# Hyperpolarizability of the hydrogen atom

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The frequency dependence of the hyperpolarizability  $(\gamma)$  of the nonrelativistic hydrogen atom is calculated for a range of third-order nonlinear optical processes using an expansion in Sturmian functions. It is shown that the quantitative relations between the various nonlinear optical processes are made much clearer when  $\gamma$  is treated as a function of an effective frequency  $\omega_L$ . The detailed, systematic exploration of the dispersion of  $\gamma$  of the hydrogen atom presented here should serve as a guide in the analysis and interpretation of experimental or theoretical results for less accessible systems.

#### INTRODUCTION

There has been much recent interest in third-order nonlinear optics, 1,2 and since the nonlinear susceptibility of an optical medium governs its nonlinear response to incident electric fields, the susceptibility has in turn become the focus of much study. In gases, a wide range of third-order nonlinear optical phenomena may be understood in terms of either the macroscopic susceptibility  $\chi^{(3)}$  or the closely related microscopic second hyperpolarizability  $\gamma$  of the constituent atoms or molecules.<sup>3,4</sup> Fourth-order perturbation theory gives an explicit expression for  $\gamma$  which applies for all third-order nonlinear optical processes, so all these optical processes are in fact intimately related. 5-7 However,  $\gamma$  is a fourth-rank tensor function of three applied field frequencies and polarizations, with contributions from electronic, vibrational, and orientational degrees of freedom of a molecule.<sup>3,8</sup> Because of these complexities it is not clear in practice precisely what will be the form of the relations between the hyperpolarizabilities for different nonlinear optical processes. While symmetry considerations may greatly reduce the number of independent tensor elements of  $\gamma$ ,<sup>4</sup> even for a spherical atom the relations between the hyperpolarizabilities for different processes are fairly unconstrained. Thus it would be instructive to examine the relations which actually exist for some particular simple atom or molecule.

Experimental measurements give only fragmentary and rather inaccurate data on the relations between  $\gamma$  for various nonlinear optical processes. A,9 And though there have been many calculations of  $\gamma$  performed for a range of atoms and molecules, the results of these calculations are almost as fragmentary and inaccurate as the experimental results. The only systems for which ab initio calculations with an accuracy of a few percent or better have been performed are the hydrogen and helium atoms and the  $H_2^+$  and  $H_2$  molecules. The static  $\gamma$  of the nonrelativistic hydrogen atom is known exactly,  $^{12,13}$  while the best static calculations for the helium atom agree to better than 1%.  $^{14-17}$  The accuracy of the best static results for  $H_2^+$  and  $H_2$  is probably better than 1%.  $^{18-22}$  Accurate dynamic calculations of  $\gamma$  have been

reported for the H and He atoms. The dynamic calculation of  $\gamma$  for third-harmonic generation (THG) in hydrogen is essentially exact.<sup>23</sup> The dynamic calculations of  $\gamma$ for the dc Kerr effect, electric-field-induced secondharmonic generation (ESHG) and THG in helium are thought to be accurate to about 1%, but the calculated values of  $\gamma$  were only reported at a few points. 16,17 More accurate and complete results for He would be most useful, especially for the calibration of experimental measurements, but a very accurate calculation of  $\gamma$ for He is likely to be difficult. On the other hand, essentially exact results are easily obtained for the hydrogen atom by extending the method of Mizuno.<sup>23</sup> In what follows we will calculate the frequency dependence of the hyperpolarizability of the hydrogen atom as a guide to the behavior which may be seen in more complicated systems.

## STURMIAN EXPANSION FOR $\gamma_H$

The hyperpolarizability of the ground-state hydrogen atom is most readily calculated using the Sturmian Coulomb Green's function.<sup>23</sup> The Sturmian expansion is preferable to the basis of hydrogenic radial functions, which they closely resemble, because the Sturmian functions form a complete discrete basis without continuum functions.<sup>24</sup> The Sturmian function  $S_{nlq}(r)$  satisfies

$$\left[ -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} - \frac{n\alpha}{r} - E \right] S_{nl\alpha}(r) = 0 , \qquad (1)$$

where

$$\alpha = (-2E)^{1/2} \ . \tag{2}$$

Atomic units,  $\hbar = e = \mu = 1$ , will be used throughout. The normalization is chosen as

$$(S_{nl\alpha} | r^{-1} | S_{n'l\alpha}) = \int_0^\infty S_{nl\alpha}(r) r^{-1} S_{n'l\alpha}(r) dr = \delta_{nn'}.$$
 (3)

The  $S_{nl\alpha}(r)$  are related to the normalized hydrogenic radial functions  $u_{nl}(Zr)$  for an atom with nuclear charge Z by

$$S_{nl\alpha}(r) = -nZ^{-1/2}u_{nl}(n\alpha r)$$
 (4)

Equation (1) differs from the Schrödinger equation for the hydrogen atom in that E is a fixed constant. For example, when considering the static hyperpolarizability, we choose E to be the hydrogenic atom ground-state energy,  $E=-\frac{1}{2}Z^2$ .

Applying diagrammatic perturbation theory, 25 ignor-

Applying diagrammatic perturbation theory,  $^{25}$  ignoring damping,  $^{7}$  and expanding in a basis of Sturmian Coulomb Green's functions and spherical harmonics,  $^{23}$  and noting that  $\Delta l = \pm 1$  for dipole-allowed transitions, the hyperpolarizability of the ground-state hydrogen atom may be written as

$$\gamma_{\alpha\beta\gamma\delta}(-\omega_{\sigma};\omega_{1},\omega_{2},\omega_{3})$$

$$=\sum_{n_{1}}P\sum_{n_{2}}\sum_{n_{3}}\sum_{l_{2}}C(\alpha\beta\gamma\delta l_{2})F(n_{1}n_{2}n_{3}\theta_{1}\theta_{2}\theta_{3}l_{2}),$$
(5)

where P is the permutation operator and  $\sum P$  denotes

summation over the 24 terms obtained by permuting the frequencies  $(-\omega_{\sigma}, \omega_1, \omega_2, \omega_3)$  along with their associated spatial subscripts  $(\alpha, \beta, \gamma, \delta)$ . The frequency of the induced polarization  $\omega_{\sigma}$  is  $\omega_{\sigma} = \omega_1 + \omega_2 + \omega_3$ . The factor  $C(\alpha\beta\gamma\delta l_2)$  contains the angular dependence of  $\gamma$  and is given by

$$C(\alpha\beta\gamma\delta l_{2}) = \sum_{m_{1}} \sum_{m_{2}} \sum_{m_{3}} \langle 00 | \hat{\mathbf{r}}_{\alpha} | 1m_{1} \rangle \langle 1m_{1} | \hat{\mathbf{r}}_{\delta} | l_{2}m_{2} \rangle$$

$$\times \langle l_{1}m_{2} | \hat{\mathbf{r}}_{\gamma} | 1m_{3} \rangle \langle 1m_{3} | \hat{\mathbf{r}}_{\beta} | 00 \rangle ,$$
(6)

where the spherical harmonics  $Y_{lm}(\theta,\phi)$  appearing in the expectation values of the various Cartesian components  $\hat{\mathbf{r}}_{\alpha}$  of the unit vector  $\hat{\mathbf{r}}$  are denoted  $|lm\rangle$ . Because of the  $\Delta l$  selection rule,  $C(\alpha\beta\gamma\delta l_2)$  vanishes unless  $l_2=0$  or 2. The dynamics are contained in the final factor,

$$F(n_{1}n_{2}n_{3}\theta_{1}\theta_{2}\theta_{3}l_{2}) = Z \frac{(S_{10Z} \mid r \mid S_{n_{1}1\alpha_{1}})(S_{n_{1}1\alpha_{1}} \mid r \mid S_{n_{2}l_{2}\alpha_{2}})(S_{n_{2}l_{2}\alpha_{2}} \mid r \mid S_{n_{3}1\alpha_{3}})(S_{n_{3}1\alpha_{3}} \mid r \mid S_{10Z})}{(n_{1}\alpha_{1} - Z)(n_{2}\alpha_{2} - Z)(n_{3}\alpha_{3} - Z)},$$

$$(7)$$

where

$$\alpha_1 = \alpha(\theta_1), \quad \theta_1 = \omega_1 + \omega_2 + \omega_3$$
 (8a)

$$\alpha_2 = \alpha(\theta_2), \quad \theta_2 = \omega_1 + \omega_2$$
 (8b)

$$\alpha_3 = \alpha(\theta_3), \quad \theta_3 = \omega_1$$
 (8c)

and

$$\alpha(\theta) = (Z^2 - 2\theta)^{1/2} \ . \tag{9}$$

The extra factor Z appears because  $S_{10Z}(r)$  has been substituted for  $u_{10}(Zr)$ .

