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Hyperpolarizability of the hydrogen atom

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The frequency dependence of the hyperpolarizability (γ) 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 γ is treated as a function of an effective frequency ω_L. The detailed, systematic exploration of the dispersion of γ 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 γ of the constituent atoms or molecules.[3,4] Fourth-order perturbation theory gives an explicit expression for γ which applies for all third-order nonlinear optical processes, so all these optical processes are in fact intimately related.[5-7] However, γ 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.[3,8] 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 γ,[4] 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 γ for various nonlinear optical processes.[4,9] And though there have been many calculations of γ performed for a range of atoms and molecules, the results of these calculations are almost as fragmentary and inaccurate as the experimental results.[10,11] 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 γ 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 γ have been reported for the H and He atoms. The dynamic calculation of γ for third-harmonic generation (THG) in hydrogen is essentially exact.[23] The dynamic calculations of γ for the dc Kerr effect, electric-field-induced second-harmonic generation (ESHG) and THG in helium are thought to be accurate to about 1%, but the calculated values of γ 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 γ 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.[23] 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 γ_H

The hyperpolarizability of the ground-state hydrogen atom is most readily calculated using the Sturmian Coulomb Green's function.[23] 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.[24] The Sturmian function $S_{nl\alpha}(r)$ 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

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

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

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

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

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

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] 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

$$\gamma_{\alpha\beta\gamma\delta}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) = \sum P \sum_{n_1}\sum_{n_2}\sum_{n_3}\sum_{l_2} C(\alpha\beta\gamma\delta l_2)F(n_1n_2n_3\theta_1\theta_2\theta_3 l_2)\ , \tag{5}$$

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 ω_σ is $\omega_\sigma=\omega_1+\omega_2+\omega_3$. The factor $C(\alpha\beta\gamma\delta l_2)$ contains the angular dependence of γ and is given by

$$C(\alpha\beta\gamma\delta l_2)=\sum_{m_1}\sum_{m_2}\sum_{m_3}\langle 00\,|\,\hat{\mathbf{r}}_\alpha\,|\,1m_1\rangle\langle 1m_1\,|\,\hat{\mathbf{r}}_\delta\,|\,l_2m_2\rangle \times\langle l_1m_2\,|\,\hat{\mathbf{r}}_\gamma\,|\,1m_3\rangle\langle 1m_3\,|\,\hat{\mathbf{r}}_\beta\,|\,00\rangle\ , \tag{6}$$

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 Δl selection rule, $C(\alpha\beta\gamma\delta l_2)$ vanishes unless $l_2=0$ or 2. The dynamics are contained in the final factor,

$$F(n_1n_2n_3\theta_1\theta_2\theta_3l_2)=Z\frac{(S_{10Z}\,|\,r\,|\,S_{n_11\alpha_1})(S_{n_11\alpha_1}\,|\,r\,|\,S_{n_2l_2\alpha_2})(S_{n_2l_2\alpha_2}\,|\,r\,|\,S_{n_31\alpha_3})(S_{n_31\alpha_3}\,|\,r\,|\,S_{10Z})}{(n_1\alpha_1-Z)(n_2\alpha_2-Z)(n_3\alpha_3-Z)}\ , \tag{7}$$

where

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

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

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

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.[4] To completely specify γ 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 γ are given in Table I. The matrix elements required for the evaluation of Eq. (7) may be expressed as

$$(S_{n1\alpha}\,|\,r\,|\,S_{n'0\alpha'}) = \frac{[(n^2-1)nn']^{1/2}}{4}\sum_{\mu=0}^{n-2}(-1)^\mu\begin{bmatrix}n-2\\ \mu\end{bmatrix}\sum_{\nu=0}^{n'-1}(-1)^\nu\begin{bmatrix}n'-1\\ \nu\end{bmatrix}\begin{bmatrix}4+\mu+\nu\\ 3+\mu\end{bmatrix}\left[\frac{(2\alpha)^2(2\alpha')}{(\alpha+\alpha')^3}\frac{4}{(\alpha+\alpha')^2}\right]\frac{(2\alpha)^\mu(2\alpha')^\nu}{(\alpha+\alpha')^{\mu+\nu}} \tag{11}$$

and

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

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.[23] 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.

