Nonlinear absorption and dispersion in a two-level system with permanent dipole moments

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We calculate the third-order nonlinear absorption and dispersion (self-phase-modulation and cross-phase modulation) of a homogeneously broadened two-level molecular system with permanent dipole moments interacting with (1) an optical field of frequency ω, and (2) two optical fields of frequency ω_1 and ω_2, i.e., the susceptibilities $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$ and $\chi^{(3)}(-\omega_1;\omega_1,-\omega_2,\omega_2)$. Sharp features in the nonlinear absorption and dispersion appear whenever one- or two-photon resonance conditions are met. Only features corresponding to one-photon resonance arise if the difference between the permanent dipole moments of the levels, $\Delta\mu$, vanishes. The $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$ spectrum has two features, one at frequency ω_{ba} dominated by contributions proportional to μ_{ab}^4, where μ_{ab} is the transition dipole moment of the two levels with transition frequency ω_{ba}, and the other at frequency $\omega_{ba}/2$ dominated by contributions proportional to $(\Delta\mu)^2\mu_{ab}^2$. Sharp features in $\chi^{(3)}(-\omega_1;\omega_2,-\omega_2,\omega_1)$ appear when ω_2 is near $\omega_{ba},\omega_1,\omega_1+\omega_{ba}$, and $|\omega_1-\omega_{ba}|$.

I. INTRODUCTION

In this paper we analyze the third-order nonlinear-optical susceptibilities for a homogeneously broadened two-level system. We treat a (molecular) system with states that are not parity eigenstates and have permanent dipole moments. It has been shown previously[1–5] that such systems exhibit wave mixing and multiphoton processes of arbitrary order when the dipole moments of the two levels are not equal. Recently, we calculated the two-photon absorption and Raman properties of such systems.[2,6] We also calculated their sum- and difference-frequency-generation (SFG and DFG) susceptibilities,[7] second-harmonic-generation (SHG) susceptibility, and the electric-field-induced second-harmonic-generation (EFISH) susceptibility.[8]

Third-order nonlinearities in such systems have contributions proportional to either of the dipole moment products $(\Delta\mu)^2\mu_{ab}^2$ and μ_{ab}^4, where $\Delta\mu\equiv\mu_{aa}-\mu_{bb}$ is the difference between the permanent dipole moments of the two levels and μ_{ab} is the transition dipole moment. Since these contributions contain only even powers of the dipole moments, they do not vanish in centrosymmetric media. We present results for media in which the molecules comprising the system are aligned. The third-order susceptibilities of a randomly aligned molecular system are two-fifths of the susceptibilities of an aligned medium. For the sake of simplicity we treat a case where $\Delta\mu$ and μ_{ab} are parallel. Other cases are analyzed in a similar manner.

Experimental measurements of two-photon absorption cross sections (proportional to $\mathrm{Im}[\chi^{(3)}(-\omega;\omega,-\omega,\omega)]$), have been carried out by Hochstrasser, Sung, and Wessel[9] in molecules and molecular crystals. Self-focusing of laser beams has been extensively studied.[10] In fact, in certain regimes self-focusing may constitute the dominant feature in propagation of light.[11] Direct and accurate measurement techniques of the nonlinear refractive index of materials have been developed.[12] Self-phase-modulation and cross-phase modulation effects in fiber lasers and fiber soliton lasers have been well documented.[13] Phase-modulation effects in third-harmonic generation have also been studied experimentally[14] and theoretically.[15] Spectra of four-wave mixing in two-level systems were studied theoretically by Mollow[16] and by Boyd *et al.*[17] Calculations of the third-order susceptibilities for two-level systems with permanent dipole moments have, to the best of our knowledge, not been heretofore undertaken.