The hyperpolarizability tensor of an isotropic system such as the spherically symmetric hydrogen atom has at most three independent components.<sup>4</sup> To completely specify  $\gamma$  in this case, it is sufficient to consider the set of four tensor components which satisfy the relation

$$\gamma_{zzzz} = \gamma_{zzxx} + \gamma_{zxzx} + \gamma_{zxxz} . \tag{10}$$

The values of  $C(\alpha\beta\gamma\delta l_2)$  required for the calculation of these tensor components of  $\gamma$  are given in Table I. The matrix elements required for the evaluation of Eq. (7) may be expressed as

 $(S_{n1\alpha} \mid r \mid S_{n'0\alpha'})$ 

$$=\frac{\left[(n^{2}-1)nn'\right]^{1/2}}{4}\sum_{\mu=0}^{n-2}(-1)^{\mu}\begin{bmatrix}n-2\\\mu\end{bmatrix}\sum_{\nu=0}^{n'-1}(-1)^{\nu}\begin{bmatrix}n'-1\\\nu\end{bmatrix}\begin{bmatrix}4+\mu+\nu\\3+\mu\end{bmatrix}\begin{bmatrix}\frac{(2\alpha)^{2}(2\alpha')}{(\alpha+\alpha')^{3}}\frac{4}{(\alpha+\alpha')^{2}}\end{bmatrix}\frac{(2\alpha)^{\mu}(2\alpha')^{\nu}}{(\alpha+\alpha')^{\mu+\nu}}$$
(11)

and

$$(S_{n2\alpha} \mid r \mid S_{n'1\alpha'}) = \frac{\left[ (n^2 - 4)(n^2 - 1)(n'^2 - 1)nn' \right]^{1/2}}{4} \sum_{\mu=0}^{n-3} (-1)^{\mu} \begin{bmatrix} n - 3 \\ \mu \end{bmatrix} \sum_{\nu=0}^{n'-2} (-1)^{\nu} \begin{bmatrix} n' - 2 \\ \nu \end{bmatrix} \begin{bmatrix} 6 + \mu + \nu \\ 3 + \mu \end{bmatrix} \frac{1}{(4 + \mu)(5 + \mu)} \times \left[ \frac{(2\alpha)^3 (2\alpha')^2}{(\alpha + \alpha')^5} \frac{4}{(\alpha + \alpha')^2} \right] \frac{(2\alpha)^{\mu} (2\alpha')^{\nu}}{(\alpha + \alpha')^{\mu + \nu}} . \tag{12}$$

The nonzero matrix elements form a band when  $\alpha = \alpha'$ . The exact static hyperpolarizability  $(\alpha = \alpha' = Z)$  is given as the sum of a finite number of terms  $(n_1, n_2, n_3 \le 5)$ .

### TREATMENT OF APPARENT DIVERGENCES

In the case that no pair of the frequencies sums to zero, Eq. (5) may be used as it stands. With  $\alpha\beta\gamma\delta = zzzz$ 

and  $\omega_1 = \omega_2 = \omega_3$  one obtains just the previously derived expression for THG.<sup>23</sup> However, if any pair of frequencies  $\omega_1, \omega_2, \omega_3$  does sum to zero, then at least one of the permuted terms in Eq. (5) will have  $\theta_2 = 0$  and  $\alpha_2 = Z$ . Then, for  $n_2 = 1$ , a factor  $(n_2\alpha_2 - Z) = 0$  appears in the denominator and the term diverges. We will show that such divergent terms cancel and that Eq. (5) may be put in a form which may be used even in the static limit.

TABLE I. Numerical values of the angular factor  $C(\alpha\beta\gamma\delta l_2)$  appearing in the expression for the atomic hyperpolarizability.

|      | 45 C      | $(\alpha\beta\gamma\delta l_2)$ |  |
|------|-----------|---------------------------------|--|
| αβγδ | $l_2 = 0$ | $l_2 = 2$                       |  |
| ZZZZ | 5         | 4                               |  |
| ZZXX | 5         | -2                              |  |
| zxzx | 0         | 3                               |  |
| zxxz | 0         | 3                               |  |

Note that the apparent divergences cannot arise if all three input frequencies are different in magnitude.

Our consideration will be restricted to processes with at most two distinct input field frequencies. The treatment becomes simpler because it is sufficient to consider just the two tensor components  $\gamma_{zzzz}$  and  $\gamma_{zxxz}$  in this case. For each value of  $l_2$  (=0 or 2) the terms in the expression for  $\gamma_{zxxz}$  may be grouped into three subsets according to the factor  $C(\alpha\beta\gamma\delta l_2)$  they contain. Thus all those permuted terms for which  $P\theta_2 = \pm(\omega_1 + \omega_2)$  contain the common factor  $C(zzxxl_2)$ . This subset of  $\sum P$  has eight terms and will be denoted  $\sum' P$ . Similarly, the subset of eight terms for which  $P\theta_2 = \pm(\omega_1 + \omega_3)$  has the common factor  $C(zxxzl_2)$ , and the final subset of eight terms for which  $P\theta_2 = \pm(\omega_2 + \omega_3)$  has the common factor  $C(zxzxl_2)$ . For  $\gamma_{zzzz}$  all subsets of  $\sum P$  have the same common factor  $C(zzzzzl_2)$ .

When  $n_2 = 1$ ,  $l_2 = 0$  the first subset of terms becomes

$$C(zzxx0) \sum_{n_1} \sum_{n_3} \sum' PF(n_1 1 n_2 \theta_1 \theta_2 \theta_3 0) ,$$
 (13)

with similar expressions for the other subsets. If  $\theta_2$ =0 every term in Eq. (13) diverges, but one finds that the divergent terms within a subset pair off and cancel in such a way as to give a finite result.

The divergent factor F is treated by taking the limit

$$\lim_{\theta_{2} \to 0} \left[ \frac{Zf(\theta_{2})}{\alpha(\theta_{2}) - Z} \right]$$

$$= \lim_{\theta_{2} \to 0} \left[ -\frac{Z^{2}f(\theta_{2})}{\theta_{2}} + \frac{f(\theta_{2})}{2} - \frac{Z^{2}df(\theta_{2})}{d\theta_{2}} \right], \quad (14)$$

where

$$f(\theta_2) = Z^{-1}[\alpha(\theta_2) - Z]F(n_1 1 n_3 \theta_1 \theta_2 \theta_3 0)$$
 (15)

When the permuted terms of Eq. (13) are written out and rearranged, the divergent first term on the right-hand side of Eq. (14) cancels identically. The derivative appearing in Eq. (14) is evaluated using the relations

$$\frac{d}{d\alpha'}(S_{n1\alpha} \mid r \mid S_{10\alpha'}) = (2\alpha')^{-1/2}(S_{n1\alpha} \mid r \mid S_{20\alpha'}) \quad (16)$$

and

$$\frac{d}{d\alpha} (S_{n1\alpha} | r | S_{10\alpha'}) 
= -(2\alpha)^{-1/2} (S_{n1\alpha} | r | S_{20\alpha'}) - \frac{2}{\alpha} (S_{n1\alpha} | r | S_{10\alpha'}) ,$$

(17)

which follow from Eq. (11). The final result is

$$G(n_{1}1n_{3}\theta_{1}0\theta_{3}0) = \lim_{\theta_{2}\to0} F(n_{1}1n_{3}\theta_{1}\theta_{2}\theta_{3}0)$$

$$= -\frac{1}{2}f(0)\left\{ \left[ \frac{Z}{\alpha_{1}} \right]^{2} \left[ 4 + \frac{n_{1}\alpha_{1}}{n_{1}\alpha_{1} - Z} \right] - 1 + \left[ \frac{Z}{\alpha_{3}} \right]^{2} \left[ 4 + \frac{n_{3}\alpha_{3}}{n_{3}\alpha_{3} - Z} \right] \right.$$

$$+ \sqrt{2} \left[ \left[ \frac{Z}{\alpha_{1}} \right]^{2} - 1 \right] \frac{(S_{n_{1}1\alpha_{1}} | r | S_{20Z})}{(S_{n_{1}1\alpha_{1}} | r | S_{10Z})} + \sqrt{2} \left[ \left[ \frac{Z}{\alpha_{3}} \right]^{2} - 1 \right] \frac{(S_{n_{3}1\alpha_{3}} | r | S_{20Z})}{(S_{n_{3}1\alpha_{3}} | r | S_{10Z})} \right\}. \tag{18}$$

In order to evaluate Eq. (5) one simply replaces F by G in those terms for which  $(n_2\alpha_2-Z)=0$ . It is convenient to compute separately the terms with  $l_2=0$ ,  $n_2=1$  (which may have apparent divergences),  $l_2=0$ ,  $n_2\geq 2$  and  $l_2=2, n_2\geq 3$ . The sums over  $n_1$  and  $n_3$  run from 2 to an upper limit  $n_{\max}$  chosen large enough to ensure convergence (the same upper limit is used for the  $n_2$  summation). The computations are done in double precision. Only the results for the hydrogen atom (Z=1) have been calculated since the results for hydrogenic ions may be obtained by scaling:  $\gamma$  simply varies as  $Z^{-10}$  if all field frequencies are simultaneously scaled by  $Z^2$ 

#### RESULTS AND DISCUSSION

The optical processes that will be specifically considered are listed in Table II. Any optical process with

at most two distinct input field frequencies may be thought of as a special case of one or the other of the last two processes listed: the ac Kerr effect or coherent anti-Stokes Raman scattering (CARS). To begin with we will consider the four processes involving a single optical field [the dc Kerr effect, degenerate four-wave mixing (DFWM), ESHG and THG], mapping out the frequency dependence and the convergence of the calculated results for  $\gamma_{zzzz}$  and the ratio  $\gamma_{zzzz}/\gamma_{zxxz}$ . [The expression for electric-field-induced optical rectification (EOR) is identical to that for the dc Kerr effect.] The first few excited levels of the hydrogen atom lie  $\frac{3}{8}$ ,  $\frac{4}{9}$ ,  $\frac{15}{32}$ , and  $\frac{24}{50}$  a.u. above the ground state, and  $\gamma$  will be resonant if  $\omega$  is equal to one of these energy differences. For DFWM and ESHG resonances will also occur when  $2\omega$  matches a transition frequency; and for THG, resonances occur when  $\omega$ ,  $2\omega$ , or  $3\omega$  matches a transition frequency. For the dc Kerr effect we have calculated  $\gamma$  up to and past