$\alpha\beta\gamma\delta$	45 $C(\alpha\beta\gamma\delta l_2)$ $l_2=0$	$l_2=2$
$zzzz$	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 γ_{zzzz} and γ_{zxxz} in this case. For each value of l_2 ($=0$ or 2) the terms in the expression for γ_{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 γ_{zzzz} all subsets of $\sum P$ have the same common factor $C(zzzzl_2)$.

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

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

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

$$\lim_{\theta_2\to 0}\left[\frac{Zf(\theta_2)}{\alpha(\theta_2)-Z}\right] = \lim_{\theta_2\to 0}\left[-\frac{Z^2 f(\theta_2)}{\theta_2}+\frac{f(\theta_2)}{2}-\frac{Z^2 df(\theta_2)}{d\theta_2}\right]\ , \tag{14}$$

where

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

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

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

and

$$\frac{d}{d\alpha}(S_{n1\alpha}\,|\,r\,|\,S_{10\alpha'}) = -(2\alpha)^{-1/2}(S_{n1\alpha}\,|\,r\,|\,S_{20\alpha'})-\frac{2}{\alpha}(S_{n1\alpha}\,|\,r\,|\,S_{10\alpha'})\ , \tag{17}$$

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

$$\begin{aligned}G(n_1 1 n_3\theta_1 0\theta_3 0)&=\lim_{\theta_2\to 0}F(n_1 1 n_3\theta_1\theta_2\theta_3 0)\\ &=-\tfrac{1}{2}f(0)\left\{\left[\frac{Z}{\alpha_1}\right]^2\left[4+\frac{n_1\alpha_1}{n_1\alpha_1-Z}\right]-1+\left[\frac{Z}{\alpha_3}\right]^2\left[4+\frac{n_3\alpha_3}{n_3\alpha_3-Z}\right]\right.\\ &\quad\left.+\sqrt{2}\left[\left[\frac{Z}{\alpha_1}\right]^2-1\right]\frac{(S_{n_1 1\alpha_1}\,|\,r\,|\,S_{20Z})}{(S_{n_1 1\alpha_1}\,|\,r\,|\,S_{10Z})}+\sqrt{2}\left[\left[\frac{Z}{\alpha_3}\right]^2-1\right]\frac{(S_{n_3 1\alpha_3}\,|\,r\,|\,S_{20Z})}{(S_{n_3 1\alpha_3}\,|\,r\,|\,S_{10Z})}\right\}\ .\end{aligned} \tag{18}$$

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: γ 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 γ_{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 γ will be resonant if ω is equal to one of these energy differences. For DFWM and ESHG resonances will also occur when 2ω matches a transition frequency; and for THG, resonances occur when ω, 2ω, or 3ω matches a transition frequency. For the dc Kerr effect we have calculated γ up to and past

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

Process	Frequency arguments	Independent tensor components	Number of laser fields	Apparent divergences
Static	$(0;0,0,0)$	1	0	yes
EOR	$(0;\omega,-\omega,0)$	2	1	yes
dc Kerr[a]	$(-\omega;0,0,\omega)$	2	1	yes
ESHG	$(-2\omega;\omega,\omega,0)$	2	1	no
THG	$(-3\omega;\omega,\omega,\omega)$	1	1	no
DFWM	$(-\omega;\omega,\omega,-\omega)$	2	1	yes
ac Kerr[a]	$(-\omega_3;\omega_1,-\omega_1,\omega_3)$	2	2	yes
CARS	$(-2\omega_1+\omega_3;\omega_1,\omega_1,-\omega_3)$	2	2	no

[a]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 $n_{\max}=10$ 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 $n_{\max}$.

The results of the γ_{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 γ_{zzzz} as resonance is approached and the change in the relative size of γ_{zzzz} and γ_{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 γ_{zzzz} obeys the relation[26]

$$\gamma_{zzzz}(-\omega_\sigma;\omega_1,\omega_2,\omega_3)=\gamma_{zzzz}(0;0,0,0)(1+A\omega_L^2)\ , \qquad (19)$$

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

$$\omega_L^2=\omega_\sigma^2+\omega_1^2+\omega_2^2+\omega_3^2 \qquad (20)$$

defines the effective "laser" frequency ω_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 γ occurs at $\omega_L^2=0.281\,25$, $0.140\,625$, $0.210\,9375$, or 0.1875, respectively. Since γ_{zzzz} will diverge at different values of ω_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 γ_{zzzz}. This suggests that we calculate γ as a function of ω_L^2 rather than as a function of ω.

