Giant impurity nonlinearities in optics of fractal clusters

A. V. Butenko

Institute of Automation and Electrometry, Siberian Division, USSR Academy of Sciences

V. M. Shalaev

Physics Institute, Siberian Division, USSR Academy of Sciences

M. I. Shtokman

Krasnoyarsk State University

(Submitted 16 March 1987)
Zh. Eksp. Teor. Fiz. **94**, 107–124 (January 1988)

A theory of the nonlinear optical properties of fractals (fractal clusters) is developed. Giant enhancement of the nonlinear susceptibilities are predicted for impurities bound to fractals. This enhancement is implemented by excitation with radiation in the intrinsic-absorption band of the fractal. The giant optical nonlinearities are due to the existence of strong local fields at the impurity centers. The enhancement of the local fields is due to the inhomogeneously broadened character of the fractal spectrum (partial preservation of the individuality of the monomers), and is proportional to the Q factor of the monomer treated as a resonator. The effects of coherent anti-Stokes Raman scattering (CARS) and of the phase conjugation are much more enhanced than generation of higher harmonics. In the general case, the nonlinear susceptibility of higher order will be enhanced to the utmost if the frequency of at least one strong field enters in the susceptibility with a minus sign. On the contrary, higher-harmonic generation is minimally enhanced. The dependence of the susceptibility on the type of effect is due to the influence of the fluctuations of its phase when averaged over an ensemble of fractals. The gain depends substantially on the fractal (Hausdorff) dimensionality and decreases when the latter tends to become trivial. The observed phenomena yield information on the spectra of the impurity particles as well as of the fractal. It is predicted that the CARS spectra of impurity centers will exhibit a system of narrow lines typical of a fractal isolated monomer.

1. INTRODUCTION

Fractals are defined as constructs having non-integer dimensionality and imbedded in three-dimensional space.[1,2] Nature abounds in fractal clusters,[3] which are physical realizations of fractals. These clusters have unique geometric, statistical and kinetic properties. Light scattering from fractals was considered by Berry and Percival[4] in the framework of the mean-field approximation. In contrast to them, two of us proposed in an earlier paper[5] a description of linear optics of fractals, with account taken of the dominant property of fractals—their fluctuating character; a theory was developed for the linear response of the fractal, and surface enhanced Raman scattering by impurities was predicted.

The method of Ref. 5 is used in the present paper to develop, for the first time, a theory of nonlinear optical properties of impurity centers connected with a fractal. We obtain the susceptibilities that account for the coherent (parametric) phenomena: coherent anti-Stokes Raman scattering (CARS) of light, phase conjugation (PC) of optical radiation in degenerate four-wave interaction, and second- and third-harmonic generation. It is shown the CARS and PC undergo giant enhancement. Higher-harmonic generation can also be enhanced, albeit considerably less.

Fractals have unusual optical properties[5] different from those of both gases and condensed media. The reason is that the integrated density of a fractal tends asymptotically to zero, but pair interaction between its constituent monomers is nonetheless not weak. These properties, mutually exclusive for a nonfractal medium, are the consequence of a power-law decrease of the pair (density-density) correlation function $g(r)$ with increase of distance between the monomers, and the scaling form of the dependence of the number N of monomers in the fractal on its radius F_c:

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

where R_0 is a constant with dimension of length and has the meaning of the characteristic distance between the nearest monomers. The exponent D is called the fractal (external Hausdorff) dimensionality. Both relations in (1) follow uniquely from each other. The $g(r)$ dependence should be understood as an intermediate asymptotic at $R_0 \lesssim r \lesssim R_c$. A fractal is called nontrivial when $D<3$. In this case, as follows from the second relation of (1), its integrated density $\bar{\rho} \propto R_c^{d-3}$ does indeed tend asympotically to zero as $R_c \to \infty$.

The Raman-scattering enhancement considered earlier,[5] and the giant nonlinearity enhancement predicted in the present paper, are the consequence of the strong local fields which are produced near the monomers of the fractal and are at resonance with the exciting radiation. The enhancement of the local field is proportional to the large Q of the monomer as a resonator. The spectrum of a fractal is inhomogeneously broadened owing to the variance of the interaction between the monomers, so that its broad absorption band contains monomers for which the resonance conditions are met. The increase of the nonlinear susceptibilities is very large, since it is determined by the value of the local field raised to high power (e.g., the sixth) for CARS and PC. As $D \to 3$, i.e., as the fractal comes close to being trivial, the

 0038-5646/88/010060-10$04.00

spectra of the fractal broaden and enhancement of the susceptibilities ceases.

We show also that the nonlinear spectra of impurities in a fractal matrix carry information on the properties of the impurity centers of the fractal as a whole, as well as of the individual monomers that make up the fractal.

2. FORMULATION OF PROBLEM AND QUALITATIVE ESTIMATES. FUNDAMENTAL FRACTAL PROPERTIES NEEDED FOR A QUANTITATIVE THEORY

Consider a fractal consisting of N particles (monomers) located at points $\{\mathbf{r}^i\}$, where the superscript indicates the number of the monomer. The coordinates $\{\mathbf{r}^i\}$ are random; the probability of finding another monomer at a distance r from a given one is determined by the pair correlation function $g(r)$ [Eq. (1)].

Monomers are dipole-polarizable (at optical frequencies) particles with linear susceptibility $\chi_0(\omega)$, where ω is the frequency of the external optical field. The induced dipoles of different monomers interact with one another via dipole-dipole forces. Bound to some monomers are impurity centers, whose number is assumed to be small and the interaction between which can be neglected. The impurities are assumed to be linearly polarizable and are characterized by a susceptibility $\chi^{(n)}$ of order n.

The reason for the giant enhancement of the nonlinear susceptibilities of impurities formed into a fractal is that the local field $\mathbf{E}^c$ acting on the impurity center bound to the monomer at resonance with the exciting radiation is much stronger that the mean field $\mathbf{E}$. Let us find the corresponding estimates. We present *in passim* the needed theoretical results of Ref. 5.

Consider one impurity bound, say, to the ith monomer of a fractal. We denote the monomer-impurity radius vector by $\mathbf{R}$ and assume it to be shorter than the characteristic distance R_0 between the nearest monomers. The local electric field $\mathbf{E}^c$ at a given impurity consists then of the field $\mathbf{E}^i$ acting on the given monomer and the field of its induced dipole[5]:

$$E_\alpha{}^c=\chi_0\Pi_{\alpha\beta}E_\beta{}^i, \quad \Pi_{\alpha\beta}=(\chi_0{}^{-1}-R^{-3})\delta_{\alpha\beta}+3R^{-5}n_\alpha{}^c n_\beta{}^c; \quad \mathbf{n}^c\equiv\mathbf{R}/R, \tag{2}$$

where the subscripts label the tensor components, and summation over repeated indices is implied.

The principal quantity that we shall estimate below and calculate later on is the gain $G^{(n)}$ for a nonlinear effect of nth order. We mean by it the ratio of the intensity of the radiation generated on the impurities bound to the fractals and the analogous intensity but for the free impurity particles. Since the amplitude of the field generated on a nonlinearity of order n is proportional to the nth power of the exciting field, the following estimate is obvious:

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

Averaging designated by angle brackets includes here and elsewhere averaging over an ensemble of fractals.

Let us emphasize a circumstance of importance in what follows. Since we are considering coherent phenomena (whose elementary act leaves the material subsystem in the initial state), the quantity averaged is not the radiation intensity (as in the description of spontaneous Raman scattering, cf. Ref. 5), but its amplitude. This accounts for the order of the averaging and for the squaring of the absolute value.

To find $\mathbf{E}^c$ and determine the method of averaging in (3), we must know the properties, especially the statistical ones, of the field $\mathbf{E}^i$ acting on the monomer. We can first attempt to estimate the difference between the effective field $\mathbf{E}^i$ and the average (macroscopic) field $\mathbf{E}$ in the usual manner, introducing the Lorentz field $\mathbf{E}_L$. To find the Lorentz field (see, e.g., Ref. 6) it must be recognized that the densities of all other monomers around the given one is not constant but is given by the function $g(r)$ [Eq. (1)]. The result is $\mathbf{E}^L=\frac{1}{3}D\chi_0\mathbf{E}^iR_0{}^{-D}R_L{}^{D-3}$, where R_L is radius of a fictitious cavity (Lorentz sphere) around the given monomer. In contrast to the case of a nonfractal medium ($D=3$), the Lorentz field for a nontrivial fractal ($D<3$) diverges as $R_L\to 0$.

The divergence of the Lorentz field at short distances shows that the main contribution to the field $\mathbf{E}^i$ acting on the given monomer is made by its nearest neighbors. Since their number is small, the field fluctuates strongly. Theories using only a field averaged over an ensemble of systems (such as the Lorentz field) are inadequate for fractals.