Using a formalism developed previously,[2,6,18] we expand the elements of the density matrix in a Fourier series. When the difference in the permanent dipole moments of the ground and excited state is nonzero ($\mu_{aa}\neq\mu_{bb}$), the *diagonal* elements of the density matrix representing the population probability densities of the levels (as well as the off-diagonal elements) have oscillating terms with frequencies equal to linear combinations of the impressed electromagnetic field(s) and contribute to the polarization at these frequencies. The microscopic polarization vector $\mathbf{P}$ of a two-level system whose levels have permanent dipole moments is given by $\mathbf{P} = \mathrm{Tr}(\underline{\rho}\,\underline{\boldsymbol{\mu}})=\boldsymbol{\mu}_{ab}(\rho_{ba}+\rho_{ab})+\boldsymbol{\mu}_{aa}\rho_{aa}+\boldsymbol{\mu}_{bb}\rho_{bb}$, where $\boldsymbol{\mu}_{ii}$ is the permanent dipole moment of level i. We present full steady-state (i.e., all the elements of the density matrix are taken to be in steady state) results for the third-order nonlinear absorption and dispersion since the appearance of diagonal elements of the density matrix in the expression for the optical polarization does not permit a quasisteady state, wherein only the polarization is taken to be in steady state, as in condensed phase systems without permanent dipole moments.[18]

The formalism is briefly reviewed in Sec. II and the resulting expressions are used in Sec. III for calculation of spectra. In Sec. IV we present a discussion on our results, and a conclusion.

II. FORMALISM

Following the treatment in Ref. 7, the state of the optically active two-level medium at any time is given by its density matrix

$$\underline{\rho}(t)=\begin{bmatrix}\rho_{aa} & \rho_{ab}\\ \rho_{ba} & \rho_{bb}\end{bmatrix}, \tag{1}$$

and its effect on the electric field is given by the wave equation

$$\frac{\partial^2}{\partial t^2}\mathbf{E}(x,t)-c^2\frac{\partial^2}{\partial x^2}\mathbf{E}(x,t)=-N\mu_0 c^2\frac{\partial^2}{\partial t^2}\mathbf{P}(x,t)\ , \tag{2}$$

where the microscopic polarization vector is given by $\mathbf{P}=\mathrm{Tr}(\underline{\rho}\,\underline{\boldsymbol{\mu}})$ and N is the density of the optically active molecules. The Liouville equation (including decay) for the density matrix is given by

$$\partial_t\underline{\rho}=(-i/\hbar)[\underline{H}_0-\eta\mathbf{E}\cdot\underline{\boldsymbol{\mu}},\underline{\rho}]-\underline{\Gamma}\,\underline{\rho}\ , \tag{3}$$

where η is the Lorentz-Lorentz correction factor, which is given by $\eta(\omega)=[n^2(\omega)+2]/3$, and the decay tensor $\underline{\Gamma}$ is taken to be diagonal and is given in terms of the phenomenological decay rates for the excited state decay to the ground state, $\gamma=1/T_1$, and for the decay of the off-diagonal density matrix elements $\Gamma=1/T_2$. The dipole moment vector matrix $\underline{\mu}$ is given by

$$\underline{\mu}=\begin{bmatrix}\mu_{aa} & \mu_{ab}\\ \mu_{ba} & \mu_{bb}\end{bmatrix}, \tag{4}$$

where we have used $\mu_{ab}=\mu_{ba}$, and each element of this matrix is the product of the magnitude of the dipole moment matrix element and the cosine of the angle between this dipole moment and the electric fields. The electric field is taken as

$$\mathbf{E}(x,t)=\mathbf{A}(x,t)\exp\{i[n(\omega_1)k_1x-\omega_1t]\}+\mathbf{B}(x,t)\exp\{i[n(\omega_2)k_2x-\omega_2t]\}+\text{c.c.} \tag{5}$$

In what follows we include the local-field correction factors in the field amplitudes. The density matrix elements can be expanded in a Fourier series of the form[1-3]

$$\rho_{ij}=\sum_{m,l}\rho_{ij}^{(m,l)}\exp\{im[n(\omega_1)k_1x-\omega_1t]+il[n(\omega_2)k_2x-\omega_2t]\}\ . \tag{6}$$