The results for γ_{zzzz} and $\gamma_{zzzz}/\gamma_{zxxz}$ calculated at several values of ω_L^2 are presented in Table IV. The results for γ_{zzzz} and γ_{zxxz} for the dc Kerr effect, DFWM, ESHG, and THG are also plotted as functions of ω_L^2 in Figs. 1 and 2. It is immediately apparent that the dispersion is very nearly the same for all four processes for γ_{zzzz} considered as a function of ω_L^2, but not for γ_{zxxz}. Plotting $\gamma_{zzzz}/\gamma_{zzzz,\ \mathrm{dc\,Kerr}}$ versus ω_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 ω_L^2, but at higher ω_L^2 the dc Kerr effect has the smallest dispersion. DFWM has the largest dispersion at all values of ω_L^2. The ratio $\gamma_{zzzz}/\gamma_{zxxz}$ is plotted versus ω_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 γ as a function of ω_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 γ, 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 γ_{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 range $\omega_L^2=5\times10^{-6}-1\times10^{-3}$ with 12-significant-figure accuracy have been used. To within the uncertainty of ±1 in the last decimal place, the leading coefficient A in the power-series expansion of γ_{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 ±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 γ_{zzzz}, and an error

TABLE III. Results for γ_{zzzz} and $\gamma_{zzzz}/\gamma_{zxxz}$ calculated as functions of ω for the dc Kerr effect, DFWM, ESHG, and THG. The accuracy of the results decreases with increasing ω because the maximum number of terms in the calculation is fixed. The ratio $\gamma_{zzzz}/\gamma_{zxxz}$ has not been tabulated for THG, because for THG the ratio is exactly equal to 3 at all frequencies. The first resonance of γ for the dc Kerr effect, DFWM, ESHG, or THG occurs at $\omega=0.375$, 0.1875, 0.1875, or 0.125, respectively.

	γ_{zzzz} (a.u.)				$\gamma_{zzzz}/\gamma_{zxxz}$		
ω (a.u.)	dc Kerr	DFWM	ESHG	THG	dc Kerr	DFWM	ESHG
0.0000	1333.125 000	1333.125 000	1333.125 000	1333.125 000	3.000 000 00	3.000 000 00	3.000 000 00
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
0.005	1333.773 300	1334.422 079	1335.071 258	1337.021 519	3.000 218 02	2.999 127 83	2.999 345 78
0.01	1335.720 917	1338.324 538	1340.934 582	1348.808 744	3.000 872 45	2.996 508 70	2.997 380 00
0.02	1343.552 374	1354.104 514	1364.761 641	1397.466 688	3.003 495 89	2.985 992 33	2.989 469 75
0.03	1356.752 064	1381.023 883	1405.846 573	1484.293 574	3.007 888 69	2.968 322 10	2.976 116 16
0.04	1375.546 510	1420.066 087	1466.417 486	1619.357 197	3.014 081 83	2.943 278 42	2.957 055 99
0.05	1400.264 462	1472.725 496	1549.966 913	1820.392 956	3.022 119 47	2.910 543 14	2.931 903 10
0.06	1431.349 391	1541.148 131	1661.722 581	2118.621 363	3.032 059 77	2.869 687 88	2.900 128 82
0.07	1469.376 896	1628.352 964	1809.430 817	2571.468 093	3.043 976 03	2.820 157 46	2.861 033 80
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
0.09	1569.371 488	1877.851 100	2265.173 665	4540.499 44	3.074 114 05	2.692 070 67	2.756 976 05
0.10	1633.403 205	2054.896 662	2618.929 335	7009.695 7	3.092 572 83	2.611 518 02	2.689 316 78
0.11	1708.603 016	2282.774 67	3112.232 63	13 352.452	3.113 486 69	2.518 193 72	2.608 754 17
0.12	1796.756 695	2581.853 17	3826.146 03	48 135.766	3.137 034 94	2.410 331 02	2.512 696 37
0.13	1900.103 840	2985.7602	4913.7672		3.163 428 25	2.285 664 99	2.397 703 0
0.14	2021.469 926	3554.5182	6695.0986		3.192 914 10	2.141 239 8	2.259 141 3
0.15	2164.446 724	4407.884	9941.5492		3.225 783 73	1.973 101 7	2.090 677 0
0.16	2333.641 865	5829.175	16 962.324		3.262 380 72	1.775 780 8	1.883 532 3
0.17	2535.028 897	8717.13	37 827.346		3.303 112 15	1.541 344	1.625 495 4
0.18	2776.445 909	18 606.30	180 213.618		3.348 462 84	1.257 479	1.300 047 8
0.19	3068.318 025				3.399 014 08		
0.20	3424.724 28				3.455 468 24		
0.21	3865.006 32				3.518 682 08		
0.22	4416.251 43				3.589 712 15		
0.23	5117.226 23				3.669 878 30		
0.24	6024.794 15				3.760 854 36		
0.25	7224.738 94				3.864 801 10		
0.26	8850.726 61				3.984 566 97		
0.27	11 119.016 23				4.124 001 51		
0.28	14 395.3462				4.288 464 70		
0.29	19 331.9121				4.485 693 23		
0.30	27 169.285				4.727 357 7		
0.31	40 465.118				5.032 056 1		
0.32	65 068.111				5.431 575 4		
0.33	116 346.59				5.985 509 0		
0.34	243 518.68				6.820 956		
0.35	661 397.3				8.267 549		
0.36	3 038 857				11.532 67		