In Ref. 5 we formulated a binary approximation that takes exact account of the contribution made to $\mathbf{E}^i$ by the fluctuating field of the monomer closest to the given one. The fields of the remaining monomers are treated as averaged; this leads, in analogy with Ref. 6, to replacement of the external field by an averaged one and in addition to the field $\mathbf{E}^i$ of a Lorentz field. The role of the latter, however, is small; the field of the nearest monomer is the strongest. We shall present below an expression obtained for $\mathbf{E}^i$ in the binary approximation, but for now we shall estimate $G^{(n)}$ [Eq. (3)] using the qualitative considerations above. We neglect for simplicity the inessential influence of the Lorentz field and the interaction of the generated radiation with the fractals (allowance for these factors leads only to small quantitative changes).

We consider for the sake of argument monomers that have an isolated resonance. Their susceptibility is

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

where ω_m and Γ are the characteristic frequency and the homogeneous excitation width of the monomer, R_m is the characteristic geometric dimension of the monomer (for a two-level system we have $\omega_m R_m{}^3=|d_{12}|^2$, where d_{12} is a transition matrix element, and Ω is the deviation of the frequency ω from resonance.

The interaction of the given monomer with its nearest neighbor shifts the frequency of the resonance (of the optical absorption) by a certain random (since the location of the monomer is radom) amount $\Delta\omega\sim\Omega_f$, where we have introduced the characteristic frequency

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

which determines the scale of the broadening and shift of the fractal spectrum compared with the spectra of the individual monomers. This estimate follows from (4) with allowance for the usual form of the dipole-dipole interaction and for the fact that the characteristic distance between nearest monomers is of order R_0. For many investigated fractals R_0 exceeds R_m insignificantly,[4] therefore $\Omega_f\lesssim\omega_m$. If the monomer is a good resonator, it has $Q\sim\omega_m/\Gamma\gg 1$, which we shall assume hereafter.

The probability of entering into resonance with a given pair of other monomers is small relative to Γ/Ω_f. Therefore different sections of the fractal will be independently absorbed. We arrive thus at the concept of a strong inhomogeneously broadened in view of the variance of the pair interactions) absorption spectrum of the fractal.

If the external-radiation frequency is located in the absorption band of the fractal, certain monomers (more accurately, pairs of them) will be at resonance with the radiation; their fraction is, obviously, $\Gamma/\Omega_f \ll 1$. The field E^c_{res} induced by the resonant monomer in its immediate vicinity is, according to (2) and (4),

$$E^c_{res} \sim \chi_0(0) E/R_m^3 \sim \omega_m E/\Gamma. \tag{6}$$

The local field E^c_{res} is ω_m/Γ times stronger than the mean field E ($\omega_m/\Gamma \gg 1$); this is in fact the cause of the giant enhancement of the nonlinear susceptibilities [cf. Eq. (3)].

A qualitative average of (3), however, cannot even be estimated. The point is that the averaged quantity $(E^c)^n$ contains an unknown phase whose fluctuations can in principle suppress strongly the enhancement (this statement is confirmed by the theory, see below). Only the upper- and lower-bound estimates can be obtained for $G^{(n)}$.

The upper-bound estimate is obviously obtained by neglecting in (3) the phase fluctuations, i.e., by changing $E^c \to |E^c|$:

$$G^{(n)} \leqslant (\langle |E^c|^n \rangle / E^n)^2 \sim [(|E^c_{res}|/E)^n \Gamma/\Omega_f]^2. \tag{7}$$

The factor $\Gamma/\Omega_f \ll 1$ is here the estimated fraction of the resonant monomers. The lower-bound estimate, on the contrary, follows from the assumption that the influence of the phase fluctuation in (3) is essentially destructive: the large contribution to E^c, proportional to the factor ω_m/Γ, is excluded and we are left only with the mean (nonfluctuating) value $\langle E^c \rangle$. Then

$$G^{(n)} \geqslant |\langle E^c \rangle / E|^{2n} \sim (E^r_{cs} \Gamma / E\Omega_f)^{2n}. \tag{8}$$

Using (5) and (6), we reduce the estimates (7) and (8) to the form

$$(R_0/R_m)^{6n} \lesssim G^{(n)} \lesssim (\Omega_f/\Gamma)^{2(n-1)} (R_0/R_m)^{6n}. \tag{9}$$

The appearance, in the upper-bound estimate, of the homogeneous width of the resonance of an isolated monomer is due to the space-frequency selection that is a feature of nonlinear interaction with radiation.

Since $R_0 \gtrsim R_m$ and $\Omega_f \gg \Gamma$, the upper- and lower-bound estimates in (9) differ very strongly. Which of the indicated estimates is approached by the value of $G^{(n)}$ for a specific effect can be determined only from the complete theory (see below). This theory describes also the spectral dependence of the factor $G^{(n)}$, a dependence not included in (9) and is determined essentially by the fractal dimensionality.

It will be shown below that generation of a higher harmonic (i.e. of radiation of the maximum possible frequency at the given external fields and the order of nonlinearity) is always described by the lower limit in (9). Processes with "subtraction" of even one photon are estimated, when the exciting fields are equal (within the limits of the width Γ) are estimated from the upper limit in (9). The same processes are characterized, when the relative frequency detunings increase from zero to $\gg \Gamma$, by values of $G^{(n)}$ with order of magnitude ranging from the upper to the lower estimates in (9).

To conclude this section, we present the results needed below for the linear response to fractals and obtained in Ref. 5 in the binary approximation. The fluctuating field $\mathbf{E}^i$ acting on the ith monomer is expressed (see below) in terms of the random response matrix M^{-1}:

$$M_{\alpha\beta}^{-1} = A\delta_{\alpha\beta} + (C-A) n_\alpha^{ij} n_\beta^{ij}, \quad A = (\chi_0^{-1} + \Phi)^{-1}, \quad C = (\chi_0^{-1} - 2\Phi)^{-1}, \tag{10}$$

where

$$\mathbf{n}^{ij} \equiv \mathbf{r}^{ij}/r^{ij}, \quad \mathbf{r}^{ij} \equiv \mathbf{r}^i - \mathbf{r}^j, \quad \Phi = \sum_k (r^{ik})^{-3}. \tag{11}$$

The random quantities in (10) are Φ and of the unit vectors $\mathbf{n}^{ij}$ that depend on the random coordinates $\mathbf{r}^{ij}$ of the monomer.

The quantities entering in M^{-1} [Eq. (10)] are averaged[5] over the ensemble of fractals (i.e., over the sets $\{\mathbf{r}^i\}$) by changing to a Laplace representation with χ_0^{-1} as the variable, and averaging over the distance between the monomer and its nearest neighbors with the aid of the distribution $g(r)$ [Eq. (1)]; the result is therefore dependent on the fractal dimensionality D. This dependence is defined by a special function $\mathbf{S}_\alpha$ of the complex variable z (Ref. 5):

$$\mathbf{S}_\alpha(z) \equiv i \int_0^\infty \exp\{izt - (it)^\alpha \Gamma(1-\alpha)\} dt, \tag{12}$$

$$\langle A \rangle = R_0^3 \mathbf{S}_\alpha(-R_0^3 \chi_0^{-1}), \quad \langle C \rangle = -\tfrac{1}{2}\mathbf{S}_\alpha(\tfrac{1}{2} R_0^3 \chi_0^{-1}),$$

where $\alpha = D/3$ (not to be confused with the vector index), and $\Gamma(\ldots)$ is the gamma function. The integral representation in (12) specifies $\mathbf{S}_\alpha$ at $\operatorname{Im} z > 0$; in the lower half plane the function is determined by the analytic continuation $\mathbf{S}_\alpha(z^*) = \mathbf{S}^*_\alpha(z)$.

The linear susceptibility of a monomer in a fractal is expressed as the mean value:

$$\chi_1 = \tfrac{1}{3}\operatorname{Sp}\langle M^{-1} \rangle = \tfrac{1}{3} R_0^3 \{2\mathbf{S}_\alpha(X) - \tfrac{1}{2}\mathbf{S}_\alpha(-\tfrac{1}{2}X)\}, \quad X \equiv -R_0^3 \chi_0^{-1}. \tag{13}$$

The final expression for the total field acting in the ith monomer is

$$E_\alpha^i = \chi_0^{-1} M_{\alpha\beta}^{-1} k_L E_\beta, \tag{14}$$

where E is the mean (macroscopic) field in the fractal, $k_L = (1 - \alpha R_0^{-3} \chi_1)^{-1}$ is a factor due to allowance for the Lorentz field (it is not of principal importance in the present theory and leads only to small corrections). If expression (14) is used. Eq. (2) determines the field $\mathbf{E}^c$ at the impurity, which is the initial quantity for the calculation of the nonlinear susceptibilities.