TABLE II. Third-order nonlinear optical processes with at most two distinct input field frequencies.

| Process  | Frequency<br>arguments                              | Independent<br>tensor<br>components | Number of laser fields | Apparent divergences |
|----------|---|-------------------------------------|------------------------|----------------------|
| Static   | (0;0,0,0)   | 1                                   | 0                      | yes                  |
| EOR      | $(0;\omega,-\omega,0)$                              | 2                                   | 1                      | yes                  |
| dc Kerra | $(-\omega;0,0,\omega)$                              | 2                                   | 1                      | yes                  |
| ESHG     | $(-2\omega;\omega,\omega,\zeta)$                    | 2                                   | 1                      | no                   |
| THG      | $(-3\omega;\omega,\omega,\omega)$                   | 1                                   | 1                      | no                   |
| DFWM     | $(-\omega;\alpha,\omega,-\omega)$                   | 2                                   | 1                      | yes                  |
| ac Kerra | $(-\omega_3;\omega_1,-\omega_1,\omega_3)$           | 2                                   | 2                      | yes                  |
| CARS     | $(-2\omega_1+\omega_3;\omega_1,\omega_1,-\omega_3)$ | 2                                   | 2                      | no                   |

<sup>&</sup>lt;sup>a</sup>The experimentally measurable quantity is actually  $(\gamma_{zzzz} - \gamma_{zxxz})$ 

the first two resonances, nearly to the ionization threshold at  $\omega = 0.5$  a.u. For DFWM, ESHG, and THG the calculations stop at the first resonance. Since damping is not included, the calculation will fail for frequencies too close to resonance. The value  $n_{\rm max} = 10$  was used as the upper limit of the  $n_1, n_2, n_3$  summations unless convergence could be obtained with a smaller value of  $n_{\rm max}$ .

The results of the  $\gamma_{zzzz}$  and  $\gamma_{zzzz}/\gamma_{zxxz}$  calculations are presented in Table III. Using a fixed upper limit on the number of terms in the summations, the accuracy of the calculation is seen to decrease as the ionization threshold is approached, as is most clearly illustrated by the dc-Kerr-effect results. The increase in  $\gamma_{zzzz}$  as resonance is approached and the change in the relative size of  $\gamma_{zzzz}$  and  $\gamma_{zxxz}$  both differ greatly for the various processes. However, it is difficult to see any simple quantitative relation between the results for the dc Kerr effect, DFWM, ESHG, and THG as they are presented in Table III.

On the basis of a crude model it has been suggested that the low-frequency dispersion of  $\gamma_{zzzz}$  obeys the relation<sup>26</sup>

$$\gamma_{zzzz}(-\omega_{\sigma};\omega_{1},\omega_{2},\omega_{3}) = \gamma_{zzzz}(0;0,0,0)(1+A\omega_{L}^{2}),$$
 (19)

where A is some constant which applies for all processes in a given atom, and where

$$\omega_L^2 = \omega_\sigma^2 + \omega_1^2 + \omega_2^2 + \omega_3^2 \tag{20}$$

defines the effective "laser" frequency  $\omega_L$  for any particular optical process. The effective frequencies for the dc Kerr effect, DFWM, ESHG, or THG are  $\omega_L^2 = 2\omega^2$ ,  $4\omega^2$ ,  $6\omega^2$ , or  $12\omega^2$ , and the first resonance in  $\gamma$  occurs at  $\omega_L^2 = 0.28125$ , 0.140625, 0.2109375, or 0.1875, respectively. Since  $\gamma_{zzzz}$  will diverge at different values of  $\omega_L^2$  for these four processes, Eq. (19) clearly must fail at some point. However, even if Eq. (19) is only valid at very low frequencies it could still be useful in organizing the results for  $\gamma_{zzzz}$ . This suggests that we calculate  $\gamma$  as a function of  $\omega_L^2$  rather than as a function of  $\omega$ .

The results for  $\gamma_{zzzz}$  and  $\gamma_{zzzz}/\gamma_{zxxz}$  calculated at several values of  $\omega_L^2$  are presented in Table IV. The results for  $\gamma_{zzzz}$  and  $\gamma_{zxxz}$  for the dc Kerr effect, DFWM, ESHG, and THG are also plotted as functions of  $\omega_L^2$  in

Figs. 1 and 2. It is immediately apparent that the dispersion is very nearly the same for all four processes for  $\gamma_{zzzz}$  considered as a function of  $\omega_L^2$ , but not for  $\gamma_{zxzz}$ . Plotting  $\gamma_{zzzz}/\gamma_{zzzz, \text{ dc Kerr}}$  versus  $\omega_L^2$  in Fig. 3 allows one to examine in more detail the relative dispersion of the various processes. One sees that the smallest dispersion in fact occurs for THG at small values of  $\omega_L^2$ , but at higher  $\omega_L^2$  the dc Kerr effect has the smallest dispersion. DFWM has the largest dispersion at all values of  $\omega_L^2$ . The ratio  $\gamma_{zzzz}/\gamma_{zxxz}$  is plotted versus  $\omega_L^2$  in Fig. 4. This ratio has been experimentally measured by ESHG for the series of inert-gas atoms, and it is interesting to note that while the experimental ratio for He slopes downward in agreement with the calculated results for H, the ratio in the case of the heavier inert-gas atoms slopes upward. 27

Treating  $\gamma$  as a function of  $\omega_L^2$  seems to be a good way of relating the results for the various nonlinear optical processes. Since the motivation for this parametrization came from the attempt to use a power series to represent  $\gamma$ , it is interesting to inspect the coefficients of the power series which fits the calculated results for hydrogen. The coefficients of the power-series expansions of  $\gamma_{zzzz}$  and  $\gamma_{zzzz}/\gamma_{zxxz}$  are given in Table V. While it is difficult to accurately obtain the higher coefficients because the number of significant terms in the power-series expansion increases very rapidly for  $\omega_L^2 > 10^{-2}$ , the first coefficient may be obtained with little difficulty. To accurately determine the leading coefficients of the fit, additional untabulated points in the  $\omega_L^2 = 5 \times 10^{-6} - 1 \times 10^{-3}$  with 12-significant-figure accuracy have been used. To within the uncertainty of  $\pm 1$  in the last decimal place, the leading coefficient A in the power-series expansion of  $\gamma_{zzzz}$  is the same for all four processes considered, which validates Eq. (19). The leading coefficient in the expansion of the ratio  $\gamma_{zzzz}/\gamma_{zxxz}$ also shows an interesting regularity. The coefficients A for DFWM, ESHG, and THG are given to within  $\pm 1$  in the last decimal place if one multiplies the A' for the dc Kerr effect by -2, -1, or 0, respectively. The convergence of these power-series expansions is illustrated by considering the results for the dc Kerr effect. The power series with the fitted coefficients has an error of  $10^{-4}\%$ at  $\omega_L^2 = 0.001$  and 1% at  $\omega_L^2 = 0.03$  for  $\gamma_{zzzz}$ , and an error

TABLE III. Results for  $\gamma_{zzz}$  and  $\gamma_{zzz}$  / $\gamma_{zxz}$  calculated as functions of  $\omega$  for the dc Kerr effect, DFWM, ESHG, and THG. The accuracy of the results decreases with increasing  $\omega$  because the maximum number of terms in the calculation is fixed. The ratio  $\gamma_{zzz}$  / $\gamma_{zxz}$  has not been tabulated for THG, because for THG the ratio is exactly equal to 3 at all