TABLE III. (*Continued*).

	γ_{zzzz} (a.u.)				$\gamma_{zzzz}/\gamma_{zxxz}$		
ω (a.u.)	dc Kerr	DFWM	ESHG	THG	dc Kerr	DFWM	ESHG
0.37	81 032 102				27.479 50		
0.38	−77 842 687				−19.931 07		
0.39	-2.48445×10^{6}				−3.965 46		
0.40	-2.4331×10^{5}				−0.6611		
0.41	3.131×10^{5}				0.8502		
0.42	1.059×10^{6}				1.7891		
0.43	4.844×10^{6}				2.5252		
0.44	$1.628\,80\times10^{8}$				3.3536		
0.45	-7.8727×10^{7}				7.2883		
0.46	2.505×10^{7}				1.9631		

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

	γ_{zzzz} (a.u.)				$\gamma_{zzzz}/\gamma_{zxxz}$		
ω_L^2 (a.u.)	dc Kerr	DFWM	ESHG	THG	dc Kerr	DFWM	ESHG
0.0000	1333.125 000	1333.125 000	1333.125 000	1333.125 000	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	3.000 436 10	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	1472.361 813	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	1633.126 963	3.092 572 83	2.816 289 77	2.907 938 83
0.03	1820.816 892	1826.805 162	1821.570 438	1820.392 956	3.143 292 12	2.716 788 16	2.857 954 35
0.04	2040.379 855	2054.896 662	2042.561 916	2040.179 747	3.197 372 39	2.611 518 02	2.805 033 18
0.05	2299.469 590	2330.693 91	2304.726 105	2300.487 778	3.255 175 05	2.499 874 67	2.748 917 01
0.06	2607.606 688	2670.311 62	2618.929 335	2611.987 417	3.317 118 69	2.381 148 00	2.689 316 78
0.07	2977.217 757	3098.3278	2999.896 787	2989.192 852	3.383 691 65	2.254 493 90	2.625 908 21
0.08	3424.724 28	3654.4493	3467.994 75	3452.302 726	3.455 468 24	2.118 894 6	2.558 326 51
0.09	3972.122 16	4407.884	4052.059 75	4030.190 73	3.533 130 09	1.973 101 7	2.486 160 41
0.10	4649.314 37	5492.545	4794.0457	4765.473 26	3.617 494 29	1.815 552 9	2.408 945 2