3. NONLINEAR IMPURITY SUSCEPTIBILITY OF A FRACTAL. GIANT CARS AND PC

With CARS and CP as examples, we construct a theory of nonlinear susceptibility of impurity centers in a fractal matrix. Consider fields that are harmonic in space and time. If the fractal dimension R_c is much shorter than the radiation wavelength λ, the waves generated by different parti-

cles in a fractal will always add up coherently. At $R_c \gg \lambda$, known phase-matching conditions must be met (see, e.g., Ref. 7). Of course, for the theory of Ref. 5 to be valid at $R_c > \lambda$ it is necessary that the characteristic distance R_0 between the nearest monomers be much shorter than the wavelength λ. Assume that the foregoing conditions are met. The oscillating exponentials are then excluded; we shall indicate below only the amplitudes that precede them. In view of the coherence, the amplitude of the generated radiation is proportional to the number of impurities, while the radiation power is proportional to the square of this number. Bearing this in mind, we shall leave out this factor for brevity (we have converted here to the amplitude per impurity center).

CARS and CP are four-wave parametric processes in the elementary act of which two photons of frequency ω_1 decay into two photons with frequencies ω_2 and ω_s. These processes are defined by a nonlinear susceptibility of third order[7]

$$\chi^{(3)}_{\alpha\beta\gamma\delta}(-\omega_s; \omega_1, \omega_1, -\omega_2), \tag{15}$$

where ω_s is the frequency of the generated radiation, and ω_1 and ω_2 are the frequencies of the nonlinearly interacting waves. In the CARS case, $\omega_s = 2\omega_1 - \omega_2$; PC corresponds to the completely degenerate case $\omega_s = \omega_1 = \omega_2$. For coherent effects it is necessary to average the field amplitude (see the preceding section) i.e., the value of the susceptibility. In the case of isotropic (in the mean) fractals, the known[8] symmetry properties lead to an expression for the averaged (impurity) susceptibility $\chi^{(3F)}_{\alpha\beta\gamma\delta}$ of the fractal in terms of two scalar functions F_s and F_a, which we write in the form

$$\begin{aligned}
&\langle \chi^{(3F)}_{\alpha\beta\gamma\delta} \rangle = F_s \Delta^{+}_{\alpha\beta\gamma\delta} + F_a \Delta^{-}_{\alpha\beta\gamma\delta},\\
&\Delta^{+}_{\alpha\beta\gamma\delta} = {}^1/_3[\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}],\\
&\Delta^{-}_{\alpha\beta\gamma\delta} = {}^1/_3[\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} - 2\delta_{\alpha\delta}\delta_{\beta\gamma}].
\end{aligned} \tag{16}$$

The terms with Δ^+ and Δ^- are respectively the completely symmetric and the incompletely symmetric (vanishing on symmetrization with respect to $\beta \leftrightarrow \delta$ and $\gamma \leftrightarrow \delta$) parts of $\chi^{(3)}$. The averaged susceptibility of an isolated impurity molecule is expressed in similar form:

$$\langle \chi^{(3c)}_{\alpha\beta\gamma\delta} \rangle = f_s \Delta^{+}_{\alpha\beta\gamma\delta} + f_a \Delta^{-}_{\alpha\beta\gamma\delta}. \tag{17}$$

The task of our theory is to express the amplitudes F_s and F_a in terms of f_s and f_a.

We take next into account the nonlinearity of the susceptibility of the impurity, and describe the fractal in the framework of the linear-response theory.[5] The nonlinear (of frequency ω_s) amplitude of the dipole-center dipole moment is then

$$d_\alpha^{NL} = \chi^{(3c)}_{\alpha\beta\gamma\delta} E^{(1)c}_\beta E^{\prime(1)c}_\gamma E^{(2)c*}_\delta, \tag{18}$$

where $\mathbf{E}^{(h)c}$ are the amplitudes of the local fields (2). The numerical exponent identifies the frequency of the corresponding field.

Inasmuch as in PC the generated and excited frequency radiations have the same frequency, the dipole moment (18) produces a field that polarizes in turn the nearest ith monomer. It is important that the distance between the two dipoles is much less than λ and the amplitudes of the waves generated by them add up coherently. The actual emitter is thus in fact the summary (effective) dipole $\mathbf{d}^{\text{eff}}$, for which it is easy to obtain the expression

$$d_\alpha^{eff} = \chi_0 \Pi_{\alpha\beta} d_\beta^{NL}. \tag{19}$$

In the CARS case the generated wave differs in frequency from the initial waves, but the difference is as a rule small. The effective nonlinear dipole is therefore likewise described by Eq. (19).

In accord with the definition of $\chi^{(3F)}$, the radiating dipole moment $\mathbf{d}^{\text{eff}}$ is expressed in terms of the average (macroscopic) wave amplitudes as

$$\langle d_\alpha^{eff} \rangle = \langle \chi^{(3F)}_{\alpha\beta\gamma\delta} \rangle E^{(1)}_\beta E^{\prime(1)}_\gamma E^{(2)*}_\delta, \tag{20}$$

where $E^{(k)}$ are the average (macroscopic) amplitudes of the exciting waves. Using (2), (14), (18), and (19) we obtain an expression for $\langle \mathbf{d}^{\text{eff}} \rangle$ in the form (20) with a nonlinear susceptibility

$$\langle \chi^{(3F)}_{\alpha\beta\gamma\delta} \rangle = \chi_0 |k_L|^2 k_L \langle \chi^{(3c)}_{\alpha'\beta'\gamma'\delta'} \Pi_{\alpha'\alpha} T_{\beta'\beta}(\omega_1) T_{\gamma'\gamma}(\omega_1) T^{*}_{\delta'\delta}(\omega_2) \rangle, \tag{21}$$

where we have introduced the matrix $T \equiv \Pi M^{-1}$; the wave frequencies are indicated where they are significant (see below).

The averaging in (21) is over random factors: the impurity orientation (the tensor $\chi^{(3c)}$, the angles of the vector $\mathbf{n}^c$ (the matrices Π), the angles of the vector $\mathbf{n}^{ij}$ of the mutual orientation of the approaching monomers, and the distances r^{ij} between these monomers (the matrices T). Assuming the averaging over these factors to be independent, we rewrite (21) in the form

$$\begin{aligned}
\langle \chi^{(3F)}_{\alpha\beta\gamma\delta} \rangle = \chi_0 |k_L|^2 k_L \langle \chi^{(3c)}_{\alpha'\beta'\gamma'\delta'} \rangle \langle \Pi_{\alpha'\alpha} \Pi_{\beta'\beta''} \Pi_{\gamma'\gamma''} \Pi^{*}_{\delta'\delta''} \rangle\\
\times \langle M^{-1}_{\beta''\beta}(\omega_1) M^{-1}_{\gamma''\gamma} M^{-1*}_{\delta''\delta} \rangle.
\end{aligned} \tag{22}$$

The product of the matrices Π (2), which enters in (22), is a polynomial in R^{-1}. The main effect of the enhancement of the nonlinear processes is due to the term with the maximum power (twelfth) of R^{-1}, which will be retained hereafter. The discarded terms are small with a smallness parameter $(R/R_0)^3$.

Using (17) and averaging over the angles (see above), we obtain the susceptibility $\langle \chi^{(3F)} \rangle$ in the form (16), with coefficients

$$F_s = {}^8/_{25} \chi_0 |k_L|^2 k_L R^{-12} [f_s \langle Q_s \rangle + {}^5/_4 f_a \langle q \rangle], \tag{23}$$

$$F_a = \chi_0 |k_L|^2 k_L R^{-12} [f_a \langle Q_a \rangle + {}^4/_5 f_s \langle q \rangle], \tag{24}$$

where it is required to average, over the mutual distances of the monomers, the quantities Q_s, Q_a, and q expressed in terms of the amplitudes A and C [see (10)]:

$$Q_s = 8A^2A^* + 3C^2C^* + {}^4/_3 AC(A^* + C^*) + {}^2/_3(A^2C^* + C^2A^*), \tag{25}$$

$$Q_a = A^2A^* + {}^1/_3 AC(A^* + C^*) + {}^2/_3(A^2C^* + C^2A^*), \tag{26}$$

$$q = {}^2/_3(C - A)(AC^* - A^*C). \tag{27}$$

The amplitudes A and C in (25)–(27) are taken at the frequency ω_1, and A^* and C^* at the frequency ω_2.