| ESHG         THG         de Kerr           1333.125 000         1333.125 000         3000 000 00           1333.436 127         1333.447 357         3000 218 02           1340,934 882         1347,021 519         3000 218 02           1340,934 882         1348.808 744         3000 872 45           1340,934 882         1348.808 744         3003 495 89           1405.846 573         1484.203 574         3003 495 89           1405.846 573         1484.203 574         3007 888 69           1406.417 486         1619.357 197         3.014 081 83           1661.722 581         1820.392 956         3.022 119 47           1661.722 581         1820.392 956         3.022 119 47           1661.722 581         1820.392 956         3.022 119 47           1661.722 581         1820.392 956         3.022 119 47           1661.722 581         1820.392 956         3.022 119 47           2004.673 80         2.251.468 093         3.024 114 05           212.235 63         3.022 119 47         3.024 186 59           4913.766         3.132.445         3.132.946           4913.766         4.185.602         3.125 488 462           4180.439         3.2518 682 08         3.2518 682 08           4  |          |               | $\gamma_{zzzz}$ (a.u.) | 1.)          |              |              | V 2227 / V 2887 |              |
|--|----------|---------------|------------------------|--------------|--------------|--------------|-----------------|--------------|
| 1333,125,000   1333,125,000   1333,125,000   1333,125,000   1333,125,000   1333,125,000   1333,125,000   1333,234,07   1333,445   1335,071,258   1335,071, | ω (a.u.) | dc Kerr       | ΝM                     |              | THG          | dc Kerr      | DFWM            | ESHG         |
| 2         1333.246         1333.3447         1333.445         77         3000.0488           5         1333.773 300         1344.42079         1335.07158         1337.021319         3000.01802           1355.720 91         1384.242079         1385.07158         1347.021519         3000.01802           1355.720 94         1384.04514         1364.0451         1347.06688         3000.01802           135.720 64         1310.02845         1460.04788         1374.0641         3000.08788           135.545 104         140.066.087         1466.417486         1693.3744         3004.0818           135.540 105         1400.066.087         1466.417486         1693.3747         3004.0818           1400.240 20         1400.066.087         1466.417486         1693.3747         3007.0888           1460.37 21 488         1731.2818         1800.044.0817         3007.0888         3002.0897           1515.73 488         1877.8311         1800.046.08         3004.0688         3007.0993           1516.75 50         1880.07         3007.046         3007.0498         3007.0993           1517.04 50         1880.07         3007.046         3007.0498         3007.0498           1517.04 50         2007.460         3007.0468         3007.0498 </td <td>0.0000</td> <td>1333.125000</td> <td>1333.125000</td> <td>1333.125000</td> <td>1333.125000</td> <td>3,000 000 00</td> <td>3.000 000 00</td> <td>3.000 000 00</td>  | 0.0000   | 1333.125000   | 1333.125000            | 1333.125000  | 1333.125000  | 3,000 000 00 | 3.000 000 00    | 3.000 000 00 |
| 5         1133,723 300         1134,22079         1133,021 519         300021802           133,520,4         138,124,237         138,124,237         1448,808,74         300021802           134,522,374         134,104,514         146,476,641         199,466,688         3003,405,89           1356,720,64         138,102,883         1405,846,73         148,295,74         300,108,18           140,249,39         1420,260,77         146,466,913         1820,395,96         300,140,18           140,27,72,46         143,148,131         166,122,881         2118,621,363         30,104,08           140,27,72,80         1541,148,131         166,122,881         2118,621,363         30,120,1947           140,27,72,80         1541,148,131         166,122,881         2118,621,363         30,137,60           156,27,148         17,72,240         180,434,081         20,146,093         30,121,104           156,27,148         187,881,060         20,148,094         30,141,105           156,27,148         187,881,060         20,188,094         30,111,106           100,010,340         20,24,496         31,22,452         31,114,105           100,103,40         20,24,406         31,22,422         31,114,105           100,104,103         20,24,406   | 0.002    | 1333.228 697  | 1333.332 407           | 1333.436 127 | 1333.747 357 | 3.000 034 88 | 2.999 860 48    | 2.999 895 36 |
| 1345.250 74         1335.25458         1340.94582         1348.08744         3000.97245           1345.52 734         1354.104814         1344.10414         1344.05274         3000.97889           1356.52 044         1356.4104814         1364.104144         1364.1048183         4005.846573         1400.2488           1356.52 044         1356.52 044         1364.1048183         1400.2489         3002.10497         3007.8889           1400.264 462         1407.272 464         1549.04981         1257.3460         302.21047         3007.8889           1400.276 866         153.52.5046         1800.450817         2186.1363         302.01947         3007.8218           156.577 488         177.851 100         2265.13665         4540.4944         307.411405         307.411405           156.57.74 48         187.851 100         2265.13665         4540.4944         307.411405         307.411405           1706.50.695         2885.150         2265.13665         4540.49944         307.411405         307.411405           1706.50.695         2885.150         2265.13665         4540.49944         307.411405         313.706.49           1900.10.80         2825.1002         460.250.986         4813.762         31.13486         31.13486           2021.466 92 <td>0.005</td> <td>1333.773 300</td> <td>1334.422079</td> <td>1335.071 258</td> <td>1337.021 519</td> <td>3.000 218 02</td> <td>2.999 127 83</td> <td>2.999 345 78</td>  | 0.005    | 1333.773 300  | 1334.422079            | 1335.071 258 | 1337.021 519 | 3.000 218 02 | 2.999 127 83    | 2.999 345 78 |
| 1356.723 74         1354.104514         1364.761641         1397.466 688         3003.458 89           1356.725 064         1381.023 883         1405.845 73         1494.295 74         3003.458 89           1356.725 064         1381.023 883         1405.845 73         1404.084 89         3003.458 89           1375.405 1         1400.264 67         1466.973 88         160.2571 97         3014081 83           1400.264 62         1427.254 96         158.352 964         1809.450 817         218.661 33         302.1047           1460.376 896         1628.352 964         1809.450 817         2271.468 93         3043.376 80         302.209.44         3074.11405           1560.371 488         1873.851 10         2264.13 665         4540.499 44         3074.11405         3072.850 89         3043.3766           1796.6016         2282.774 67         3112.226 3         313.245.2         3113.486 69         313.704.94         3092.146         3092.146         3092.140   | 0.01     | 1335.720917   | 1338.324538            | 1340.934 582 | 1348.808 744 | 3.00087245   | 2.996 508 70    | 2.997 380 00 |
| 1375.546.10   1300.888.5   1400.884.573   1442.93574   3.007.888.69     1375.546.11   1420.066.087   1466.4174.86   1619.357197   3.007.888.69     1400.264.62   1472.735.496   1446.4174.86   1619.357197   3.002.0937     1401.249.391   1541.148.131   1661.722.881   1820.392.56   3.022.1994     1403.376.896   1628.352.994   1809.43081   2.571.468.993   3.043.976.03     1515.078.11   1738.580.286   2004.607.189   3.043.9944   3.074.114.05     1636.371.488   1877.881   100   2265.173.665   4540.49944   3.074.114.05     1506.371.489   2282.74.46   3112.225.63   313.24.52   3.113.488.69     1706.756.695   2282.74.46   3112.225.63   313.24.52   3.113.488.69     1706.756.695   2282.74.46   312.24.63   3.13.70.494   3.074.114.05     1706.756.695   2382.74.46   349.44   3.074.114.05     1706.756.695   2382.74.46   3112.225.63   313.24.52   3.113.70.494     1706.756.695   2382.74.46   349.44   3.094.54.92     2011.469.246   3385.176   38.54.16.03   48.135.766   3.143.94.94     2011.465.244   4407.884   9941.5492   3.257.83   3.254.818     2022.33.44   30.20.32   3.454.62.84   3.454.62.84     2022.33.44   30.20.32   3.454.62.84   3.454.62.84     2022.34.34   3.454.724   3.454.62.84   3.454.62.84     2022.34.34   3.454.724   3.454.84   3.454.84   3.454.84   3.454.84     2022.34.34   3.454.724   3.454.84   3.45 | 0.02     | 1343.552 374  | 1354.104514            | 1364.761 641 | 1397.466 688 | 3.003 495 89 | 2.985 992 33    | 2.989 469 75 |
