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Indices governing optical self-focusing and self-induced changes in the state of polarization in N_2, O_2, H_2, and Ar gases

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We employ recently published data on the dc Kerr effect and electric-field-induced second-harmonic generation in N_2, O_2, H_2, and Ar gases to calculate the nonlinear-optical indices governing self-focusing, self-induced changes in the state of polarization, and third-harmonic generation, over a wide range of wavelengths in these gases. We construct a new, one-parameter, dispersion formula that not only fits all existing data on the above gases, but also fits recent quantum calculations of each tensor component of the third-order optical susceptibility of helium, over a wide range of frequency arguments. We compare the difference between the predictions of this formula and the predictions of a previously used formula based only on linear refractive-index dispersion. The difference is negligible at 1053 nm but becomes significant at blue or shorter wavelengths (<350 nm), where it indicates the uncertainty in our dispersion calculations. We find the coefficient for self-induced polarization changes in one atmosphere of air to be $c_{1221}(-\omega,\omega,\omega,-\omega)=(24\pm2)\times10^{-19}$ esu, at 1053 nm and 20 °C. This is consistent with one of two reported measurements of this coefficient.

I. INTRODUCTION

The intensity-dependent change in the state of polarization (ICSP) of a high-power laser beam as it propagates through the amplifiers, lenses and air paths of a large laser system such as Nova[1] has been observed to cause various unwanted effects, such as a reduction in the efficiency of harmonic generation and energy loss from polarizing surfaces.[2,3] These and other effects of nonlinear refraction, such as the self-focusing of a high-power laser beam in an isotropic transparent medium are described by two medium coefficients, which by common convention are called $c_{1111}(-\omega,\omega,\omega-\omega)$ and $c_{1221}(-\omega,\omega,\omega-\omega)$, and are often referred to as the "c coefficients" for degenerate four-wave mixing (DFWM).[4,5] Two published, independently measured, values of c_{1221} for air at 1053 and 1064 nm differ by a factor of 2.[6,7] In this paper, we use recently published measurements at 515 nm of the dc Kerr effect[8] and electric-field-induced second-harmonic generation[9] to calculate the ICSP (Ref. 10) and self-focusing coefficients over a wide range of wavelengths for N_2, O_2, H_2, air, and argon gases. We construct two methods to predict the dispersion of nonlinear coefficients, and compare their predictions to assess their uncertainties. The first method is old, having been tested with Kerr data in gases as early as 1924.[11] This simple method requires a knowledge of linear-index dispersion only. The second method is new. It requires only a single accurate string of nonlinear dispersion data (e.g., for the Kerr constant) to determine a single parameter (an effective ultraviolet resonance frequency ω_0) in the formulas we have constructed. This second method fits all the past calculations for all beam polarizations of self-focusing, ICSP, electric-field-induced second-harmonic generation (ESHG), third-harmonic generation, and Kerr effect in helium gas, to ultraviolet (uv) wavelengths. It also fits all other known experimentally observed dispersion, especially the recent ESHG measurements in the gases of interest here.[9] The difference between the predictions of the two methods is not great throughout the visible. We use this difference to estimate the uncertainties in our calculations. Our calculation of $c_{1221}(-\omega,\omega,\omega,-\omega)$ at 1053 nm for air agrees with the measured value reported by us in Ref. 7. We predict high dispersion in the blue and uv for this and other indices.

There is in the literature some variation in the definitions of nonlinear coefficients. Therefore we first review the exact definitions we will employ in Sec. II. Then in Sec. III we relate these coefficients to physically measurable effects in the long wavelength limit (LWL) where coefficients approach their LWL values asymptotically. In Sec. IV we review the existing literature on dc Kerr and ESHG measurements, summarizing the results relevant for the gases of interest here. In Sec. V we construct two methods for estimating dispersion of nonlinear indices, whose formulas we apply in Sec. VI to the determination of Kerr effect, self-focusing, ICSP, ESHG, and third-harmonic generation coefficients throughout the visible for the gases of interest.