The quantities (25)–(27) can be reduced by identity transformations to a from that merits calculation of their

averages with the aid of (12). For example,

$$\langle A^2A^*\rangle=\langle[\chi_0^{-1}(\omega_1)+\Phi]^{-2}[\chi_0^{-1*}(\omega_2)+\Phi]^{-1}\rangle$$
$$=\Lambda R_0^3\langle[\chi_0^{-1}(\omega_1)+\Phi]^{-2}\rangle$$
$$-\Lambda^2R_0^6\{\langle[\chi_0^{-1}(\omega_1)+\Phi]^{-1}\rangle-\langle[\chi_0^{-1*}(\omega_2)+\Phi]^{-1}\rangle\}, \quad (28)$$

where we have introduced a resonant (see below) factor Λ that contains no random quantities:

$$\Lambda\equiv(X_1-X_2^*)^{-1}, \quad X_{1,2}=-R_0^3\chi_0^{-1}(\omega_{1,2}). \quad (29)$$

The first term in (28) is transformed by differentiation with respect to the parameter χ_0^{-1} after which, using (12), we obtain

$$\langle A^2A^*\rangle=\Lambda R_0^9\frac{d}{dX_1}\mathbf{S}_\alpha(X_1)-\Lambda^2R_0^9[\mathbf{S}_\alpha(X_1)-\mathbf{S}_\alpha^*(X_2)]. \quad (30)$$

We use, for the sake of argument, the form (4) of χ_0 (cf. Ref. 5) and express Λ of (29) in the patently resonant form

$$\Lambda(\Delta\omega)=\Omega_f(\Delta\omega+2i\Gamma)^{-1}, \quad \Delta\omega=\omega_1-\omega_2, \quad (31)$$

where Ω_f is given by Eq. (5). We assume a relatively small detuning $|\Delta\omega|\ll\Omega_f$ and recognize that $\Gamma\gg\Omega_f$. The factor Λ (31) is then large in terms of the parameter $\Omega_f/\max(\Gamma,\Delta\omega)$.

Recognizing that the functions $\mathbf{S}_\alpha(X)$ and their derivatives are of the order of unity, we separate from (30) the leading terms with respect to the parameter Λ and obtain

$$\langle A^2A^*\rangle=-R_0^9\Lambda^2[\mathbf{S}_\alpha(X_1)-\mathbf{S}_\alpha^*(X_2)]. \quad (32)$$

Since the frequency-variation interval of the factors $\mathbf{S}_\alpha(x)$ is $\sim\Omega_f$ (cf. Ref. 5) we can set at $\Omega_f\gg\Gamma$ the frequencies ω_1 and ω_2 in these factors equal to some mean value ω and rewrite (32) in the final form

$$\langle A^2A^*\rangle=-2iR_0^9\Lambda^2(\Delta\omega)\operatorname{Im}\mathbf{s}_\alpha(x), \quad x\equiv-R_0^3\operatorname{Re}\chi_0^{-1}(\omega), \quad (33)$$

where we use a complex function of a real argument $\mathbf{s}_\alpha(x)\equiv\mathbf{S}_\alpha(x+i0)$ (see Ref. 5 for its properties). In perfect analogy with the foregoing, we obtain in the leading order in Λ:

$$\langle C^2C^*\rangle=-iR_0^9\Lambda^2(\Delta\omega)\operatorname{Im}\mathbf{s}_\alpha(-x/2). \quad (34)$$

The interference terms containing products of A and turn out to be small compared with (33) and (34) relative to the parameter Γ/Ω_f. For example, for the term $\langle A^2C^*\rangle$ we obtain, in full analogy with the derivation of (30),

$$\langle A^2C^*\rangle=\frac{R_0^9}{2X_1+X_2^*}\frac{d}{dX}\mathbf{S}_\alpha(X)$$
$$+\frac{2R_0^9}{(2X_1+X_2^*)^2}\left[\mathbf{S}_\alpha(X_1)-\mathbf{S}_\alpha\left(-\frac{1}{2}X_2^*\right)\right]. \quad (35)$$

The maximum value of (35) is reached at $\Omega\lesssim\Gamma$. The estimate $\langle A^2C\rangle\sim R_0^9\Lambda$ is then valid, i.e., (35) is indeed smaller than (33) and (34) by a factor $\Gamma/\Omega_f\ll1$.

As a result we get from (23), (24), (33), and (34) in principal order in Γ/Ω_f

$$F_s=\frac{8i}{25x}f_s|k_L|^2k_L\left(\frac{R_0}{R}\right)^{12}\Lambda^2(\Delta\omega)\operatorname{Im}\left[16\mathbf{s}_\alpha(x)+3\mathbf{s}_\alpha\left(-\frac{x}{2}\right)\right], \quad (36)$$

$$F_a=\frac{2i}{x}f_a|k_L|^2k_L\left(\frac{R_0}{R}\right)^{12}\Lambda^2(\Delta\omega)\operatorname{Im}\mathbf{s}_\alpha(x). \quad (37)$$

The amplitudes (36) and (37) of the nonlinear susceptibility, together with its form (15), are the principal result of the theory for giant CARS. They determine the susceptibility of the impurity introduced into the fractal matrix in terms of the susceptibility of an isolated impurity molecule. The corresponding expression for PC are obtained from (36) and (37) by putting $\Delta\omega=0$ (or course, the initial single-particle amplitudes f_s and f_a will be different for these two effects).

Let us discuss briefly the basic expressions (36) and (37). The nonlinear-response amplitudes F_s and F_a, carry information on the impurity center (the ampltudes f_s and f_a), on the fractal absorption spectrum (the functions $\mathbf{s}_\alpha$), and on the unperturbed spectrum of the individual monomer (the factor Λ). The most complete information can obviously be obtained with the aid of CARS (since it is possible to vary $\Delta\omega$).

A distinctive property of the amplitudes (36) and (37) is their proportionality to the imagninary pact of the susceptibility of the fractal [cf. (13)] and hence to its absorption [at a given sign of the detuning, only one of the quantities, $\operatorname{Im}\mathbf{s}_\alpha(x)$ or $\operatorname{Im}\mathbf{s}_\alpha(-x/2)$, differs from zero, see the properties of the function $\mathbf{s}_\alpha$ in Ref. 5]. Thus, the predicted giant (see below) enhancement of the CARS and PC effects on impurities are realized only when the exciting radiation lands in the fractal's intrinsic absorption bands.

The symmetry of the susceptibility of an isolated impurity [see (17) and the discussion following that equation] is duplicated, as expected, by the impurity susceptibility of the fractal (16). In the leading order in Γ/Ω_f, the completely symmetric part of the impurity susceptibility "generates" a completely symmetric part of the fractal susceptibility ($F_s\propto f_s$); the same holds for the incompletely symmetric parts. It is interesting that in the long-wave absorption band of the fractal (at $\Omega<0$) the amplitude F_a vanishes, i.e., the linear response becomes completely symmetric. We point out that both amplitudes F_s and F_a, and hence the symmetry of the response, can be directly measured in polarization experiments.

The gain $G^{(3)}$ is given by

$$G^{(3)}=|\langle\chi_{\alpha\beta\gamma\delta}^{(3F)}\rangle e_\beta^{(1)}e_\gamma'^{(1)}e_\delta^{(2)*}/\langle\chi_{\alpha\beta\gamma\delta}^{(3c)}\rangle e_\beta^{(1)}e_\gamma'^{(1)}e_\delta^{(2)*}|^2, \quad (38)$$

where $\mathbf{e}^{(1)}$, $\mathbf{e}'^{(1)}$, $\mathbf{e}^{(2)}$ are the polarization vectors of the incident waves. The amplitudes (36) and (37) increase rapidly with decrease of R and reach a maximum at the limiting (from the standpoint of applicability of the dipole-dipole interaction model) small value $R\sim R_m$. For a monomer in the form of a macroscopic sphere it is permissible to put $R=R_m$ (R_m is the radius of the sphere). Assuming, to be definite, identical linear polarizations of the waves, we obtain from (17), (36), and (37) for the maximum value of CARS again

$$G_{max}^{CARS}=G_0^{CARS}L^{CARS}(\Omega),$$
$$G_0^{CARS}=|k_L|^6\left(\frac{R_0}{R_m}\right)^{24}\left(\frac{\Omega_f}{\Gamma}\right)^4g^2(\Delta\omega),$$
$$g(\Delta\omega)=\left[1+\left(\frac{\Delta\omega}{2\Gamma}\right)^2\right]^{-1},$$
$$L^{CARS}(\Omega)=\left(\frac{2}{25x}\right)^2\{[16\operatorname{Im}\mathbf{s}_\alpha(x)]^2+[3\operatorname{Im}\mathbf{s}_\alpha(-x/2)]^2\}. \quad (39)$$

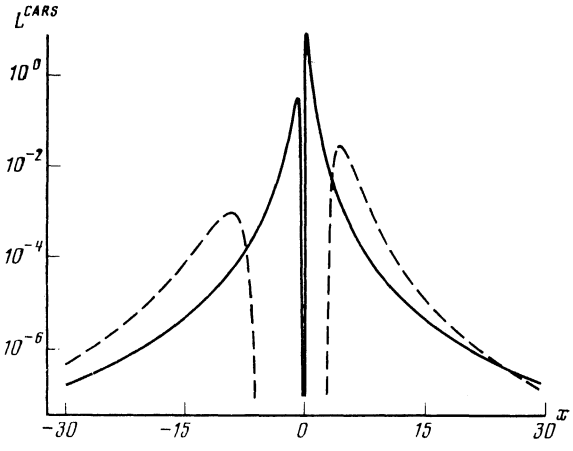

FIG. 1. Gain for CARS and PC (values of L^{CARS}) vs the parameter $x \approx \Omega/\Omega_f$ (Ω is the detuning of the exciting-radiation frequency). Solid line—$D = 1.5$, dashed—$D = 2.5$.