| 1400.264462   1472.725 496   1466.417486   1610.357197   3.012101947     1401.264462   1472.725 496   1549.969   13   1820.392.956   3.022.01947     1431.349.316 890   1621.342.944   1541.148131   1661.722.881   2118.62136.33   3.032.05937     1491.349.316 890   1622.32.2944   1800.4308.87   2211.468.093   3.043.976.03     150.978.211   1738.580.268   2.064.676.180   3.293.219.445   3.057.918     150.978.211   1738.580.268   2.064.676.180   3.293.219.445   3.057.918     163.4013.02   2.024.896.662   2.0618.929.335   7.009.695 7   3.079.278.83     1708.603.016   2.228.774.6 7   311.222.6 3   3.137.044.94     2.021.469.22   2.288.776.2   4913.767.2   481.35.766   3.137.044.94     2.021.469.24   4407.884   941.349.2   481.35.76   3.137.044.94     2.021.469.25   3.245.784   4407.884   941.349.2   3.225.783     2.021.469.25   3.222.77   3.122.24   3.225.783     2.021.469.25   3.222.77   3.18.68.89   3.225.784     2.021.473.89   18.66.30   180.213.61   8.257.84     2.021.473.89   18.66.30   180.213.61   8.257.84     2.021.26   2.021.24   2.021.24   2.021.24     2.021.26   2.021.24   2.021.24   2.021.24     2.021.26   2.021.24   2.021.24   2.021.24     2.021.26   2.021.24   2.021.24   2.021.24     2.021.26   2.021.24   2.021.24   2.021.24     2.021.26   2.021.24   2.021.24   2.021.24     2.021.26   2.021.24   2.021.24   2.021.24     2.021.26   2.021.24   2.021.24   2.021.24     2.021.26   2.021.24   2.021.24   2.021.24     2.021.26   2.021.24   2.021.24   2.021.24     2.021.26   2.021.24   2.021.24   2.021.24     2.021.26   2.021.24   2.021.24   2.021.24     2.021.26   2.021.24   2.021.24   2.021.24     2.021.26   2.021.24   2.021.24   2.021.24     2.021.26   2.021.24   2.021.24   2.021.24     2.021.26   2.021.24   2.021.24   2.021.24     2.021.26   2.021.24   2.021.24   2.021.24     2.021.26   2.021.24   2.021.24   2.021.24     2.021.27   2.021.24   2.021.24   2.021.24     2.021.27   2.021.24   2.021.24   2.021.24     2.021.27   2.021.24   2.021.24   2.021.24     2.021.27   2.021.24   2.021.24   2.021.24     2.021. | 0.03     | 1356.752 064  | 1381.023 883           | 1405.846573  | 1484.293 574 | 3.007 888 69 | 2.968 322 10    | 2.976 116 16 |
| 1400.264 402   | 0.04     | 1375.546510   | 1420.066087            | 1466.417 486 | 1619.357 197 | 3.014 081 83 | 2.943 278 42    | 2.957 055 99 |
| 1431.349.391   1541.148   1166.1722.581   2118.621.363   30.021.059.77     1469.376.896   1628.350.264   1809.430.817   2.571.468.093   3.045.976.03     1515.078.211   17.885.02.86   2.004.657.180   3.293.219.456   3.057.988.06     1569.371.488   1877.8511.00   2.265.173.665   4540.499.44   3.074.1140.5     1708.603.016   2.22.774.67   3112.22.56   48.135.766   3.137.03.49     1706.756.695   2.281.853.17   3826.146.03   48.135.766   3.137.03.49     1706.756.695   2.281.853.17   3826.146.03   48.135.766   3.137.03.49     1706.756.695   2.281.853.17   3826.146.03   48.135.766   3.137.03.49     2.235.028.897   377.73   37.827.346   3.205.378.37     2.235.028.897   8777.13   37.827.346   3.399.014.08     3.348.40.244   3.348.342   3.348.40.28     4.46.251.43   3.348.342   3.348.40.28     4.46.251.43   3.348.342   3.348.342   3.348.40.10     4.486.30   3.348.342   3.348.342   3.348.342   3.348.342     4.46.251.43   3.348.342   3.34 | 0.05     | 1400.264 462  | 1472.725 496           | 1549.966913  | 1820.392 956 | 3.022 119 47 | 2.910 543 14    | 2.931 903 10 |
| 1469,376 896         1628,332 964         1809 430817         2571,468 093         3.043 976 03           1815,078 211         1738,580 268         2004,676 180         3293,219 436         3.057 958 06           1653,402 205         2054,896 662         2.618,929 335         700.685 7         3.074 11405           1633,402 205         2282,774 67         3.12,236 53         13.35,452         3.137 03494           1708,603 016         2282,774 67         3.13,1236 53         13.35,452         3.117 03494           1900,103 840         2985,7602         4913,762         48 135,766         3.163,428 25           201,409,26         288,5182         66,95,086         3.157,344         3.137 03494           216,447,24         440,784         9941,5492         3.164,284         3.164,284           233,641,865         5829,175         16,962,324         3.225,383,73         3.225,833,73           234,445,243         817,13         37,827,346         3.339,014,08         3.349,014,08         3.349,014,08           346,244         366,30         180,213,618         3.385,012,15         3.345,46,24         3.345,46,24           4416,251,43         366,206,30         180,213,61         3.266,37         3.266,37         3.266,37           4172,   | 90.0     | 1431.349 391  | 1541.148131            | 1661.722 581 | 2118.621 363 | 3.032 059 77 | 2.869 687 88    | 2.900 128 82 |
| 1515.078 2.11   1738.580.268   2004.676 180   339.2.19436   3.077 958 06     1569.371 488  | 0.07     | 1469.376 896  | 1628.352 964           | 1809.430817  | 2571.468093  | 3.043 976 03 | 2.820 157 46    | 2.86103380   |
| 1569,371,488         187,881 100         2265,173 665         4540,499,44         3.074 11405           1634,340,205         2054,896 662         261,933         7009,695 7         3.092,572.83           1708,603 016         2282,746         2112,232.63         1337,432         3.113,486 69           1706,103,840         228,7360.2         491,357.2         481,357.66         3.113,486 69           1706,103,840         228,736.2         491,376.7         481,357.66         3.113,486 69           2021,409,926         3554,518.2         490,182,49         3.113,486 69           2104,446,724         4407,884         9941,549.2         3.225,783.7           215,50,28         8717,13         37,827,346         3.225,783.7           215,445,509         18 606.30         180,213,618         3.399,112 15           3068,318,025         8717,13         37,827,346         3.348,462,84           4416,251,43         3865,006,32         3.148,462,84           5117,226,23         4416,251,43         3867,206         3.248,401,10           1119,016,23         4416,218         3.248,401,10         3.248,401,10           1119,016,23         4416,218         3.248,401,10         3.248,461,10           1119,016,23         442,218  | 0.08     | 1515.078 211  | 1738.580 268           | 2004.676 180 | 3293.219 436 | 3.057 958 06 | 2.761 247 03    | 2.813 708 21 |
| 163,403.05   | 60.0     | 1569.371 488  | 1877.851 100           | 2265.173 665 | 4540.499 44  | 3.074 114 05 | 2.692 070 67    | 2.75697605   |
| 1708.603.016     2282.774.67     3112.236.53     1332.452     3113.486.69       1796.756.695     2281.833.17     3826.146.03     48 135.766     3.3170.3494       1900.103.80     2958.7602     4913.762     48 135.766     3.1370.3494       1900.103.80     3554.5182     6695.0986     3.192.914.0       2021.469.926     3554.5182     6695.0986     3.192.914.0       2164.46.724     4407.884     9941.5492     3.257.83.73       235.028.897     8717.13     37 827.346     3.205.783.73       2776.445.909     18 606.30     18 05.324     3.344 46.284       366.318.025     37827.346     3.348 46.284       344.724.28     346.826.8     3.358.712.15       4416.251.43     346.826.8     3.569.830       604.774.15     3.867.726.61     3.864.801.10       880.726.61     4.385.932     4.485.693.23       1119.016.23     4.385.462     3.247.24       4046.118     65.081.11     5.331.912       4046.118     5.60.813     5.385.500       2431.575.4     5.032.056       661.397.3     661.397.3       11.534.68     661.397.3       11.532.67     11.532.67   | 0.10     | 1633.403 205  | 2054.896 662           | 2618.929 335 | 7009.6957    | 3.092 572 83 | 2.611 518 02    | 2.689 316 78 |
| 1796,756695       2581,88317       3826,14603       48135,766       3.103 0494         1900,103 840       2985,7602       4913,7672       3.103 941         2104,446 724       4407,884       9941,5492       3.122 914 10         2164,446 724       4407,884       9941,5492       3.202 783 73         233,3041 865       5829,175       16.962,324       3.262 380 72         233,502 897       8717,13       37827,346       3.303 112 15         275,445 909       18.606,30       180213.618       3.399 014 08         3424,724 28       3865,006 32       3.7827,346       3.399 014 08         346,274 28       3865,006 32       3.445 462       3.569 882 08         411,226 23       416,251 43       3.569 883 0       3.569 883 0         6024,794 15       5.17,226 23       3.569 887 30       3.569 887 30         1119,016 23       1119,016 23       4.124 001 51       4.124 001 51         19 33.1921       4.06,218       5.431 574       4.124 001 51         40 465,118       65.068 111       5.431 574       5.025 056         661 397.3       3.088 57       661 397.3       11.532 67   | 0.11     | 1708.603016   | 2282.77467             | 3112.232 63  | 13 352.452   | 3.113 486 69 | 2.518 193 72    | 2.608 754 17 |
| 1900.103 840         298.7602         4913.7672         3.163.428.25           2021.469 926         3554.5182         6695.0986         3.152.91410           216.469 926         3554.5182         6695.0986         3.129.91410           216.446 926         3824.175         16.962.324         3.262.380.72           233.502 897         8717.13         37.827.346         3.303.1215           2776.445 909         18.606.30         180.213.618         3.348.46.284           3468.318 025         18.606.30         180.213.618         3.348.46.284           3468.318 025         344.62.34         3.348.46.284         3.455.468.24           4416.251 43         3865.006.32         3.517.266.23         3.518.682.08           517.226.23         6024.794 15         3.584.801.10         3.894.869.11           8850.726.61         11119.016.23         4.124.001.51         4.426.01.54           1119.016.23         27.162.285         4.277.337.7         4.277.337.7           40.465.118         65.086.111         5.431.875.4         5.032.056.1           66.83.11         66.83.13         66.83.24         6.820.56           861.34.68         85.7         11.532.67         11.532.67   | 0.12     | 1796.756 695  | 2581.85317             | 3826.14603   | 48 135.766   | 3.137 034 94 | 2.410 331 02    | 2.512 696 37 |