II. REVIEW OF NONLINEAR SUSCEPTIBILITY TENSOR DEFINITIONS

Maxwell's equations govern the nonlinear propagation of a real-valued optical electric field vector $\mathcal{E}(\mathbf{r},t)$ which creates a real polarization density vector $\mathcal{P}(\mathbf{r},t)$ in the medium. It is always possible (and often convenient) to express these real vector fields in terms of complex amplitudes $\mathbf{E}(\mathbf{r},\omega_i)$ and $\mathbf{P}(\mathbf{r},\omega_i)$ of (a possibly infinite number of) components having (temporal) frequencies ω_i $(i=1,2,\ldots)$ as follows:

$$\mathcal{E}(\mathbf{r},t)=\mathrm{Re}\sum_i{}^{+}\,\mathbf{E}(\mathbf{r},\omega_i)e^{-i\omega_i t} \tag{1}$$

and

$$\mathcal{P}(\mathbf{r},t)=\mathrm{Re}\sum_i{}^{+}\,\mathbf{P}_i(\mathbf{r},\omega_i)e^{-i\omega_i t}\ . \tag{2}$$

Here the plus subscripts on the sums indicate that they are over positive frequencies ω_i only. In general, the sums extend to an infinite number of frequencies, and they may sometimes be most conveniently represented as integrals over frequency. In what follows, we will suppress the space variable $\mathbf{r}$ when it is understood that it is the same in every term. Electrostatic units (esu) will be used throughout. Note that some authors express the fields in terms of Fourier amplitudes which are one-half of the ordinary $\mathbf{E}$ and $\mathbf{P}$ amplitudes in (1) and (2).

We will treat isotropic media (gases, liquids, and glasses) for which the linear relation holds for all frequencies ω in the limit $|\mathbf{E}|\rightarrow 0$:

$$\mathbf{P}(\omega)=\chi(\omega)\mathbf{E}(\omega)\ . \tag{3}$$

The linear susceptibility χ is related to the linear refractive index n by $n=(1+4\pi\chi)^{1/2}$. In isotropic media there is no "second-order" component of the complete "nonlinear" polarization density $\mathcal{P}$ that is proportional to $\mathbf{E}^2$ due to the requirement of spatial inversion symmetry. The lowest-order nonlinear response, and the only order we need consider for the effects of interest here, is a "third-order" polarization density $\mathcal{P}$ that is proportional to $\mathbf{E}^3$. To express this we will use the commonly employed nonlinear susceptibility function, or "c tensor" $c_{\alpha\beta\gamma\delta}(\omega_i,\omega_j,\omega_k,\omega_l)$, defined by Maker and Terhune,[5] which relates different frequency components as follows. First, we express the complex vector amplitudes $\mathbf{E}(\omega)$ and $\mathbf{P}(\omega)$ in terms of their Cartesian spatial components E_α and P_α $(\alpha=x,y,z)$. Then the nonlinear part of the αth space component of the polarization density amplitude $P_\alpha^{\mathrm{NL}}(\omega)$ is related to the impressed electric vector components $E_\beta(\omega_j)$ by

$$P_\alpha^{\mathrm{NL}}(\omega)=Dc_{\alpha\beta\gamma\delta}(\omega_i,\omega_j,\omega_k,\omega_l)E_\beta(\omega_j)E_\gamma(\omega_k)E_\delta(\omega_l)\ . \tag{4}$$

The summation convention is assumed for repeated space indices β, γ, and δ. Also, by convention, the coherence of the nonlinear response is expressed in the requirements

$$\omega_i+\omega_j+\omega_k+\omega_l=0 \tag{5a}$$

and

$$\omega=-\omega_i\ . \tag{5b}$$

Although it is customary to make ω positive (and ω_i negative), one or two of the field frequency arguments could be negative. If, for example, ω_j were negative, we would find from (1) that