An equation for PC is obtained from (39) by putting $\Delta\omega = 0$. We indicte that the singularity in (39) at $x = 0$ is only apparent: Im $\mathbf{s}(x)$ vanishes at this point faster than any power of x.[5]

The value of the factor $G_{\max}^{\mathrm{CARS}}$ is determined by the constant $(\omega_m^2/\Omega_f\Gamma)^4 = (R_0^6\Omega_f/R_m^6\Gamma)^4 \gg 1$, and its spectral dependence is determined by the smoothly varying factor $L^{\mathrm{CARS}}(\Omega)$ and the resonant circuit $g(\Delta\omega)$. A feature of the latter is its small spectral width, equal to 2Γ (cf. the width Γ of an isolated monomer vs the width $\Omega_f \gg \Gamma$ of the spectrum of the fractal). The factor $G_{\max}^{\mathrm{CARS}}$ (39) agrees, accurate to insignificant factors $|k_L|^6$ (influence of the Lorentz field) and $(R_0/R_m)^6$ (effect of interaction of the generated radiation with the fractal) with the upper-bound estimate in (9) for $n = 3$ [cf. the discussion following Eq. (9)].

The variable x (33) in terms of which the gain $G_{\max}^{\mathrm{CARS}}$ (39) depends smoothly on the exciting-radiation frequency, is equal, if Eq. (4) is used, to the relative detuning Ω/Ω_f from resonance. Figure 1 shows the factor L^{CARS} (39) which describes this smooth dependence. It has the form of a doublet consisting of short- and long-wave peaks. In the fractal absorption region shown in the figure, the gain changes by seven orders of magnitude. A strong dependence on the fractal dimensionality is seen: for example, when D changes grom 1.5 to 2.5 the long-wave maximum is shifted by a decade in frequency and decreases by approximately three decades in size.

It is expedient to compare (39) with the maximum Raman-scattering gain G^{RS}. The corresponding theory developed in Ref. 5 for the case of large frequency shifts by scattering yields[1)]

$$G^{RS} = \frac{1}{3}\mathrm{Sp}\langle TT^+\rangle = \frac{1}{3}\left(\frac{R_0}{R}\right)^6\frac{\Omega_f}{\Gamma}|k_L|^2\mathrm{Im}\{4s_\alpha(x)+s_\alpha(-x/2)\}. \quad (40)$$

Generalization of (40) to the case of small shifts, when the interaction between the fractal and the impurity at the frequency of the scattered radiation is substantial, can be carried out in analogy with the derivation of Eq. (19). The result is

$$G^{RS} = {}^1/_3|\chi_0|^2|k_L|^2\,\mathrm{Sp}\langle\Pi^+\Pi TT^+\rangle. \quad (41)$$

Calculation of the mean values in (41) yields

$$G_{max}^{RS} = |k_L|^2\left(\frac{R_0}{R}\right)^{12}\frac{\Omega_f}{\Gamma}\frac{1}{x^2}\left\{4s_\alpha(x)+s_\alpha\left(-\frac{1}{2}x\right)\right\}. \quad (42)$$

The maximum value of the Raman scattering gain is $G_{\max}^{\mathrm{RS}} = G^{\mathrm{RS}}|_{R=R_m}$; comparison of (39) with (42) leads to the estimate

$$G_{max}^{CARS} \sim (G_{max}^{RS})^2(\Omega_f/\Gamma)^2 g^2(\Delta\omega). \quad (43)$$

A typical value is $G^{\mathrm{RS}} \gtrsim 10^5$ (Ref. 9); the main parameter that determines this value is Ω_f/Γ. Diverting the factor $\sim 10^3$ to the remaining parameters, we obtain the estimate $\Omega_f/\Gamma \sim 10^2$. We get then from (43) the estimate $G_{\max}^{\mathrm{CARS}} \sim 10^{14}$ for PC on fractally bound molecules, and also for CARS at $\Delta\omega \lesssim \Gamma$. In the case of CARS, if the detuning $\Delta\omega$ lies in the usual IR band, then $\Delta\omega/\Gamma \sim 10^2 - 10^3$, and the estimate (43) gives $G_{\max}^{\mathrm{CARS}} \sim 10^6 - 10^2$. Such values will be reached, of course, if the local fields (which can exceed the external ones by several orders) do not saturate the susceptibilities of either the impurities or the fractal monomer.

4. ENHANCED HARMONIC GENERATION

We begin with third-harmonic generation. This effect is also determined by a linearity of third order. The nonlinear dipole moment of the impurity is

$$d_\alpha^{NL} = \overset{(3c)}{\chi}_{\alpha\beta\gamma\delta}(-\omega_s;\omega,\omega,\omega)E_\beta^c E_\gamma^c E_\delta^c, \quad \omega_s = 3\omega, \quad (44)$$

where $E^{(c)}$ is the local amplitude of the exciting field at the frequency ω at the impurity location. The nonlinear impurity susceptibility of the fractal and of the individual impurity take respectively the form

$$\langle\overset{(3F)}{\chi}_{\alpha\beta\gamma\delta}\rangle = F\Delta^+_{\alpha\beta\gamma\delta}, \quad \langle\overset{(3c)}{\chi}_{\alpha\beta\gamma\delta}\rangle = f\Delta^+_{\alpha\beta\gamma\delta}. \quad (45)$$

Note that the susceptibilities (45) are fully symmetric and each of them is characterized by one amplitude $F(f)$. In this case, in contrast to the descriptions of the CARS and PC effects, we can neglect the interaction between the generated radiation (of frequency ω_s) with the fractal, i.e., we can put $d^{\mathrm{eff}} = d^{\mathrm{NL}}$.

The expression for $\chi^{(3F)}$ is obtained in full analogy with (21):

$$\langle\overset{(3F)}{\chi}_{\alpha\beta\gamma\delta}\rangle = k_L^3\langle\overset{(3c)}{\chi}_{\alpha\beta'\gamma'\delta'}T_{\beta'\beta}T_{\gamma'\gamma}T_{\delta'\delta}\rangle. \quad (46)$$

Next, just as in the transition from (21) to (22), we "uncouple" the averagings and reduce (46) to the form

$$\langle\overset{(3F)}{\chi}_{\alpha\beta\gamma\delta}\rangle = k_L^3\langle\overset{(3c)}{\chi}_{\alpha\beta'\gamma'\delta'}\rangle\langle\Pi_{\beta'\beta''}\Pi_{\gamma'\gamma''}\Pi_{\delta'\delta''}\rangle\langle M^{-1}_{\beta''\beta}M^{-1}_{\gamma''\gamma}M^{-1}_{\delta''\delta}\rangle. \quad (47)$$

Averaging over the angles of the vectors $\mathbf{n}^c$ and $\mathbf{n}^{ij}$, we verify that the structure (45) is duplicated; the expression for the response amplitude is

$$F = {}^4/_{75}fR^{-9}k_L^3\langle 8A^3+3C^3+2AC(A+C)\rangle. \quad (48)$$

We average in (48) over the distances between the monomers, using (12), in full analogy with the calculation of the amplitudes, (25)–(27). The result is

$$F=\frac{4}{75}f\left(\frac{R_0}{R}\right)^9 k_L{}^3\left\{\frac{d^2}{dx^2}\left[4\mathbf{s}_\alpha(x)-\frac{3}{4}\mathbf{s}_\alpha{}^*\left(-\frac{1}{2}x\right)\right]\right.$$
$$\left.-\frac{2}{3}\frac{1}{x}\left(\frac{d}{dx}-\frac{1}{x}\right)\left[\mathbf{s}_\alpha(x)-\mathbf{s}_\alpha{}^*\left(-\frac{x}{2}\right)\right]\right\}. \qquad (49)$$

Note that, just as in (39) above, there is no singularity at $x=0$.