| 2021.469 926       3554.5182       6695.0986       3.192 91410         2104.467 24       4407.884       9941.3492       3.192 91410         2333.641 865       5829.175       16 962.324       3.252.38072         2535.028 897       8717.13       37 827.346       3.364.02 84         3068.318 025       18 606.30       180 213.618       3.38 462.84         344.742 8       3424.742 8       3.38 462.84       3.39 01408         344.6251 43       365.006 32       3.416.28       3.55 462         410.251 43       3.58 500       3.56 98.83       3.56 98.83         6024.794 15       3.88 50.75 61       3.864 801 10         880.75 61       11 119.016 23       4.124 501 51         14 395.3462       4.28 464       4.28 464         19 331.912       5.33 1.92       5.33 1.92         40 465.118       5.032 056 1       5.032 056 1         66 13 46.59       661 397.3       11.532 67         3038 857       11.532 67  | 0.13     | 1900.103 840  | 2985.7602              | 4913.7672    |              | 3.163 428 25 | 2.285 664 99    | 2.397 703 0  |
| 2164.446724       4407.884       9941.5492       3.225 783 73         2333.641 865       5829.175       16 962.324       3.262 780 72         235.621 8077       16 962.324       3.364 862       3.303 112 15         2776.445 909       18 606.30       18 0213 618       3.399 014 08         346.724 28       3.45 462 84       3.399 014 08         3424.724 28       3.45 468 24       3.59 014 08         346.506 32       416.251 43       3.51 862 08         416.251 43       3.51 862 08       3.51 862 08         6024.794 15       3.50 863 08       3.760 884 36         7224.738 94       3.864 801 10       3.864 801 10         8850.726 61       8850.726 61       4.124 001 51         11 119.016 23       4.284 464 70         19 331.911       4.285 693 23         27 169.285       4.727 357 7         4.65 08       5.032 056 1         66 1307.3       8.267 349         8.66 1397.3       8.267 349         8.378 67       11.532 67   | 0.14     | 2021.469 926  | 3554.5182              | 9860:5699    |              | 3.19291410   | 2.141 239 8     | 2.259 141 3  |
| 233.641 865       5829.175       16 962.324       3.262.380 72         235.502 897       8177.13       37 827.346       3.303 112 15         2776.445 909       18 606.30       180 213.618       3.348 462 84         3424.724 28       3.486 5006 32       3.48 462 84         3865.006 32       3.517 226 23       3.518 682 08         4416.251 43       3.517 226 23       3.669 878 30         6024.794 15       3.589 712 15         5117.226 23       3.698 878 30         6024.794 15       3.569 878 30         11 119.016 28       3.564 801 10         8850.726 61       4.124 001 51         14 395.346 2       4.124 001 51         19 331.912 1       4.128 464 70         19 331.912 1       5.988 509 0         40.65.118       5.020 056 1         661 34.53       661 397.3         3038 857       11.532 67  | 0.15     | 2164.446 724  | 4407.884               | 9941.5492    |              | 3.225 783 73 | 1.973 101 7     | 2.090 677 0  |
| 2535.028 897       8717.13       37827.346       3.303 112 15         2776.445 909       18 606.30       180213 618       3.348 462 84         3068.318 025       3608.318 025       3.484 462 84         3477.24 28       3.455 468 24       3.455 468 24         386.500 632       4416.251 43       3.589 712 15         5117.25 63       3.589 712 15       3.589 712 15         5117.26 61       3.580 712 15       3.569 878 30         6024.794 15       3.589 712 15       3.569 878 30         6024.794 15       3.580 712 15       3.569 878 30         1119.016 23       1119.016 23       3.760 854 566 97         19 331.9121       4.124 001 51       4.124 001 51         40 465.118       4.228 464 70       4.485 693 23         27 169.285       2.43 518.68       5.985 509 0         243 518.68       661 397.3       11.532 67         3038 857       11.532 67   | 0.16     | 2333.641865   | 5829.175               | 16 962.324   |              | 3.262 380 72 | 1.775 780 8     | 1.883 532 3  |
| 2776.445 909     18 606.30     180213.618     3.348 462 84       3068.318 025     3068.318 025     3.399 014 08       3424.724 28     3455.066 32     3.455 468 24       3865.006 32     4416.231 43     3.518 682 08       4416.214 3     3.518 682 08     3.518 682 08       4416.214 3     3.589 712 15     3.669 878 30       6024.794 15     3.669 878 30     3.669 878 30       6024.794 15     3.864 801 10     3.984 566 97       11119.016 23     4.124 001 51     4.124 001 51       14 395.346 2     4.288 464 70     4.485 693 23       19 331.912 1     4.485 693 23     4.772 357 7       40 465.118 65 068.111     5.985 509 0     5.985 509 0       243 518.68 61397.3 3     8.267 549       661 397.3 3     11.532 67   | 0.17     | 2535.028 897  | 8717.13                | 37 827.346   |              | 3.303 112 15 | 1.541 344       | 1.625 495 4  |
| 3068.318 025 3424.724 28 3865.006 32 4416.251 43 5117.226 23 6024.794 15 7224.738 94 8850.726 61 11119.016 23 14 395.3462 19 331.9121 27 169.285 40 465.118 65 068.111 116 346.59 243 518.68 661 397.3   | 0.18     | 2776.445 909  | 18 606.30              | 180 213.618  |              | 3.348 462 84 | 1.257 479       | 1.300 047 8  |
| 3424.724 28 3865.006 32 4416.251 43 5117.226 23 6024.794 15 7224.738 94 8850.726 61 11119.016 23 14 395.3462 19 331.9121 27 169.285 40 465.118 65 068.111 116 346.59 243 518.68 661 397.3  | 0.19     | 3068.318 025  |                        |              |              | 3.39901408   |                 |              |
| 3865.006 32 4416.251 43 5117.226 23 6024.794 15 7224.738 94 8850.726 61 11 119.016 23 14 395.3462 19 331.9121 27 169.285 40 465.118 65 068.111 116 346.59 243 518.68 661 397.3 3 038 857   | 0.20     | 3424.72428    |                        |              |              | 3.455 468 24 |                 |              |
| 4416.25143 5117.22623 6024.79415 7224.73894 8850.72661 11119.01623 14.395.3462 19.331.9121 27.169.285 40.465.118 65.068.111 116.346.59 243.518.68 661.397.3  | 0.21     | 3865.00632    |                        |              |              | 3.518 682 08 |                 |              |
| 5117.226 23<br>6024.794 15<br>7224.738 94<br>8850.726 61<br>11 119.016 23<br>14 395.3462<br>19 331.9121<br>27 169.285<br>40 465.118<br>65 068.111<br>116 346.59<br>243 518.68<br>661 397.3   | 0.22     | 4416.25143    |                        |              |              | 3.589 712 15 |                 |              |
| 6024.79415<br>7224.738 94<br>8850.726 61<br>11 119.016 23<br>14 395.3462<br>19 331.9121<br>27 169.285<br>40 465.118<br>65 068.111<br>116 346.59<br>243 518.68<br>661 397.3   | 0.23     | 5117.22623    |                        |              |              | 3.66987830   |                 |              |
| 7224.738 94 8850.726 61 11 119.016 23 14 395.3462 19 331.9121 27 169.285 40 465.118 65 068.111 116 346.59 243 518.68 661 397.3 3 038 857   | 0.24     | 6024.79415    |                        |              |              | 3.760 854 36 |                 |              |
| 8850.726 61 11 119.016 23 14 395.3462 19 331.9121 27 169.285 40 465.118 65 068.111 116 346.59 243 518.68 661 397.3 3 038 857   | 0.25     | 7224.738 94   |                        |              |              | 3.864 801 10 |                 |              |
| 11 119.016 23<br>14 395.3462<br>19 331.9121<br>27 169.285<br>40 465.118<br>65 068.111<br>116 346.59<br>243 518.68<br>661 397.3   | 0.26     | 8850.72661    |                        |              |              | 3.984 566 97 |                 |              |
| 14 395.3462 19 331.9121 27 169.285 40 465.118 65 068.111 116 346.59 243 518.68 661 397.3 3 038 857   | 0.27     | 11 119.016 23 |                        |              |              | 4.124 001 51 |                 |              |
| 19 331.9121<br>27 169.285<br>40 465.118<br>65 068.111<br>116 346.59<br>243 518.68<br>661 397.3   | 0.28     | 14 395.3462   |                        |              |              | 4.288 464 70 |                 |              |
| 27 169.285<br>40 465.118<br>65 068.111<br>116 346.59<br>243 518.68<br>661 397.3<br>3 038 857   | 0.29     | 19 331.9121   |                        |              |              | 4.485 693 23 |                 |              |
| 40 465.118<br>65 068.111<br>116 346.59<br>243 518.68<br>661 397.3  | 0.30     | 27 169.285    |                        |              |              | 4.727 357 7  |                 |              |
| 65 068.111<br>116 346.59<br>243 518.68<br>661 397.3<br>3 038 857   | 0.31     | 40 465.118    |                        |              |              | 5.032 056 1  |                 |              |
| 116 346.59<br>243 518.68<br>661 397.3<br>3 038 857   | 0.32     | 65 068.111    |                        |              |              | 5.431 575 4  |                 |              |
| 243 518.68<br>661 397.3<br>3 038 857   | 0.33     | 116 346.59    |                        |              |              | 5.985 509 0  |                 |              |
| 661 397.3<br>3 038 857   | 0.34     | 243 518.68    |                        |              |              | 6.820956     |                 |              |
| 3 038 857  | 0.35     | 661 397.3     |                        |              |              | 8.267 549    |                 |              |
|  | 0.36     | 3 038 857     |                        |              |              | 11.532 67    |                 |              |