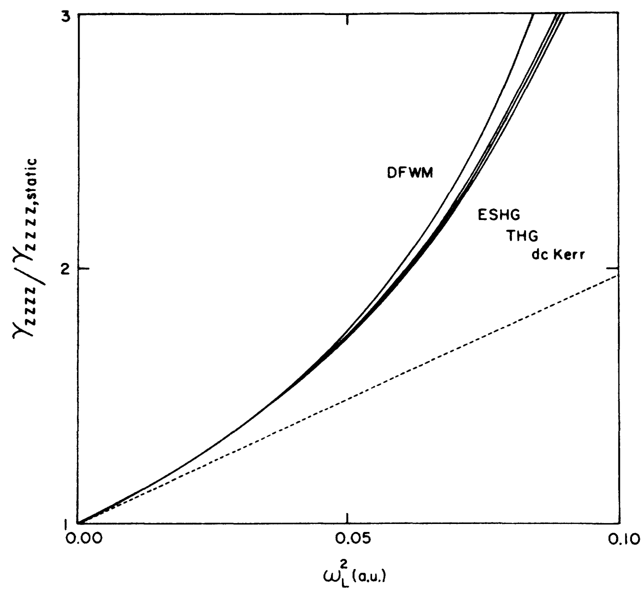

FIG. 1. Variation of γ_{zzzz}, normalized to its static value, is shown as a function of ω_L^2 for the dc Kerr effect, DFWM, ESHG, and THG. The dashed straight line is the lowest-order dispersion term from Table V.

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

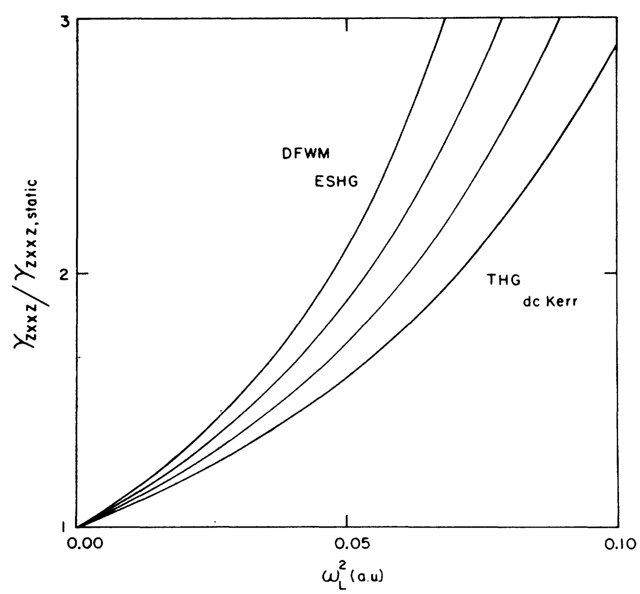

FIG. 2. Variation of γ_{zxxz}, normalized to its static value, is shown as a function of ω_L^2 of the dc Kerr effect, DFWM, ESHG, and THG.

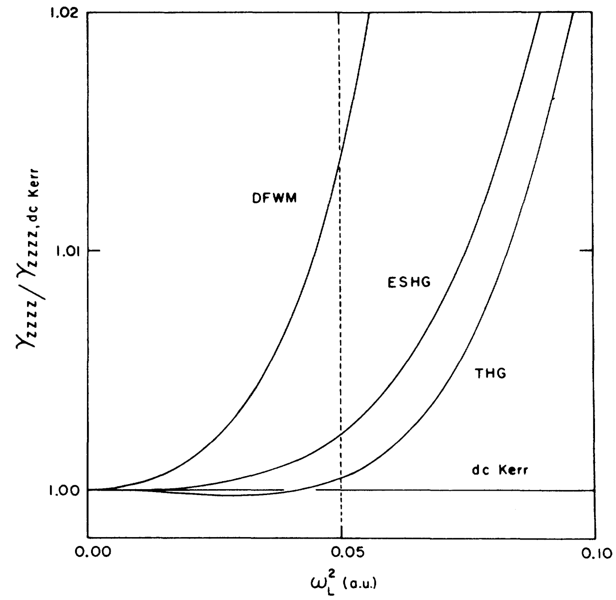

FIG. 3. Variation of γ_{zzzz}, normalized to γ_{zzzz} for the dc Kerr effect, is shown as a function of ω_L^2 for the dc Kerr effect, DFWM, ESHG, and THG. The results presented in Figs. 5 and 6 are calculated at the value of ω_L^2 indicated by the vertical dashed line.