The Maxwellian gain $G_{\max}^{TH}$ is calculated in analogy with (39):

$$G_{max}^{TH}=\left(\frac{R_0}{R_m}\right)^{18}|k_L|^6L^{TH}(\Omega),\quad L^{TH}=\left(\frac{4}{75}\right)^2\left|\frac{d^2}{dx^2}\left[4\mathbf{s}_\alpha(x)\right.\right.$$
$$\left.-\frac{3}{4}\mathbf{s}^*\left(-\frac{x}{2}\right)\right]-\frac{2}{3}\frac{1}{x}\left(\frac{d}{dx}-\frac{1}{x}\right)$$
$$\left.\times\left[\mathbf{s}_\alpha(x)-\mathbf{s}_\alpha{}^*\left(-\frac{x}{2}\right)\right]\right|^2. \qquad (50)$$

The main differences between (50) and the analogous result (39) for CARS and PC is the following. There are no large factors (powers of the ratio Ω_f/Γ nor narrow spectral structures in (50). Moreover, $G_{\max}^{TH}$ is determined by both the imaginary and real parts of the function $\mathbf{s}_\alpha$, leading to a slower decrease as a function of frequency with increased distance from the center of the absorption band.

The order of magnitude of $G_{\max}^{TH}$ in (50) coincides with the lower estimate (9) at $n=3$ [apart from the smooth spectral dependence and to the Lorentz-field contribution, which were neglected in the derivation of (9)]. The value of $G_{\max}^{TH}$ is determined by a high power of the ratio R_0/R_m, which can exceed unity but in general by not much (cf. Ref. 4). The ratio R_0/R_m can be large only for a fractal in which the polarizable monomers just joined by "neutral" long bonds. In any case, comparing (50) with (39) we can state that third-harmonic generation is much less enhanced than the CARS and PC effects.

The spectral dependence of the third-harmonic generation gain is illustrated in Fig. 2. It is smooth; the dependence on the fractal dimensionality is just as strong as for CARS and PC (cf. Fig. 1).

Second-harmonic generation is described by the second-order impurity susceptibility. The amplitude of the nonlinear dipole moment for this process is of the form [cf. (44)]

$$d_\alpha{}^{NL}=\chi_{\alpha\beta\gamma}^{(2F)}(-\omega_s;\omega,\omega)E_\beta^{(c)}E_\gamma^{(c)},\quad \omega_s=2\omega. \qquad (51)$$

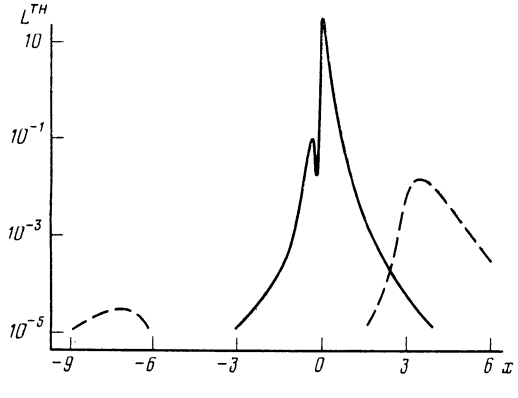

FIG. 2. Third-harmonic generation gain L^{TH} vs the parameter x. Solid curve—$D=1.5$, dashed—$D=2.5$.

The symmetry properties of the susceptibilities $\chi^{(2c)}$ of an isolated impurity and $\chi^{(2F)}$ of the fractal are determined by the noncentral symmetry of the system, viz., by the presence of the polar unit vector $\mathbf{m}$. In view of these properties, each of the indicated susceptibilities is expressed in terms of three independent amplitudes: $F_1,F_2,F_3(f_1,f_2,f_3)$. It is convenient to express the tensor structure of the susceptibility in the form

$$\langle\chi_{\alpha\beta\gamma}^{(2F)}\rangle=m_\alpha[F_1\delta_{\beta\gamma}+F_2(\delta_{\beta\gamma}-3m_\beta m_\gamma)$$
$$+F_3(^2/_3m_\alpha\delta_{\beta\gamma}-m_\gamma\delta_{\alpha\beta}-m_\beta\delta_{\alpha\gamma}), \qquad (52)$$

$$\langle\chi_{\alpha\beta\gamma}^{(2c)}\rangle=m_\alpha[f_1\delta_{\beta\gamma}+f_2(\delta_{\beta\gamma}-3m_\beta m_\gamma)$$
$$+f_3(^2/_3m_\alpha\delta_{\beta\gamma}-m_\gamma\delta_{\alpha\beta}-m_\beta\delta_{\alpha\gamma}). \qquad (53)$$

The direction of $\mathbf{m}$ can be determined, in particular, by the anisotropy *oc* the matrix (crystal) in which the fractal is immersed, or by the normal to the surface on which the fractal is located, or else by the external electric field.

The expression for $\langle\chi^{(2F)}\rangle$ is obtained in full analogy with (47):

$$\langle\chi_{\alpha\beta\gamma}^{(2F)}\rangle=k_L{}^2\langle\chi_{\alpha\beta'\gamma'}^{(2c)}\rangle\langle\Pi_{\beta'\beta''}\Pi_{\gamma'\gamma''}\rangle\langle M_{\beta''\beta}^{-1}M_{\gamma''\gamma}^{-1}\rangle. \qquad (54)$$

Retaining the terms that are maximal in the parameter $(R_0/R_m)^3$ and averaging over the vectors $\mathbf{n}^c$ and $\mathbf{n}^{ij}$, we obtain an expression for the amplitudes F_i in terms of f_i $(i=1,2,3)$:

$$F_1=^2/_3f_1R^{-6}k_L{}^2\langle 2A^2+C^2\rangle,$$
$$F_{2,3}=^1/_{75}f_{2,3}R^{-6}k_L{}^2\langle 7A^2+2C^2+6AC\rangle. \qquad (55)$$

Just as above, the susceptibility of the fractal duplicates the symmetry of the isolated impurity, while the tensor structures in Eqs. (52) and (53) turn out to be eigenfunctions of the transformations from an isolated impurity to a fractal (each amplitude F_i is expressed only in terms of the corresponding f_i).

Averaging over $\{\mathbf{r}^i\}$ makes it possible to obtain from (55) final expressions for the amplitudes of the susceptibility (52)

$$F_1=\frac{2}{3}f_1\left(\frac{R_0}{R}\right)^6 k_L{}^2\frac{d}{dx}\left[2\mathbf{s}_\alpha(x)-\frac{1}{2}\mathbf{s}_\alpha{}^*\left(-\frac{x}{2}\right)\right], \qquad (56)$$

$$F_{2,3}=\frac{1}{75}f_{2,3}\left(\frac{R_0}{R}\right)^6 k_L{}^2\left\{\frac{d}{dx}\left[7\mathbf{s}_\alpha(x)-\mathbf{s}_\alpha{}^*\left(-\frac{x}{2}\right)\right]\right.$$
$$\left.-\frac{2}{x}\left[\mathbf{s}_\alpha(x)-\mathbf{s}_\alpha{}^*\left(-\frac{x}{2}\right)\right]\right\}. \qquad (57)$$

For the sake of argument, we calculate the second-harmonic gain for circularly polarized radiation. With allowance for (57), we obtain for it from (52)

$$G_{max}^{SH}=|k_L|^4(R_0/R_m)^{12}L^{SH}(\Omega),$$
$$L^{SH}(\Omega)=\left(\frac{1}{75}\right)^2\left|\frac{d}{dx}\left[7\mathbf{s}_\alpha(x)-\mathbf{s}_\alpha{}^*\left(-\frac{x}{2}\right)\right]\right.$$
$$\left.-\frac{2}{x}\left[\mathbf{s}_\alpha(x)-\mathbf{s}_\alpha{}^*\left(-\frac{x}{2}\right)\right]\right|^2. \qquad (58)$$

The factor L_{SH} as a function of the detuning Ω/Ω_f (of the parameter x) is shown in Fig. 3. Note that the dependence on the fractal dimensionality is also strong, albeit weaker than for the third harmonic (cf. Fig. 2). This is understandable, since the higher the order of the linearity the stronger the effect of the system properties.

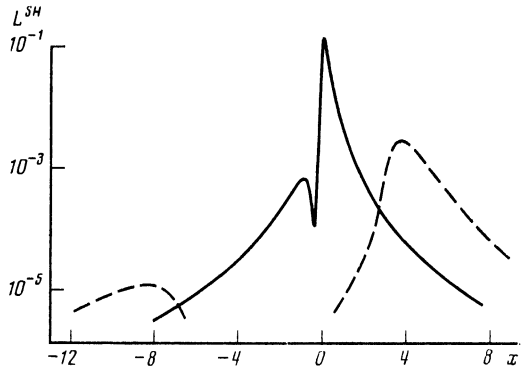

FIG. 3. Second-harmonic generation gain L^{SH} vs the parameter x. Solid line—$D = 1.5$; dashed—$D = 2.5$.