TABLE III. (Continued).

| ω (a.u.)     dc Kerr       0.37     81 032 102       0.38     -77 842 687       0.39     -2.48445×10 <sup>6</sup> 0.40     -2.4331×10 <sup>3</sup> 0.41     3.131×10 <sup>3</sup> | DFWM   |      |     |           | 7447 / 7777 / |      |
|---|--|------|-----|-----------|---------------|------|
|   | The state of the s | ESHG | THG | dc Kerr   | DFWM          | ESHG |
|   |  |      |     | 27.479 50 |               |      |
|   |  |      |     | -19.93107 |               |      |
|   | 9  |      |     | -3.96546  |               |      |
|   | 8  |      |     | -0.6611   |               |      |
|   | 8  |      |     | 0.8502    |               |      |
|   | 9  |      |     | 1.7891    |               |      |
|   | <b>9</b>   |      |     | 2.5252    |               |      |
|   | 90   |      |     | 3.3536    |               |      |
|   | 1  |      |     | 7.2883    |               |      |
|   | 7  |      |     | 1.9631    |               |      |

TABLE IV. Results for  $\gamma_{zzz}$  and  $\gamma_{zzz}/\gamma_{zxzz}$  calculated as functions of  $\omega_L^2$  for the dc Kerr effect, DFWM, ESHG, and THG. The ratio  $\gamma_{zzzz}/\gamma_{zxzz}$  has not been tabulated for THG, because for THG the ratio is exactly equal to 3 at all frequencies.

|                     |              | γ zzzz (a.u.) | (a.u.)       |              |              | V 2222 / V 2882 |              |
|---------------------|--------------|---------------|--------------|--------------|--------------|-----------------|--------------|
| $\omega_L^2$ (a.u.) | dc Kerr      | DFWM          | ESHG         | THG          | dc Kerr      | DFWM            | ESHG         |
| 0.0000              | 1333.125000  | 1333.125000   | 1333.125000  | 1333.125000  | 3.000 000 00 | 3.000 000 00    | 3.000 000 00 |
| 0.0001              | 1334.422 052 | 1334.422 079  | 1334.422 052 | 1334.422 043 | 3.00043610   | 2.999 127 83    | 2.999 563 91 |
| 0.001               | 1346.177 515 | 1346.180 292  | 1346.177 531 | 1346.176 622 | 3.004 372 41 | 2.991 258 50    | 2.995 628 70 |
| 0.005               | 1400.264 462 | 1400.342 736  | 1400.266 655 | 1400.242 783 | 3.022 119 47 | 2.955 845 23    | 2.977 909 04 |
| 0.01                | 1472.361813  | 1472.725 496  | 1472.380 994 | 1472.279 420 | 3.044 900 35 | 2.910 543 14    | 2.955 218 07 |
| 0.02                | 1633.403 206 | 1635.367 457  | 1633.587 569 | 1633.126963  | 3.092 572 83 | 2.816 289 77    | 2.907 938 83 |
| 0.03                | 1820.816892  | 1826.805 162  | 1821.570438  | 1820.392 956 | 3.143 292 12 | 2.71678816      | 2.857 954 35 |
| 0.04                | 2040.379 855 | 2054.896 662  | 2042.561 916 | 2040.179747  | 3.197 372 39 | 2.61151802      | 2.805 033 18 |
| 0.05                | 2299.469 590 | 2330.69391    | 2304.726 105 | 2300.487 778 | 3.255 175 05 | 2.499 874 67    | 2.74891701   |
| 90:0                | 2607.606 688 | 2670.31162    | 2618.929 335 | 2611.987417  | 3.317 118 69 | 2.381 148 00    | 2.68931678   |
| 0.07                | 2977.217 757 | 3098.3278     | 2999.896 787 | 2989.192852  | 3.383 691 65 | 2.254 493 90    | 2.625 908 21 |
| 80.0                | 3424.72428   | 3654.4493     | 3467.99475   | 3452.302 726 | 3.455 468 24 | 2.118 894 6     | 2.558 326 51 |
| 60.0                | 3972.122 16  | 4407.884      | 4052.059 75  | 4030.19073   | 3.533 130 09 | 1.973 101 7     | 2.486 160 41 |
| 0.10                | 4649.31437   | 5492.545      | 4794.0457    | 4765.473 26  | 3.617 494 29 | 1.815 552 9     | 2.408 945 2  |

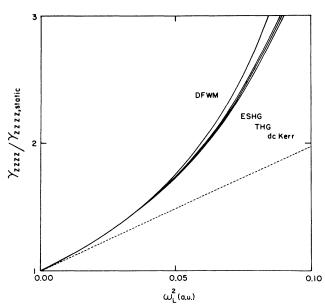


FIG. 1. Variation of  $\gamma_{zzzz}$ , normalized to its static value, is shown as a function of  $\omega_L^2$  for the dc Kerr effect, DFWM, ESHG, and THG. The dashed straight line is the lowest-order dispersion term from Table V.

of  $10^{-4}\%$  at  $\omega_L^2 = 0.005$  and 1% at  $\omega_L^2 = 0.1$  for the ratio  $\gamma_{zzzz}/\gamma_{zxxz}$ . If only the lowest-order dispersion term is retained, giving expressions with the form of Eq. (19), one obtains the results shown as the dashed lines in Figs. 1 and 4. The lowest-order dispersion formula is fairly good for the ratio  $\gamma_{zzzz}/\gamma_{zxxz}$ , but it is quite poor for

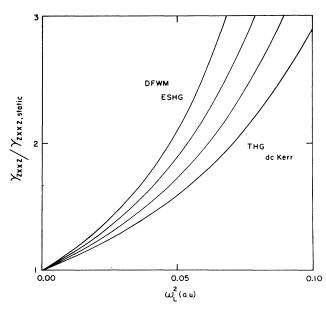


FIG. 2. Variation of  $\gamma_{zxxz}$ , normalized to its static value, is shown as a function of  $\omega_L^2$  of the dc Kerr effect, DFWM, ESHG, and THG.

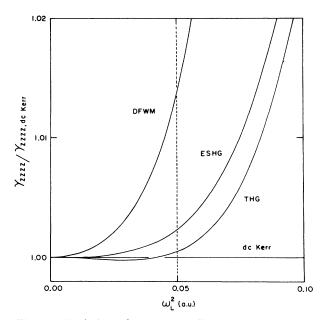


FIG. 3. Variation of  $\gamma_{zzzz}$ , normalized to  $\gamma_{zzzz}$  for the dc Kerr effect, is shown as a function of  $\omega_L^2$  for the dc Kerr effect, DFWM, ESHG, and THG. The results presented in Figs. 5 and 6 are calculated at the value of  $\omega_L^2$  indicated by the vertical dashed line.

 $\gamma_{zzzz}$  except at very small values of  $\omega_L^2$ . If one wishes to accurately extrapolate experimental dispersion measurements one should bear this in mind.

The four processes so far considered are just particular special cases of the ac Kerr effect or CARS. To investigate the wider range of processes we will vary  $\omega_1$ 

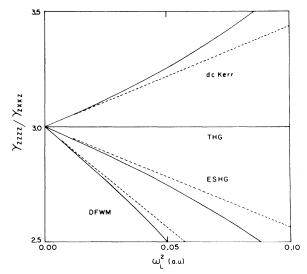


FIG. 4. Variation of  $\gamma_{zzzz}/\gamma_{zxxz}$  is shown as a function of  $\omega_L^2$  for the dc Kerr effect, DFWM, ESHG, and THG. The dashed straight lines are the lowest-order dispersion terms from Table V

TABLE V. Coefficients of the power-series expansions  $(\gamma_{zzzz}/\gamma_{zzzz,static}) = (1 + A\omega_L^2 + B\omega_L^4 + C\omega_L^6 + D\omega_L^8)$  and  $1/3(\gamma_{zzzz}/\gamma_{zxxz}) = (1 + A'\omega_L^2 + B'\omega_L^4 + C'\omega_L^6 + D'\omega_L^8)$  for the dc Kerr effect, DFWM, ESHG, and THG.

| Process | A         | В      | С   | D                   | Α'        | В'     | C'  | D'                 |
|---------|-----------|--------|-----|---------------------|-----------|--------|-----|--------------------|
| dc Kerr | 9.722 617 | 67.893 | 405 | $2.4 \times 10^{3}$ | 1.453 243 | 4.213  | 13  | $4\times10^{1}$    |
| DFWM    | 9.722 616 | 69.916 | 464 | $3.5 \times 10^{3}$ | -2.906485 | -7.329 | -21 | $-7 \times 10^{1}$ |
| ESHG    | 9.722 617 | 67.893 | 416 | $2.6 \times 10^{3}$ | -1.453242 | -3.848 | -10 | $-3 \times 10^{1}$ |
| THG     | 9.722 616 | 67.221 | 408 | $2.6 \times 10^{3}$ | 0         | 0      | 0   | 0                  |

and  $\omega_3$  while holding  $\omega_L^2$  constant. The results of such calculations will be presented for the single selected value  $\omega_L^2 = 0.05$ , corresponding to the vertical dashed line across the center of Fig. 3. For the ac Kerr effect,  $\gamma(-\omega_3;\omega_1,-\omega_1,\omega_3)$  the constraint of constant  $\omega_L^2$  requires that

$$\omega_1^2 = \frac{1}{2}(\omega_L^2 - 2\omega_3^2) , \qquad (21)$$

so  $0 \le (\omega_3/\omega_L)^2 \le \frac{1}{2}$  parametrizes the range of possible ac Kerr processes. For CARS,  $\gamma(-2\omega_1+\omega_3;\omega_1,\omega_1,-\omega_3)$ , the constraint of constant  $\omega_L^2$  requires that

$$\omega_1 = \frac{1}{3} \left[ \omega_3 \pm \left( \frac{3}{2} \omega_L^2 - 2\omega_3^2 \right)^{1/2} \right], \tag{22}$$

with solutions for  $0 \le (\omega_3/\omega_L)^2 \le \frac{3}{4}$ . For CARS, for a given value of  $\omega_3$  there are two possible solutions for  $\omega_1$ . The solutions will be labeled  $\omega_1^+$  or  $\omega_1^-$  according to whether the + or - sign is chosen in Eq. (22). The in-

put frequency arguments of the CARS processes on the  $\omega_1^-$  branch for  $0 \le (\omega_3/\omega_L)^2 \le \frac{1}{2}$  all have the same sign, and such processes may be termed sum-wave mixing (SWM). For both the ac Kerr effect and CARS we have assumed that  $\omega_3$  is positive. Since  $\gamma$  is unchanged when the signs of all its frequency arguments are reversed together, there is no loss of generality by this assumption.