After substitution of the expansion (6) and Eqs. (4) and (5) into Eq. (3), and making the steady-state approximation, we obtain the Fourier components that enter the expressions for the optical polarization at the frequencies ω_1 and ω_2. This formalism and the full expressions for the polarization are presented in detail in Refs. 2 and 7. By substituting the expansions in Eqs. (3)–(5) for $\mathbf{E}$, $\underline{\mu}$, and $\underline{\rho}$, and making the slowly varying envelope approximation for the field at the generated frequency (i.e., assuming $|\nabla^2G|\ll 2ink\nabla G|$ and $|\partial_t^2G|\ll 2i\omega\partial_tG|$ where G is either A or B) we obtain

$$\left[\frac{n(\bar\omega_1)}{c}\frac{\partial}{\partial t}+\frac{\partial}{\partial x}\right]A(\bar\omega_1,x,t)=i\frac{2\pi N\bar\omega_1}{cn(\bar\omega_1)}P(\bar\omega_1,x,t)\equiv[\alpha_{\mathrm{l,nl}}(\bar\omega_1,A,B)/2-in_{\mathrm{l,nl}}(\bar\omega_1,A,B)k]A(\bar\omega_1,x,t)\ , \tag{7}$$

$$\left[\frac{n(\bar\omega_2)}{c}\frac{\partial}{\partial t}+\frac{\partial}{\partial x}\right]B(\bar\omega_2,x,t)=i\frac{2\pi N\bar\omega_2}{cn(\bar\omega_2)}P(\bar\omega_2,x,t)\equiv[\alpha_{\mathrm{l,nl}}(\bar\omega_2,A,B)/2-in_{\mathrm{l,nl}}(\bar\omega_2,A,B)k]B(\bar\omega_2,x,t)\ , \tag{7'}$$

where the bar over the ω indicates that this is the central laser frequency of the field, $n(\bar\omega)$ is the background refractive index of the medium at frequency $\bar\omega$, and $\alpha_{\mathrm{l,nl}}$ and $n_{\mathrm{l,nl}}$ denote the linear and nonlinear absorption coefficient and refractive index of the fields. The optical polarizations at these frequencies are given by

$$P(\bar\omega_1)=\mu_{ab}(\rho_{ba}^{(1,0)}+\rho_{ab}^{(1,0)}-\Delta\mu(\rho_{aa}^{(1,0)}-\rho_{bb}^{(1,0)})/2\ , \tag{8}$$

$$P(\bar\omega_2)=\mu_{ab}[\rho_{ba}^{(0,1)}+\rho_{ab}^{(0,1)})-\Delta\mu(\rho_{aa}^{(0,1)}-\rho_{bb}^{(0,1)})/2\ . \tag{9}$$

We shall from now on drop the bar over the ω's. Equations (8) and (9) contain first- and third-order contributions to the polarization at the frequencies of the impressed fields. Extraction of the nonlinear contributions is performed as follows. In the case of $\chi^{(3)}(-\omega_1;\omega_1,-\omega_2,\omega_2)$, $P(\omega_1)$ is calculated twice for weak $A(\omega_1)$, in one case $|B(\omega_2)|^2$ is taken to be zero and in the second case it is given a small value. The third-order susceptibility $\chi^{(3)}(-\omega_1;\omega_2,-\omega_2,\omega_1)$ is determined from the equation

$$\frac{2\pi N}{c}[P(\omega_1,A,|B|^2)-P(\omega_1,A,0)]=n(\omega_1)\chi^{(3)}(-\omega_1;\omega_2,-\omega_2,\omega_1)A|B|^2\ . \tag{10}$$

The susceptibility $\chi^{(3)}(-\omega_1;\omega_1,-\omega_1,\omega_1)$, when only one field with frequency ω_1 is present is obtained by a similar procedure.

We present results of calculations with the background indices of refraction taken as unity and therefore the product of all local-field correction factors is also unity. In general, these local-field correction factors depend upon the dispersion of the medium which includes bulk contributions of the refractive index, and are therefore sample specific.

III. RESULTS

Each of the contributions to the third-order susceptibilities is proportional to a product of four dipole and three frequency denominators. Sharp features in the susceptibilities occur whenever a frequency denominator is on resonance.

We first consider third-order processes arising from the interaction of a single frequency field with the medium (see Table I). Only two such processes exist. In the first process the third-order optical response is due to population changes induced by a one-photon process. The modified population interacts again with the field and the overall process results in no net photon absorption. This process has a resonance at frequency ω_{ba} and does not involve $\Delta\mu$. The second process involves two-photon ab-

TABLE I. Parameters of the medium.