γ_{zzzz} except at very small values of ω_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 ω_1

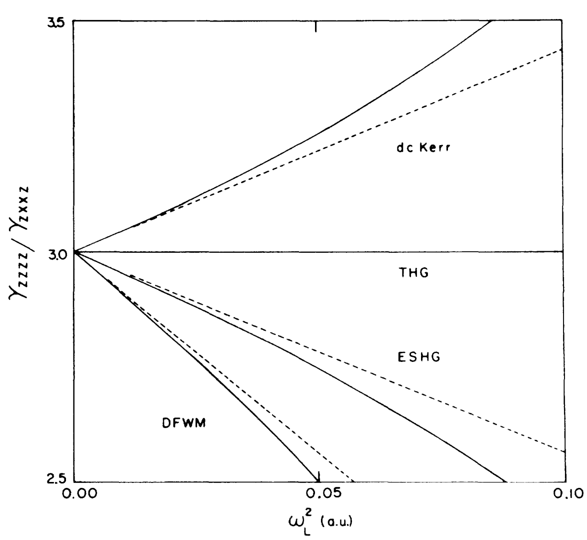

FIG. 4. Variation of $\gamma_{zzzz}/\gamma_{zxxz}$ is shown as a function of ω_L^2 for the dc Kerr effect, DFWM, ESHG, and THG. The dashed straight lines are the lowest-order dispersion terms from Table V.

TABLE V. Coefficients of the power-series expansions $(\gamma_{zzzz}/\gamma_{zzzz,\text{static}})=(1+A\omega_L^2+B\omega_L^4+C\omega_L^6+D\omega_L^8)$ 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	B	C	D	A'	B'	C'	D'
dc Kerr	9.722 617	67.893	405	2.4×10^3	1.453 243	4.213	13	4×10^1
DFWM	9.722 616	69.916	464	3.5×10^3	−2.906 485	−7.329	−21	-7×10^1
ESHG	9.722 617	67.893	416	2.6×10^3	−1.453 242	−3.848	−10	-3×10^1
THG	9.722 616	67.221	408	2.6×10^3	0	0	0	0

and ω_3 while holding ω_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 ω_L^2 requires that

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

so $0\leqq(\omega_3/\omega_L)^2\leqq\frac{1}{2}$ 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 ω_L^2 requires that

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

with solutions for $0\leqq(\omega_3/\omega_L)^2\leqq\frac{3}{4}$. For CARS, for a given value of ω_3 there are two possible solutions for ω_1. The solutions will be labeled ω_1^+ or ω_1^- according to whether the + or − sign is chosen in Eq. (22). The input frequency arguments of the CARS processes on the ω_1^- branch for $0\leqq(\omega_3/\omega_L)^2\leqq\frac{1}{2}$ 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 ω_3 is positive. Since γ 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 γ_{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 $\gamma_{zzzz}/\gamma_{zzzz,\text{ dc Kerr}}$ 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 $\gamma_{zzzz}/\gamma_{zzzz,\text{ dc Kerr}}$ in Fig. 5. From Fig. 5 one sees that the value of γ_{zzzz} 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 γ_{zzzz} and $\gamma_{zzzz}/\gamma_{zxxz}$ 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 ω_1^+ branch for CARS, $(\omega_3/\omega_L)^2=0$ gives ESHG and $(\omega_3/\omega_L)^2=\frac{1}{4}$ gives DFWM. The ω_1^- branch of CARS for $0\leqq(\omega_3/\omega_L)^2\leqq\frac{1}{2}$ corresponds to the sum-wave-mixing processes of ESHG, THG, and the dc Kerr effect when $(\omega_3/\omega_L)^2=0$, $\frac{1}{12}$, and $\frac{1}{2}$, respectively.