$$E_\beta(\omega_j)=E_\beta^*(|\omega_j|)\ , \tag{6}$$

which follows from $\mathcal{E}$ being a real electric field. The degeneracy factor D in (4) takes on the values 1, 3, or 6 when either all three, or any two, or none of the last three frequency arguments of $c_{\alpha\beta\gamma\delta}$, respectively, are equal. This factor ensures that all tensor components approach the limit $c_{\alpha\beta\gamma\delta}(0,0,0,0)$ uniformly as their frequency arguments approach zero in any order. The coefficients $c_{\alpha\beta\gamma\delta}$ are sometimes denoted $\chi^{(3)}_{\alpha\beta\gamma\delta}$ with the same frequency arguments, and sometimes written $4\chi^{(3)}_{\alpha\beta\gamma\delta}$ when field conventions differ by a factor of 2, and occasionally written otherwise by authors who omit the degeneracy factor D.

It will sometimes be convenient to use the abbreviated notation $(ijkl)$ for the argument set $(\omega_i,\omega_j,\omega_k,\omega_l)$ of the c tensor in (4). From the form of (4) it follows that the c tensor must be invariant to simultaneous interchange of any of its last three space and frequency indices[5,12]

$$c_{\alpha\gamma\beta\delta}(ikjl)=c_{\alpha\beta\gamma\delta}(ijkl)=\cdots\ . \tag{7}$$

For isotropic materials (gases, liquids, and glasses) the c tensor must have the form

$$\begin{aligned}c_{\alpha\beta\gamma\delta}(ijkl)=&\delta_{\alpha\beta}\delta_{\gamma\delta}c_{1122}(ijkl)+\delta_{\alpha\gamma}\delta_{\beta\delta}c_{1212}(ijkl)\\&+\delta_{\alpha\delta}\delta_{\beta\gamma}c_{1221}(ijkl)\ ,\end{aligned} \tag{8}$$

where $\delta_{\alpha\beta}$ is the Kronecker delta (unity for $\alpha=\beta$ and zero otherwise). This says that three independent complex tensor elements c_{1122}, c_{1212}, and c_{1221} for every frequency argument set $(ijkl)$ are enough to determine all 81 elements of the c tensor for isotropic media. Here, the indices 1 and 2 represent any two orthogonal space directions.

As one consequence of (7) and (8), the ICSP coefficient can be written in several equivalent forms

$$\begin{aligned}c_{1221}(-\omega,\omega,\omega-\omega)&=c_{1122}(-\omega,-\omega,\omega,\omega)\\&=c_{1212}(-\omega,\omega,-\omega,\omega)\ ,\end{aligned} \tag{9}$$

with similar equivalences for other coefficients. One must specify both space and frequency arguments to specify a c coefficient. Here we will use the ordering where the last two arguments are identical, unless stated otherwise.

In this paper, we will need to consider the c coefficients which describe the following five effects: (i) self-focusing of linearly polarized beams (SF), (ii) intensity-induced change in the state of polarization, (iii) electric-field-induced second-harmonic generation, (iv) dc Kerr effect, and (v) third-harmonic generation (THG). All five of these effects will be seen below to be described by argument sets $(ijkl)$ in which two of the last three arguments are equal. This fact, with (7) and (8), allows these cases to enjoy the extra symmetry

$$c_{1212}(\omega_i,\omega_j,\omega_k,\omega_k)=c_{1221}(\omega_i,\omega_j,\omega_k,\omega_k) \qquad (10)$$

so that there are only two independent tensor elements required in (8) to describe these effects. We now review the coefficients that describe these five effects.

Self-focusing of a linear-polarized beam is often described in terms of a nonlinear-index coefficient n_2, which is related to the change Δn in refractive index experienced by a monochromatic optical field at frequency ω due to its own intensity by[5]

$$\Delta n = n_2\langle \mathcal{E}^2\rangle = \tfrac{1}{2}n_2\mathbf{E}^*(\omega)\cdot\mathbf{E}(\omega)\ , \qquad (11)$$

where the time average $\langle\ \rangle$ is to be taken over several optical cycles. Of course, n_2, like n, experiences "dispersion," i.e., some, usually weak, dependence on ω at optical frequencies. Comparing (11) with (4) gives

$$n_2=(12\pi/n)c_{1111}(-\omega,-\omega,\omega,\omega)\ , \qquad (12)$$

in which the subscripts "1" indicate any single space direction. There is, in general, no relation between this tensor element $c_{1111}(-\omega,-\omega,\omega,\omega)$ and the element $c_{1122}(-\omega,-\omega,\omega,\omega)$ which we noted above governs the ICSP.