Parameters	Symbol	(a.u.)	(cgs)
transition dipole moment	μ_{ab}	3.0	7.62×10^{-18} esu cm
permanent dipole moment	$\Delta\mu$	3.0	7.62×10^{-18} esu cm
resonance frequency	ω_{ab}	0.1	4.13×10^{15} sec^{-1}
decay time	$T_1=\gamma^{-1}$	2.74×10^5	6.62 psec
dephasing time	$T_2=\Gamma^{-1}$	1001.4	0.0242 psec
population density	N	2.96×10^{-9} bohr^{-3}	2.00×10^{16} cm^{-3}
refractive index	n	1.0	1.0

sorption resulting in optical excitation. It is proportional to $(\Delta\mu)^2\mu_{ab}^2$ and has a resonance at frequency $\omega_{ba}/2$. Figures 1 and 2 show the nonlinear absorption and dispersion of the system where the optical field contains only one frequency ω, which is scanned around ω_{ba} and $\omega_{ba}/2$, respectively. In Fig. 1 the nonlinear contribution to the absorption is positive (i.e., the absorption is reduced via the nonlinear process) since the near resonance optical field burns a hole in the population and partially saturates the absorption. In Fig. 2, stimulated absorption adds to the linear absorption near $\omega=\omega_{ba}/2$, and the nonlinear contribution to the absorption is negative. The width of the nonlinear absorption in Figs. 1 and 2 are different; both are smaller than Γ. The nonlinear dispersion in Figs. 1 and 2 has opposite behavior, as is the case with the nonlinear absorption of these spectra. If $\mu_{aa}=\mu_{bb}$ the features shown in Fig. 1 remain nearly unchanged but the nonlinear absorption and nonlinear dispersion in Fig. 2 nearly vanish.

Let us now consider the nonlinear third-order processes involving interaction of the medium with light of two frequencies, ω_1 and ω_2. In general there are four possible processes which must be considered. The first process is similar to the first process described above for the single frequency case. The medium is excited by a one-photon process, then the modified population interacts with the field of the second frequency. Two other processes involve stimulated two-photon excitation (or deexcitation). In such processes a photon of one frequency is absorbed and a photon of the second frequency is either absorbed (stimulated two-photon-absorption–second process described above for the single-frequency case) or emitted (stimulated Raman scattering). Such two-photon processes become efficient when $\omega_{ba}\approx\omega_1+\omega_2$ and $\omega_{ba}\approx\omega_2-\omega_1$, respectively, and require a nonvanishing $\Delta\mu$. The fourth process is similar to the Raman process. It involves absorption of a photon of one frequency and emission of a photon of the second frequency. However this process does not involve any transition in the system and is therefore more efficient when the two frequencies are close to each other. This process does not involve $\Delta\mu$ but if $\Delta\mu\neq0$, the process is accompanied by difference frequency generation.

Figure 3 shows the cross-phase modulation and nonlinear absorption (gain) induced at frequency $\omega_1=\omega_{ba}/2-6\Gamma$ by a field at frequency ω_2, where ω_2 is scanned around $\omega_{ba}/2$. As expected, there are resonance features at $\omega_2=\omega_{ba}-\omega_1$ with width Γ (type-2 process described above). Much sharper features appear in both spectra at $\omega_2\approx\omega_1$ (type-4 process). A blowup of this region is shown in the inset of Fig. 6. Note that the nonlinear absorption has a dispersion-type profile and the nonlinear dispersion has an absorption-type profile. These features arise from second-order diagonal elements of Eq. (6) which are proportional to the frequency denominator $(\omega_1-\omega_2-i\gamma)^{-1}$. This denominator is small when $\omega_2\approx\omega_1$, especially since we have taken $\gamma\ll\Gamma$ as is the case in condensed phases. Only the sharp features around $\omega_2\approx\omega_1$ are present when $\mu_{aa}=\mu_{bb}$.

