, the large enhancement predicted for CARS intensity (see discussion of (36)) would certainly extend the capability of the method to reduce the radiation intensities and molecular concentrations and, hence, would improve its analytical application potential.

Since, being enhanced, the four-wave parametric processes can be observed at a substantially lower molecular concentrations, the impurity-containing fractals seem to be promising nonlinear media, especially to meet the requirements of miniaturization of the sample.

Besides the parametric processes, the theory is capable of describing nonlinear absorption determined by the imaginary part of the nonlinear susceptibility. The latter refers to the processes with photons substraction and hence is maximally enhanced, according to (55). In particular, the two-photon absorption index is proportional to $\mathrm{Im}\,\chi^{(3)}(-\omega_1, \omega_1, \omega_2-\omega_2)$ (see (30), (31)). According to the theory presented, the effects determined by the nonlinear absorption are enhanced as well: these are nonlinear impurity photochemistry, ionization, dissociation, photoeffect, etc.

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