The index governing ESHG ($D=3$) is $c_{1111}(-2\omega,0,\omega,\omega)$ for the usual geometry in which all optical fields are polarized parallel to an applied dc electric field whose direction in the isotropic medium is represented by the subscript "1." Again, there is, in general, no relation between this coefficient and that in (12) describing self-focusing. The dc Kerr effect ($D=3$) is governed by $c_{1221}(-\omega,\omega,0,0)$.[12] Parallel-polarized third-harmonic generation ($D=1$) is governed by $c_{1111}(-3\omega,\omega,\omega\omega)$.[5] For these five effects at long wavelengths in a gas of atoms like argon, all the above coefficients are very close to the two "limit" coefficients $c_{1111}(0,0,0,0)$ and $c_{1221}(0,0,0,0)$ which are necessarily real-values since there is no dissipation in this limit. For atoms, the latter becomes one-third the former, as will become evident in Sec. III.

However, for molecular gases such as O_2, normal optical frequencies are well above the rotational and vibrational Raman frequencies of the molecules, and therefore the coefficients need *not* be near the two independent limiting values $c_{1111}(0,0,0,0)$ and $c_{1221}(0,0,0,0)$ that are approached when all frequencies are below the Raman frequencies. We will review the well-known phenomenology for dealing with this type of "strong dispersion" in Sec. III. This phenomenology, together with "weak dispersion" corrections, will allow us to infer the c coefficients for self-focusing and ICSP over the visible region from those that have been reported for Kerr effect and second-harmonic generation for N_2, O_2, and H_2. The desired coefficients for air are obtained from these by a weighted sum of those for N_2 and O_2. Since atoms like argon have no low-frequency vibrational or rotational excitations, their nonlinear coefficients have much simpler dispersion at optical frequences and we can deduce similar values for argon even more easily.

III. PHENOMENOLOGICAL THIRD-ORDER SUSCEPTIBILITY PARAMETERS FOR NONPOLAR GASES

It has been customary to study relations among c coefficients for nonpolar molecular gases (and liquids) by starting from their values in the long-wavelength limit, i.e., where the optical frequency ω is above the molecular vibration frequency ω_V but far below an effective electronic excitation frequency ω_S. In this limit, the real third-order polarization density $\mathcal{P}^{\rm NL}(t)$ is related to the electric field $\mathcal{E}(t)$ (at the same position $\mathbf{r}$) by a particular form of expression that results from the Born-Oppenheimer (BO) approximation.[15] Terms that deviate from this are fractionally smaller by the order $(\omega_V/\omega_S)^2$, which is always much less than 1%. This estimate follows from our treatment of dispersion in Sec. V. The form dictated by the BO approximation is generally written (omitting acoustic terms) as[12]

$$\mathcal{P}^{\rm NL}(t)=\tfrac{1}{2}\sigma\boldsymbol{\mathcal{E}}(t)\mathcal{E}^2(t) + \int_{-\infty}^{\infty} ds[a(t-s)\boldsymbol{\mathcal{E}}(t)\mathcal{E}^2(s) + b(t-s)\boldsymbol{\mathcal{E}}(s)\boldsymbol{\mathcal{E}}(t)\cdot\boldsymbol{\mathcal{E}}(s)]\ . \qquad (13)$$

Here the real constant σ describes the electronic contribution to the nonlinear response, i.e., that which would occur if all the nuclei were frozen in some typical configuration. This coefficient (divided by density) does not depend on temperature. The impulse response functions $a(t)$ and $b(t)$ describe the "isotropic" and "anisotropic" components of the nuclear contribution to the nonlinear polarization density. These "nuclear" terms are much larger for gases of molecules than of atoms, and they depend strongly on temperature. For example, $a(t)$ describes the modulation of the optical susceptibility by the "symmetric" Raman vibrations (such as the stretching vibrations in N_2 and O_2), while $b(t)$ describes the modulation of the optical susceptibility by the rotation of the anisotropic molecule.[12] These functions obey causality so that $a(t)=b(t)=0$ for $t<0$.