It is seen from (58) that, just as for third-harmonic generation, in contrast to CARS and PC, the gain contains no information on the initially small spectral width of the monomer; it contains no large coefficient (power of the parameter Ω_f/Γ). The value of $G^{SH}_{\max}$ agrees in order of magnitude with the lower estimate in (9). We can thus expect the harmonic generation to be much less enhanced than the CARS and CP effects.

5. ESTIMATE OF THE GAIN FOR PROCESSES OF ARBITRARY ORDER

Let us estimate the gain G for coherent linear processes of higher orders. In particular, let us ascertain in which cases G is proportional to the large factor—a power of Ω_f/Γ (as is the case for CARS and CP, but not for harmonic generation, see above); cf. the discussion of the estimates (9).

The nth order susceptibility is of the form

$$\chi^{(n)}(-\omega_s;\ \omega_{11},\ \omega_{12},\ \ldots,\ \omega_{1p},\ -\omega_{21},\ -\omega_{22},\ \ldots,\ -\omega_{2m}), \quad (59)$$

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

We consider first the case $m > 0$, i.e., processes accompanied by photon emission to external fields (such as CARS and PC). We assume for simplicity in (59) that all the absorbed photons have the same frequency $\omega_1 = \omega_{1k}$ and all the emitted ones have $\omega_2 = \omega_{2k}$. Following next the derivation of (22) and neglecting interference terms such as (35), which contain products of A and C, we estimate the impurity susceptibility of the fractal at

$$\langle\chi^{(nF)}\rangle \sim \langle\chi^{(nc)}\rangle k_L{}^p k_L{}^{*m} \max\,(1,\ a_0\chi_{0s}R_m{}^{-3})R_m{}^{-3n} \times[a_1\langle A^p(\omega_1)A^{*m}(\omega_2)\rangle + a_2\langle C^p(\omega_1)C^{*m}(\omega_2)\rangle], \quad (60)$$

Where a_0, a_1, and a_2 are numerical coefficients that depend only on m, p, and the type of symmetry of the considered part of the susceptibility [cf., e.g., the form of (23)–(26)]; χ_{0s} is the susceptibility of an individual monomer at the frequency of the generated radiation: $\chi^{(nc)}$ is the impurity-center susceptibility part that corresponds to $\chi^{(nF)}$. The max function in (60) describes the possible additional gain due to the impurity-fractal interaction at the frequency of the generated radiation [cf. the discussion of Eq. (19)]. This enhancement takes place in those cases when ω_s lands in the intrinsic-absorption band of the cluster.

Using form (10) for A and C, expression (12) for the mean values, and definition (29) of X_1 and X_2, we rewrite (60) in the form

$$\langle\chi^{(nF)}\rangle \sim \langle\chi^{(nc)}\rangle k_L{}^p k_L{}^{*m} \max\left[1, \frac{a}{x_s}\left(\frac{R_0}{R_m}\right)^3\right] \times\left(\frac{R_0}{R_m}\right)^{3n} \frac{1}{(p-1)!\,(m-1)!} \frac{\partial^{(p-1)}}{\partial X_1^{(p-1)}} \frac{\partial^{(m-1)}}{\partial X_2^{*(m-1)}} \Lambda(X_1, X_2) \times\left\{a_1[\mathbf{S}_\alpha(X_1) - \mathbf{S}_\alpha(X_2^*)] - \frac{a_2}{2}\left[\mathbf{S}_\alpha\left(-\frac{X_1}{2}\right) - \mathbf{S}_\alpha\left(-\frac{X_2^*}{2}\right)\right]\right\}, \quad (61)$$

where $x_s \equiv -R_0^3\,\mathrm{Re}\chi_{0s}^{-1}$. The functions $\mathbf{S}_\alpha$ in (61) vary with the frequencies ω_1 and ω_2 in a characteristic interval $\sim\Omega_f$. The strongest spectral dependence in (61) is contained in the factor Λ.

Differentiation of Λ in (61) leads to the appearance of maximum powers of the large parameter Ω_f/Γ. In the arguments of the smoothly varying functions $\mathbf{S}_\alpha$ we can neglect the frequency differences, i.e., put $\omega_1 = \omega_2 = \omega$. With this in mind, we obtain from (61) the estimate

$$\langle\chi^{(nF)}\rangle \sim \langle\chi^{(nc)}\rangle k_L{}^p k_L{}^{*m} \max\left[1, \frac{a_0}{x_s}\left(\frac{R_0}{R_m}\right)^3\right]\left(\frac{R_0}{R_m}\right)^{3n} \times C_{n-2}^{m-1}\,\Lambda^{n-1}(\Delta\omega)\,\mathrm{Im}\left\{2a_1\mathbf{s}_\alpha(x) + a_2\mathbf{s}_\alpha\left(-\frac{x}{2}\right)\right\}, \quad (62)$$

where C_k^l is a binomial coefficient and x is defined in (33).

A comparison with (13) shows that the spectral dependence of the amplitude gain $\langle\chi^{(nF)}\rangle/\langle\chi^{(nc)}\rangle$ for a given sign of the detuning duplicates the form of Im χ_1, i.e., of the absorption coefficients. Thus, giant impurity nonlinearities should be observed only in the fractal's intrinsic absorption band.

The second argument of the max function in (62) predominates when the frequency ω_s is close to ω, i.e., at $p - m = 1$. In the opposite case the first argument predominates. An order-of-magnitude estimate of the gain of the effect (i.e., of the intensity of the generated radiation) follows from (62) for the considered case $m > 0$

$$G_{max}^{(n)} \sim \left|\frac{\langle\chi^{(nF)}\rangle}{\langle\chi^{(nc)}\rangle}\right|^2 \sim |k_L|^{2n}\left(\frac{R_0}{R_m}\right)^{6(n+\delta_{p-m,\,1})} \times\left(\frac{\Omega_f}{\Gamma}\right)^{2(n-1)} g^{n-1}(\Delta\omega)\,|J_\alpha(\omega)|^2, \quad (63)$$

where $J_\alpha(\omega)$ denotes the smooth (in the fractal's intrinsic-absorption band) frequency dependence given in (62) by the functions $\mathbf{s}_\alpha$.

In the case $m = 0$, i.e., when radiation of the maximum frequency (i.e. of the highest harmonic) is generated, we can verify in full analogy with the preceding case that the amplitude of the effect is a homogeneous polynomial of degree n in A and C:

$$\langle\chi^{(nF)}\rangle \sim \langle\chi^{(nc)}\rangle R_m{}^{-3} k_L{}^n \sum_{j=0}^{n} a_j\langle A^j C^{n-j}\rangle, \quad (64)$$

where a_j are numerical coefficients that depend on n [cf. (48) and (55)].

The averaging in (64) is in the same manner as above. Since, however, (64) does not contain the complex-conjugate amplitudes A^* and C^*, the susceptibilities do not con-

tain large factors $\sim\Lambda^{n-1}$. The spectral dependence of the gain of the amplitude $\langle\chi^{(nF)}\rangle/\langle\chi^{(nc)}\rangle$ is given by the functions $\mathbf{s}_\alpha(x)$ and $\mathbf{s}_\alpha(-x/2)$ and by their derivatives up to the $(n-1)st$ [cf. (49) and (56)]; we denote it by $\tilde{J}_\alpha(\omega)$. This function varies over a characteristic frequency interval Ω_f; it is of the order of unity in the absorption band of the cluster. As a result, we obtain for the gain of the higher-harmonic generation the simple estimate

$$G_{max}^{(n)} \sim |\langle\chi^{(nF)}\rangle/\langle\chi^{(nc)}\rangle|^2 \sim |k_L|^{2n}(R_0/R_m)^{6n}|\mathcal{J}_\alpha(\omega)|^2. \quad (65)$$

The nth order nonlinear impurity susceptibility of the fractal is thus larger than that for free impurity molecules by the factor (63) which is proportional to the $2(n-1)$ st power of the larger parameter Ω_f/Γ. The only exception is the case higher-harmonic generation (65), which does not contain this large parameter [cf. (9) and the discussion that follows].

6. CONCLUDING REMARKS

Let us briefly summarize and discuss the main results and principles of the present paper. We have developed a theory for nonlinear susceptibilities of impurity molecules bound to a fractal. The results for CARS (PC) and for third- and second-harmonic generation are given by Eqs. (16), (36)–(39); (45), (49), (50); (52), and (56)–(58) respectively.