	γ_{zzzz} (a.u.)			$\gamma_{zzzz}/\gamma_{zxxz}$		
$(\omega_3/\omega_L)^2$	ac Kerr	CARS, ω_1^+ branch	CARS, ω_1^- branch	ac Kerr	CARS, ω_1^+ branch	CARS, ω_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

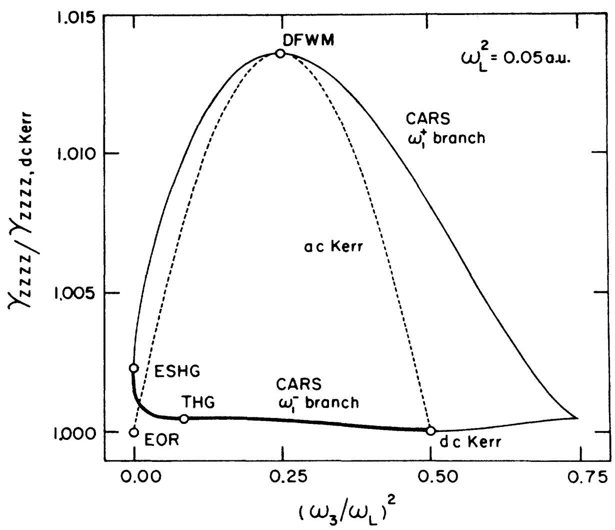

FIG. 5. Variation of γ_{zzzz}, at $\omega_L^2=0.05$ a.u. and normalized to γ_{zzzz} for the dc Kerr effect, is shown as a function of $(\omega_3/\omega_L)^2$ for the ac Kerr effect (dashed curve) and CARS (solid curve). The part of the ω_1^- branch for CARS which corresponds to sum-wave mixing has been drawn with a heavier line. The open circles mark particular special cases of the ac Kerr effect and CARS.

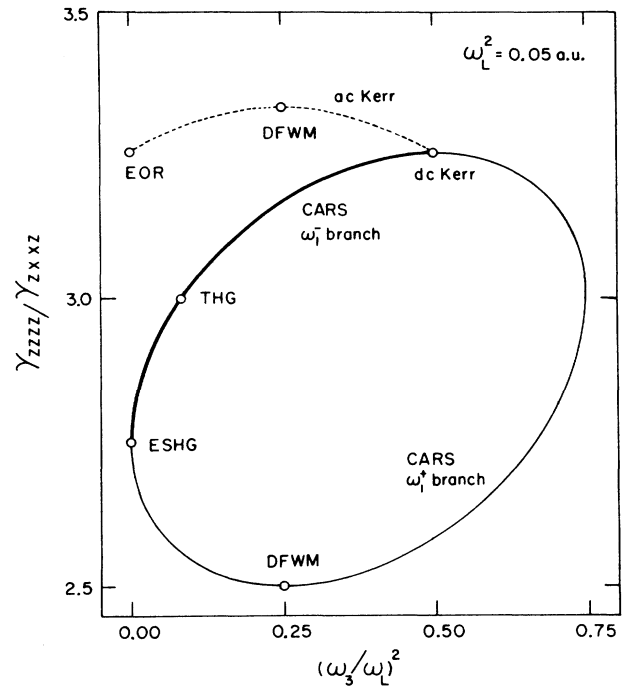

FIG. 6. Variation of $\gamma_{zzzz}/\gamma_{zxxz}$, at $\omega_L^2=0.05$ a.u., is shown as a function of $(\omega_3/\omega_L)^2$ for the ac Kerr effect (dashed curve) and CARS (solid curve). The part of the ω_1^- branch for CARS which corresponds to sum-wave mixing has been drawn with a heavier line. 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 $\omega_L^2\leqq 0.042$ the lower limit of γ_{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 γ_{zxzx} 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 $\gamma_{zzzz}/\gamma_{zxzx}$ 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 ω_L^2. The two processes for which only a single input field frequency is involved are DFWM and THG. It seems a reasonable conjecture, for the hydrogen atom at small values of ω_L^2, that DFWM and THG will give the upper and lower bounds for γ_{zzzz}, and that the ratios $\gamma_{zzzz}/\gamma_{zzxx}$, $\gamma_{zzzz}/\gamma_{zxzx}$, 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.

ACKNOWLEDGEMENT

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