The form (13) which we will use to interrelate Kerr effect, self-focusing, ICSP, ESHG, and third-harmonic generation is the expression in real time of commonly used frequency domain expressions, such as Eqs. (2), (3), and (9) of Ref. 19 for a gas of nonpolar molecules. In Eq. (9) of Ref. 19 one sees the same separation into electric and nuclear (rotational and vibrational) terms which we have in (13). Our equation (13), however, expresses the general form for obtaining model-independent, experimentally determined, coefficients. These coefficients are commonly expressed as one or a few of the frequency components of the Fourier transforms A_ν and B_ν of $a(t)$ and $b(t)$ defined by

$$A_\nu \equiv A'_\nu + iA''_\nu = \int_{-\infty}^{\infty} dt\, e^{i\nu t}a(t)\ , \qquad (14)$$

and similarly for B_ν. The function B''_ν has peaks at pure rotational Raman frequencies as well as at the O and S rovibrational-branch frequencies. The function A''_ν has in addition, peaks at the frequencies of the vibrational Raman Q branch. The magnitudes of the functions A_ν

and B_ν fall rapidly toward zero as the frequency ν increases beyond all Raman, acoustic, and absorption frequencies.

In practice, for optical waves propagating in optically transparent media at the longest wavelengths where the medium is still transparent, (13) gives the third-order nonlinear polarization density to within $\sim 1\%$. (Actually, if acoustic effects, like stimulated Brillouin scattering, become involved, one must extend the time integral to a space-time integral over $d\mathbf{r}'$, as well as ds, in which a and b become functions of $\mathbf{r}-\mathbf{r}'$ as well as $t-s$.[13]) This asymptotic region (where waves have frequencies ω far below ultraviolet resonances but still above acoustic, Raman, and infrared-absorption frequencies) is the region we will call the "long-wavelength limit" (LWL). In this region we can always neglect any terms in $\mathbf{P}^{\mathrm{NL}}$ containing A_ν and B_ν in which ν is of the order of the optical frequency ω or larger.

Most nonlinear measurements are at visible wavelengths where the form of (13) is quite good but the values of σ, $a(t)$, and $b(t)$ have shifted significantly ($\sim 1-100\%$) from their long-wavelength limit. Therefore much of the later sections of this paper will be devoted to estimating these weak dispersion corrections to the long-wavelength parameters in the already dispersive (13).

When one uses (13) to analyze the "nonlinear index" n_2 (for self-focusing of a linearly polarized monochromatic beam), or the related c coefficient of (8), one finds that, in the LWL,[12]

$$c_{1111}(-\omega,-\omega,\omega,\omega)_{\mathrm{LWL}}=\sigma/8+(A_0+B_0)/6 \ . \qquad (15)$$

Here and below, the subscript LWL indicates that the quantity is evaluated in the long-wavelength limit where the frequency argument ω is small but still well above any Raman, acoustic, or infrared absorption frequencies of the medium. The real numbers A_0 and B_0 are the values of A_ν and B_ν at $\nu=0$. For simple molecules such as we consider here, pure vibrational ($\Delta J=0$) Raman transitions (Q branch) contribute a negligible fraction to A_0 as compared to the rotational and rovibrational Raman transitions. In this limit theory predicts that[12]

$$A_0=-B_0/3 \ . \qquad (16)$$

Experiments have verified this relation to within a few percent.[14] We will proceed using (16) as if it contributes no error to the analysis.