Interesting phenomena occur also in the nonlinear interaction of two optical fields with the medium when one

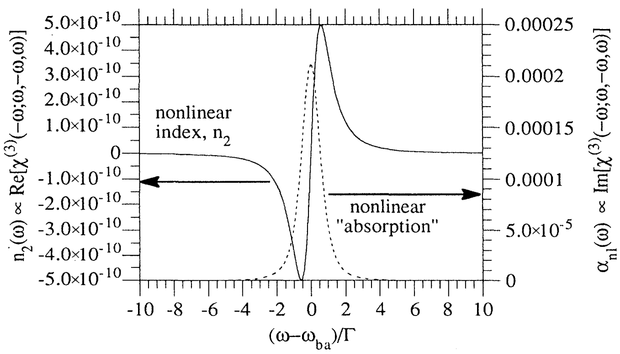

FIG. 1. Nonlinear dispersion and absorption, $n_2(\omega)$ and $\alpha_{nl}(\omega)$, of a two-level system, $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$, scanned around $\omega=\omega_{ba}$. These quantities are proportional to the real and imaginary parts of the susceptibility $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$.

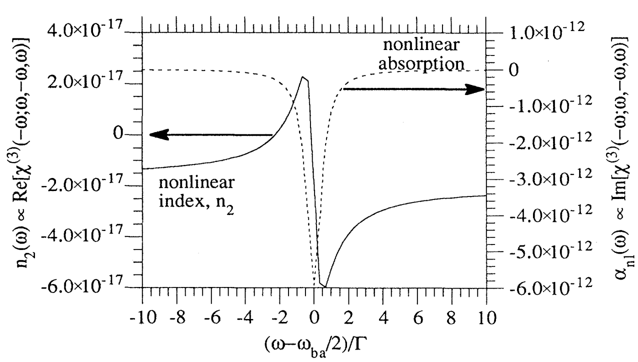

FIG. 2. Same as Fig. 1 but scanned around $\omega=\omega_{ba}/2$.

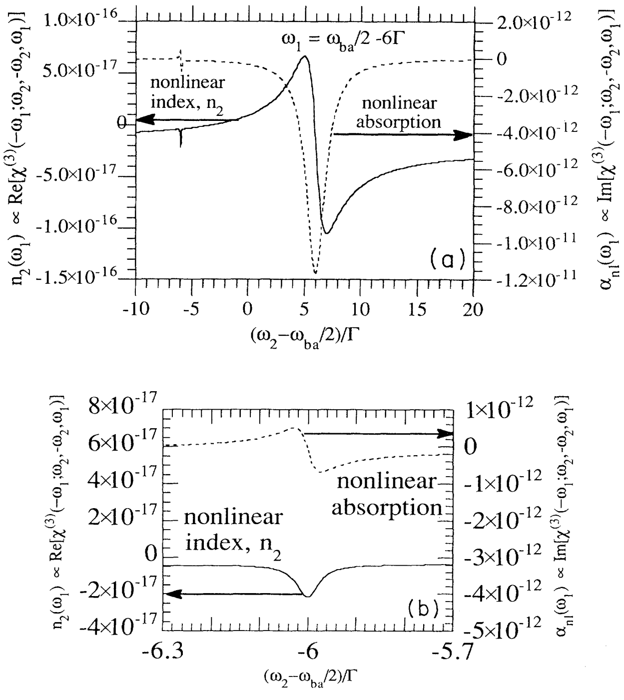

FIG. 3. (a) Nonlinear refractive index and nonlinear absorption, $n_2(\omega_1)$ and $\alpha_{\rm nl}(\omega_1)$, vs ω_2 with $\omega_1=\omega_{ba}/2-6\Gamma$. These quantities are proportional to the real and imaginary parts of $\chi^{(3)}(-\omega_1;\omega_2,-\omega_2,\omega_1)$, respectively. (b) describes in more detail the features in the region $\omega_2\approx\omega_1$.