The results for  $\gamma_{zzzz}$  and  $\gamma_{zzzz}/\gamma_{zxxz}$ , for the ac Kerr effect and CARS at  $\omega_L^2 = 0.05$  are presented in Table VI and plotted in Figs. 5 and 6 as functions of  $(\omega_3/\omega_L)^2$ . For the ac Kerr effect the curves for  $\gamma_{zzzz}/\gamma_{zzzz}$ , decemple and  $\gamma_{zzzz}/\gamma_{zxxz}$  are both symmetric about  $(\omega_3/\omega_L)^2 = \frac{1}{4}$  and both curves are nearly parabolic in shape. For CARS the curves are more complicated in shape, particularly that for  $\gamma_{zzzz}/\gamma_{zzzz}$ , decemple at  $\omega_L^2 = 0.05$ , for any process with at most 2 input field frequencies, will fall between the corresponding values for DFWM as an upper

TABLE VI. Results for  $\gamma_{zzzz}$  and  $\gamma_{zzzzz}/\gamma_{zxxz}$  calculated as functions of  $(\omega_3/\omega_L)^2$  at constant  $\omega_L^2 = 0.05$  a.u. for the ac Kerr effect and CARS. Special cases of the ac Kerr effect are EOR at  $(\omega_3/\omega_L)^2 = 0$ , DFWM at  $(\omega_3/\omega_L)^2 = \frac{1}{4}$ , and the dc Kerr effect at  $(\omega_3/\omega_L)^2 = \frac{1}{2}$ . On the  $\omega_1^+$  branch for CARS,  $(\omega_3/\omega_L)^2 = 0$  gives ESHG and  $(\omega_3/\omega_L)^2 = \frac{1}{4}$  gives DFWM. The  $\omega_1^-$  branch of CARS for  $0 \le (\omega_3/\omega_L)^2 \le \frac{1}{2}$  corresponds to the sum-wave-mixing processes of ESHG, THG, and the dc Kerr effect when  $(\omega_3/\omega_L)^2 = 0$ ,  $(\omega_3/\omega_L)^2 = 0$ ,  $(\omega_3/\omega_L)^2 \le 1$ , respectively.

|                         |              | $\gamma_{zzzz}$ (a.u.)    |                           |              | Y zzzz /Y zxxz            |                           |
|-------------------------|--------------|---------------------------|---------------------------|--------------|---------------------------|---------------------------|
| $(\omega_3/\omega_L)^2$ | ac Kerr      | CARS, $\omega_1^+$ branch | CARS, $\omega_1^-$ branch | ac Kerr      | CARS, $\omega_1^+$ branch | CARS, $\omega_1^-$ branch |
| 0.00                    | 2299.469 590 | 2304.726 105              | 2304.726 105              | 3.255 175 05 | 2.748 917 01              | 2.748 917 01              |
| 0.01                    |              | 2309.439 931              | 2301.907 724              |              | 2.671 328 59              | 2.833 385 23              |
| 0.02                    |              | 2311.900 478              | 2301.244 624              |              | 2.641952 98               | 2.869 640 69              |
| 0.05                    | 2310.189 185 | 2317.371 196              | 2300.592 708              | 3.282 591 37 | 2.589 716 92              | 2.942 514 88              |
| 0.10                    | 2318.925 868 | 2323.676 139              | 2300.498 277              | 3.304 496 79 | 2.542 625 65              | 3.023 987 40              |
| 0.15                    | 2325.387 822 | 2327.733 366              | 2300.550 020              | 3.320 467 62 | 2.516 947 56              | 3.084 006 49              |
| 0.20                    | 2329.355 857 | 2329.989 107              | 2300.516 915              | 3.330 183 50 | 2.503 827 52              | 3.131 402 13              |
| 0.25                    | 2330.693 91  | 2330.693 91               | 2300.377 076              | 3.333 444 75 | 2.499 874 67              | 3.169 538 75              |
| 0.30                    | 2329.355 857 | 2330.056 451              | 2300.161 617              | 3.330 183 50 | 2.503 446 95              | 3.200 031 01              |
| 0.35                    | 2325.387 822 | 2328.278 855              | 2299.916 914              | 3.320 467 62 | 2.513 706 20              | 3.223 688 91              |
| 0.40                    | 2318.925 868 | 2325.567 516              | 2299.691 462              | 3.304 496 79 | 2.530 290 32              | 3.240 845 90              |
| 0.45                    | 2310.189 185 | 2322.136 817              | 2299.529 962              | 3.282 591 37 | 2.553 199 84              | 3.251 472 53              |
| 0.50                    | 2299.469 590 | 2318.210 919              | 2299.469 590              | 3.255 175 05 | 2.582 799 63              | 3.255 175 05              |
| 0.55                    |              | 2314.025 914              | 2299.536 266              |              | 2.619 936 38              | 3.251 078 15              |
| 0.60                    |              | 2309.834 332              | 2299.738 915              |              | 2.666 273 29              | 3.237 490 52              |
| 0.65                    |              | 2305.916 012              | 2300.057 811              |              | 2.725 250 76              | 3.210 944 41              |
| 0.70                    |              | 2302.609 252              | 2300.413 071              |              | 2.805 857 19              | 3.162 425 07              |
| 0.73                    |              | 2301.121 741              | 2300.547 571              |              | 2.878 502 55              | 3.108 856 23              |
| 0.74                    |              | 2300.752 706              | 2300.547 540              |              | 2.914 838 71              | 3.078 848 45              |
| 0.75                    |              | 2300.487 778              | 2300.487 778              |              | 3.000 000 00              | 3.000 000 00              |

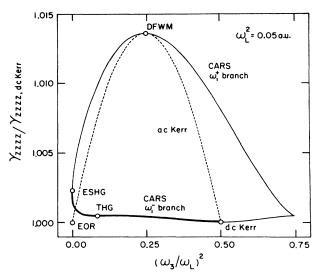


FIG. 5. Variation of  $\gamma_{zzzz}$ , at  $\omega_L^2=0.05$  a.u. and normalized to  $\gamma_{zzzz}$  for the dc Kerr effect, is shown as a function of  $(\omega_3/\omega_L)^2$  for the ac Kerr effect (dashed curve) and CARS (solid curve). The part of the  $\omega_1^-$  branch for CARS which corresponds to sum-wave mixing has been drawn with a heavier line. The open circles mark particular special cases of the ac Kerr effect and CARS.

limit and the dc Kerr effect as a lower limit. Referring to Fig. 4, it seems likely that this is the situation for all  $\omega_L^2 > 0.042$ , while for  $\omega_L^2 \leq 0.042$  the lower limit of  $\gamma_{zzzz}$  is given by the value for THG instead. In Fig. 6 two points labeled DFWM appear. The point on the ac Kerr curve has frequency arguments permuted with respect to the definition given in Table II, and so corresponds to the tensor component  $\gamma_{zxzz}$  by that definition. From Fig. 6 it would seem that the value of  $\gamma_{zzzz}/\gamma_{zxxz}$  for any process with at most 2 distinct input field frequencies will fall between  $\gamma_{zzzz}/\gamma_{zxxz}$  and  $\gamma_{zzzz}/\gamma_{zxzz}$  for DFWM.

The more general case where the magnitude of all three input frequencies are different has not been systematically explored, but the results for processes with a nearly degenerate pair of input frequencies may be expected to lie near the results calculated here, when the comparison is made at a common value of  $\omega_L^2$ . The two processes for which only a single input field frequency is

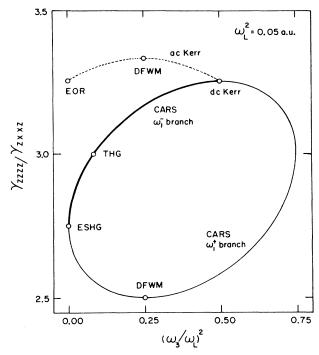


FIG. 6. Variation of  $\gamma_{zzzz}/\gamma_{zxxz}$ , at  $\omega_L^2=0.05$  a.u., is shown as a function of  $(\omega_3/\omega_L)^2$  for the ac Kerr effect (dashed curve) and CARS (solid curve). The part of the  $\omega_1^-$  branch for CARS which corresponds to sum-wave mixing has been drawn with a heavier line. The open circles mark particular special cases of the ac Kerr effect and CARS.

involved are DFWM and THG. It seems a reasonable conjecture, for the hydrogen atom at small values of  $\omega_L^2$ , that DFWM and THG will give the upper and lower bounds for  $\gamma_{zzzz}$ , and that the ratios  $\gamma_{zzzz}/\gamma_{zxxx}$ ,  $\gamma_{zzzz}/\gamma_{zxzx}$ , and  $\gamma_{zzzz}/\gamma_{zxxz}$  for any process will fall within the range spanned by  $\gamma_{zzzz}/\gamma_{zxzx}$  and  $\gamma_{zzzz}/\gamma_{zxxz}$  for DFWM.

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