When one uses (13) to analyze intensity-induced changes in the state of polarization of a monochromatic beam, one finds[12]

$$c_{1122}(-\omega,-\omega,\omega,\omega)_{\mathrm{LWL}}=(\sigma+2B_0)/24 \qquad (17a)$$

and

$$c_{1212}(-\omega,-\omega,\omega,\omega)_{\mathrm{LWL}}=(\sigma+2A_0+B_0)/24 \ . \qquad (17b)$$

When one uses (13) to analyze electric-field-induced second-harmonic generation, one finds for nonpolar molecules and atoms that[12]

$$c_{1111}(-2\omega,\omega,\omega,0)_{\mathrm{LWL}}=\sigma/8 \ . \qquad (18a)$$

Similarly, for third-harmonic generation, one finds in the long-wavelength limit[12]

$$c_{1111}(-3\omega,\omega,\omega,\omega)_{\mathrm{LWL}}=\sigma/8 \ . \qquad (18b)$$

Our nonlinear-index values for molecules will be found to depend heavily on recent measurements of the dc Kerr constant. In these measurements a static dc field E_0 is applied to the gas, and the small difference between the optical refractive indices parallel ($n_\parallel$) and perpendicular ($n_\perp$) to this field are determined by measuring transmission through a crossed polarizer. The results are expressed in Ref. 8 in terms of a quantity K defined as $(n_\parallel-n_\perp)\rho E_0^2$, where ρ is the number density of atoms or molecules. Now $n_\parallel-n_\perp$ is proportional to $c_{1111}(ijkk)-c_{1122}(ijkk)$ which, by (8) and (10), equals $2c_{1221}(ijkk)$. Therefore we obtain the well-known relation[12]

$$\frac{n_\parallel-n_\perp}{2\pi E_0^2}=24c_{1221}(-\omega,\omega,0,0)/n \ . \qquad (19)$$

By comparing $\mathcal{P}^{\mathrm{NL}}$ as obtained from (4) and from (13), one obtains the well-known relation for the long-wavelength limit[12]

$$24c_{1221}(-\omega,\omega,0,0)_{\mathrm{LWL}}=\sigma+B_0 \ . \qquad (20)$$

Our analysis will be built upon Kerr measurements that, after correction for dispersion, yield $\sigma+B_0$, and also upon ESHG measurements that yield σ. These give together the value of $\sigma+2B_0$ which, with (17) and further dispersion corrections, will enable us to compute the desired ICSP coefficient as well as the self-focusing coefficient over a wide range of wavelengths.

Most measurements of nonlinear coefficients in gases are partly or entirely normalized to a similar measurements in helium gas. Helium is by far the best calibrated of all gases, by virtue of careful experimental confirmations of even more precise theoretical calculations made over the past twenty years by many workers. The main body of existing results is reviewed by Bishop and Lam (BL) who contributed extensive theoretical checks and refinements.[15] Our confidence in these results is high since many of the results have been calculated independently by other workers, and agree closely. Their results are given in terms of single-atom coefficients, expressed in "atomic units," which they call $\gamma_{zzzz}(\omega_4,\omega_1,\omega_2,\omega_3)$ and $\gamma_{xxzz}(\omega_4,\omega_1,\omega_2,\omega_3)$. They calculated these elements for all the effects we have mentioned above. Since these all have $\omega_2=\omega_3$ and obey (10), these are all of the independent tensor elements for these cases. For frequency arguments approaching zero, γ_{zzzz} approaches the single electronic nonlinearity parameter γ, defined in Ref. 16 along with the conversion factor for converting atomic units (a.u.) to electrostatic units (esu). One may convert the important results for helium to our parameters, using the atomic number density $\rho(\mathrm{cm}^{-3})$, and the relation[16]

$$\begin{aligned}5.036\times10^{-40}&\gamma_{zzzz}(\omega_4,\omega_1,\omega_2,\omega_3)\ \text{a.u.}\\ &=24\rho^{-1}c_{1111}(\omega_4,\omega_1,\omega_2,\omega_3)\ \text{esu} \ . \qquad (21)\end{aligned}$$

TABLE I. Compendium of relevant data on dc Kerr effect in five gases. Values in parentheses are limits of error of last figures given by source. All other values have estimated error limits of ±10% for reasons explained in text. When both absolute values and helium-based values are available at the same wavelength, the average given was obtained by weighting the former three times more than the latter, as this was our estimate of the relative accuracy of the two values.