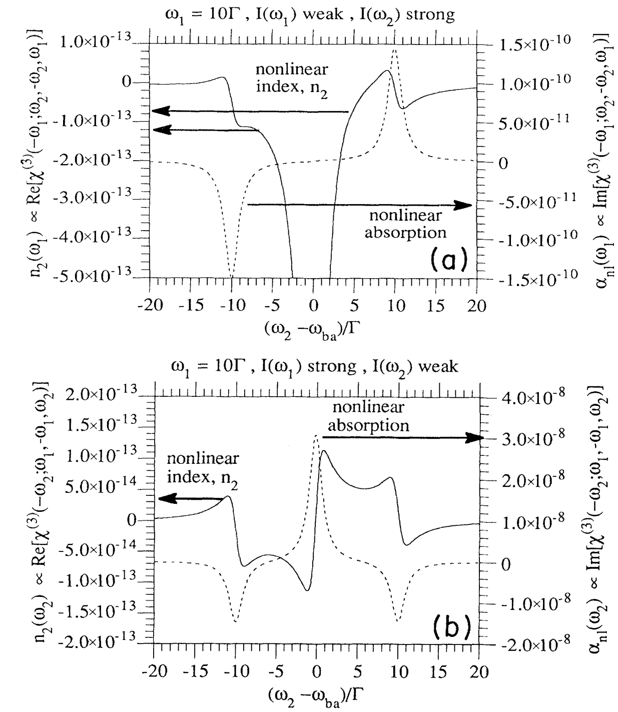

FIG. 4. Third-order susceptibilities induced in the medium due to its nonlinear interaction with two optical fields. One field is low frequency $\omega_1=10\Gamma$ and the other frequency ω_2, is scanned around ω_{ba}. (a) $\chi^{(3)}(-\omega_1;\omega_2,-\omega_2,\omega_1)$; (b) $\chi^{(3)}(-\omega_2;\omega_1,-\omega_1,\omega_2)$.

of the frequencies is small ($\omega_1=10\Gamma$ in this case) and the other frequency is close to ω_{ba}. In this regime the nonlinear absorption (gain) spectrum is resolved but the features corresponding to nonlinear dispersion overlap. Figures 4(a) and 4(b) show the third-order susceptibilities, $\chi^{(3)}(-\omega_1;\omega_2,-\omega_2,\omega_1)$ and $\chi^{(3)}(-\omega_2;\omega_1,-\omega_1,\omega_2)$, induced in the medium due to its nonlinear interaction with fields of frequencies ω_1 and ω_2. In both figures, ω_2 is scanned through the same region around ω_{ba}. The center of Fig. 4(a) is mainly affected by the population changes induced by the field with near-resonance frequency ω_2 (type-1 process). In this region, the linear absorption of level a and the gain of level b at the small frequency ω_1 are weak. Therefore, population changes do not affect $\mathrm{Im}[\chi^{(3)}(-\omega_1;\omega_1,-\omega_2,\omega_2)]$ and only peaks corresponding to two-photon absorption and Raman scattering are obtained. However, although unable to affect the absorption, population changes modify the center of the nonlinear dispersion by introducing a hole shown in Fig. 4(a). This is due to nonzero contributions of levels a and b to the refractive index at frequency ω_1. Also in this spectrum, the contributions of stimulated two-photon and Raman processes interfere constructively and destructively with the red and blue edges of the central hole, respectively. A similar interference occurs also in Fig. 4(b) except that here the central feature in the spectrum of the nonlinear dispersion is not induced through population changes but by introducing power effects on the linear absorption.

IV. CONCLUSION

We investigated the third-order susceptibilities of two-level systems with unequal permanent dipole moments. We showed that the $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$ spectrum has only two features, one at frequency ω_{ba} dominated by contributions proportional to μ_{ab}^4, and the other at frequency $\omega_{ba}/2$ dominated by contributions proportional to $(\Delta\mu)^2\mu_{ab}^2$.

The four processes affecting the cross-induced susceptibility $\chi^{(3)}(-\omega_1;\omega_2,-\omega_2,\omega_1)$ were discussed and their effects on the spectra were elucidated. Sharp features in $\chi^{(3)}(-\omega_1;\omega_2,-\omega_2,\omega_1)$ appear whenever ω_2 is scanned in the vicinity of $\omega_{ba},\omega_1,\omega_1+\omega_{ba}$, and $|\omega_1-\omega_{ba}|$.

We described the nonlinear absorption and dispersion of a two-level system arising from the third order susceptibility $\chi^{(3)}$. We did not consider the description of the nonlinear response of molecular systems including more than two levels. Whenever coupling between the ground level and a second level is much stronger than coupling to other levels in the system over a frequency range of interest, our two-level description should be adequate to describe the nonlinear optical properties of the system. Otherwise, the actual behavior of the nonlinear absorption and dispersion may be radically different.

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