The enhancement of the nonlinear effects is due to the presence, near the fractal's monomers, of strong local fields greatly exceeding (by up to several orders) the mean (macroscopic) field. The strong local fields are due in turn to the following interrelated properties of the fractal: the quasiresonant character of the spectrum (partial preservation of the individuality of the isomers) and the (mainly) inhomogeneous origin of its broadening, the disorder of the structure, and the strong fluctuations. Strong local fields are produced in the vicinities of monomers that are at resonance with the external field (and for which the inhomogeneous frequency shift of the resonance compensates for the detuning). The strengths of these fields are proportional to the Q factor of the monomer.

Using the foregoing qualitative picture, we obtained simple upper- and lower-bound estimates of the value of the effect (9). These two estimates differ substantially: the upper contains the large factor $(\Omega_f/\Gamma)\gg 1$, but the lower does not. These estimates are valid apart from inessential factors that account for the influence of the Lorentz field and for the interaction of the generated radiation with the fractal.

The results (63) and (65) of the complete theory, obtained for nonlinearity of any order, indicate which of the limiting estimates (9) correspond to the different parametric effects [cf. the discussion following Eq. (65)]. Namely, for the generation of higher harmonics (in which the frequencies of all the photons are additive) the estimate of the gain $G_{max}^{(n)}$ (65) is always the lower limit of (9). This follows formally from the fact all the poles of the averaged susceptibility as a complex function of the frequency lie in one (lower) half-plane [c.f., e.g., the analytic properties of (47) and (48) with (10) taken into account]. Physically, this fact means destructive influence of the fluctuating phase of the generated field when the latter is averaged over an ensemble of fractals.

Another result (63) was obtained for processes in which the susceptibility (59) contains at least one negative frequency. When the excitation is almost degenerate in frequency (the frequencies of all the exciting fields are equal to within Γ), the value of $G_{max}^{(n)}$ (63) is estimated by the upper limit in (9), i.e., the phase fluctuations of the susceptibility $\chi^{(nF)}$ are insignificant. Effects of this type are of third order, such as PC and also CARS at small differences between the frequencies of the two exciting fields. When the detuning increases and reaches almost the total width Ω_f of the fractal spectrum, the value of $G_{max}^{(n)}$ decreases to the lower-bound estimate (9), a fact described by the factor $g(\Delta\omega)$ in (39) and (63). Thus, at finite detunings the destructive effect of the susceptibility phase fluctuations begins to influence also effects with photon subtraction.

The indicated dependence of the form of the gain on the character of the processes is not obvious beforehand, for in all cases the local fields are equally enhanced (by ω_m/Γ times) compared with the mean field [see the estimate (6)]. The actually considered effects, however, are coherent ones in which the amplitude of the field is averaged and the important role in the averaging over the fractal ensemble is played by the fluctuations of the phase. (The enhancement of the coherent effects was estimated earlier[10] only from the increase of the modulus of the local field, while the phase was disregarded; nor was the spectrum broadening due to the disorder of the medium taken into account.)

The dependence [see (39) and (63)] of the gains of effects that include photon subtraction on the photon frequency difference $\Delta\omega$ is contained in the factor g. The contour of $g(\Delta\omega)$ has the character of a two-photon resonance: it is determined by the value of $\Delta\omega$ compared with 2Γ (we emphasize that Γ is the natural resonance width of an isolated monomer) and is independent of the positions of the system levels. It is this last circumstance that causes the immunity of this resonance to inhomogeneous broadening, meaning its natural width and its contribution to the gain. The onset of such a nonlinear resonance, notwithstanding the assumed linearity of the monomer susceptibility, is due to the interaction between the monomer and the nonlinear impurity.

The gain $G^{(n)}$ and its smooth dependence on the frequency of the exciting radiation depend strongly on the fractal dimensionality. These dependences are illustrated in Figs. 1–3 for effects of third and second order. With increase of the fractal dimensionality, the value of $G^{(n)}$ decreases and its spectral profile broadens. When the fractal dimensionality tends to the trivial $D\to 3$, the gain of the nonlinear susceptibilities vanishes (our theory, however, is no longer valid in this case).

In sum, we can state that effects with photon subtraction are much more enhanced than higher-harmonic generation. It is important that the gain estimate (63) does not depend on the number of the subtracted photons. The spectral dependence of the effects discussed reveals resonances of impurity centers as well as a nonlinear monomer resonance. To our knowledge, these nonlinear resonances have heretofore not been considered. Their distinctive features are due to the interaction between strong fields and an entity consisting of a nonlinear impurity and linear element (a monomer contained in a disordered fractal medium). The enhancement of the nonlinear susceptibility depends substantially on

the Hausdorff dimensionality of the fractal.

We have obtained above the nonlinear susceptibilities averaged over an ensemble of fractals. Since the fluctuations in the fractal are strong, the mean squared fluctuations of the susceptibilities can be of the order of the mean values. This, of course, does not make the mean values meaningless; when radiation interacts with $M \gg 1$ independent fractal particles (e.g., with a coloidal solution or a suspension), the measured fluctuations decrease by a factor $M^{1/2}$. Nonetheless, if M is not very large, these fluctuations are observable, and therefore their calculation is of independent interest. We hope to consider this calculation in the future.

Experimental observation of the predicted effects will permit a study of the properties of the monomers that make up the fractal (the question of what is a monomer is generally speaking not trivial, cf. Ref. 5), and in particular to find the spectral width Γ from the contour $g(\Delta\omega)$. Substitution of Γ in the expression for G allows us to calculate this factor and to compare it with the value obtained independently in experiment.

The most promising fractal objects for first experiments are apparently clusters made from noble metals, for example particles in colloidal solutions. Interest attaches also to fractal surfaces produced by sputtering thin films, although the theory requires certain modifications to be applicable to them.

The spectral properties of impurity particles that can be studied with the aid of CARS on fractally-bound molecules are similar to those obtained on free molecules. However, the much larger predicted enhancement of the CARS intensity [see the discussion of Eq. (43)] will undoubtedly add to the capabilities of this method at lower frequencies and will accordingly enhance its analytic capabilities.

Inasmuch as four-wave parametric processes can be observed in the presence of amplification with a much smaller number of molecules, fractals with impurity centers constitute a promising nonlinear medium, especially if miniaturization of samples is required.

Besides parametric processes, our theory describes also the nonlinear absorption, which is determined by the imaginary part of the nonlinear susceptibility. The latter pertains to processes with subtraction of photons and is therefore maximally enhanced in accordance with (62). In particular, the two-photon-absorption coefficient is proportional to $\mathrm{Im}\,\chi^{(3)}(-\omega_1, \omega_1, \omega_2, -\omega_2)$ [see (16), (36), and (37)]. According to our theory effects determined by nonlinear absorption are also enhanced, viz., nonlinear-impurity photochemistry, ionization, dissociation, photoeffect, and others.

The authors are deeply grateful to Yu. E. Nesterikhin, A. K. Popov, and S. G. Rautian for helpful discussions and constant help with the work. We thank also S. Yu. Novozhilov and A. M. Shalagin for valuable remarks.

[1)] The numerical factor in the trace Sp (TT^+) of Ref. 5 is in error. The correct value is given in Eq. (40).

[1]B. M. Mandelbrot, Fractals, Form, Chance, and Dimensions, Freeman, 1977. The Fractal Geometry of Nature, Freeman, 1972.
[2]Ya. B. Zel'dovich and L. D. Sokolov, Usp. Fiz. Nauk **146**, 493 (1985) [Sov. Phys. Usp. **28**, 608 (1985)].
[3]B. M. Smirnov, Usp. Fiz. Nauk **149**, 481 (1986) [**29**, 481 (1986)].
[4]M. V. Berry and I. C. Percival, Opt. Acta **33**, 577 (1986).
[5]V. M. Shalaev and M. I. Shtokman, Zh. Eksp. Teor. Fiz. **92**, 509 (1987) [Sov. Phys. JETP **65**, 287 (1987)]. Preprint No. 39, Phys. Inst. Siberian Div. USSR Acad. Sci., Krasnoyarsk, 1986.
[6]C. Kittel, *Elementary Solid State Physics*, Wiley, 1962.
[7]N. Bloembergen, *Nonlinear Optics*, Benjamin, 1965.
[8]L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media*, Pergamon, 1984.
[9]M. Moskovits, Rev. Mod. Phys. **57**, Part 1, 785 (1965).
[10]J. P. Heritage and A. M. Glass, in: *Surface Enhanced Raman Scattering*, R. K. Chang and T. E. Furtak, eds., Plenum, 1982.

Translated by J. G. Adashko