Gas	λ	$\frac{n_{\parallel}-n_{\perp}}{2\pi E_0^2}$ (10^{-19} esu)		
(20 °C, 760 Torr)	(nm)	Normalized to He	Absolute	Average
N_2	515	129^{a}	236^{b}	252
			257^{c}	
	633		$251(36)^{d}$	$251(36)^{d}$
O_2	515	281^{a}	515^{b}	549
			559^{c}	
Ar	515	25.5^{a}	46.7^{b}	49.7
			50.7^{c}	
	633	$22(3)^{e}$	$40(6)^{b}$	$40(6)^{b}$
H_2	515	3.2^{a}	59^{b}	63
			64.1^{c}	
	633		52.5^{f}	52.5^{f}
He	515	1	1.83^{g}	
			$1.99(13)^{c}$	
	633	1	1.80^{g}	
	∞	1	1.76^{g}	

[a] Values of Ref. 8 divided by their value for helium.

[b] Obtained by multiplying the value to the left by the theoretical value given for helium in this table.

[c] Absolute value given in Ref. 8.

[d] From Ref. 17 which has no value for He by which to calibrate the static electric field.

[e] Value as quoted in Ref. 18, divided by the helium value also given there.

[f] From Ref. 19 which has no value for He by which to calibrate the static electric field.

[g] From the value per atom calculated from Eqs. (14) and (16) of Ref. 15, assuming ideal gas law; error estimated as ~±3%.

When converted to esu, the γ parameter of Ref. 16 equals $3\sigma/p$. Fortunately for our dispersion estimates, BL calculated γ_{zzzz} and γ_{xxzz} for Kerr effect, self-focusing, ICSP, and THG over a a wide range of frequency arguments, so that we have an accurate example of dispersion with which to compare the two different dispersion correction methods we will describe in Sec. V. First we summarize the Kerr and ESHG data upon which our final results will be built.

IV. SUMMARY OF EXISTING DATA FOR FIVE GASES

We will base our complete specification of the c tensor of N_2, O_2 (and air), Ar, and H_2 on existing Kerr data (absolute and relative to He) and on electric-field-induced second-harmonic data (relative to helium). We will assume, for the purpose of normalizing the data, that the results of BL (Ref. 15) for helium are perfectly accurate. The estimated errors there (a few percent) are well below the experimental errors involved. Their results are for $c_{1111}(ijkk)$ and $c_{1122}(ijkk)$ for the four arguments sets $(ijkk)$ corresponding to $(3\omega,\omega,\omega,\omega)$ $(2\omega,0,\omega,\omega)$, $(-\omega,-\omega,\omega,\omega)$ and $(-\omega,\omega,0,0)$. The range of ω calculated is from zero to near the first resonance (uv). These helium data are the main data by which we can evaluate our extrapolation and dispersion formulas.

The dc Kerr data and their sources are given in Table I. The most important data of Carusotto *et al.*[8] at 515 nm were quoted absolutely by them with errors around 2–3 %, except for the value for helium where an error of ±7% was quoted. Their helium value is, unfortunately, 9% above the value obtained from the later calculation of BL,[15] and 6% above the value from a more recent update.[15] This discrepancy is no doubt due in part to the difficulty of measuring the unusually small Kerr effect in helium. However, there is likely to be an additional, although probably smaller, error arising from the uncertainty in calculating the spatial rms value of the dc electric field $\overline{E}_0$ over the path of the probing optical beam. Carusotto *et al.*[8] do not comment on how they corrected for the non-uniform field distribution between their electrodes, so their high helium Kerr constant may in part be due to their $\overline{E}_0$ being smaller than they estimated. To deal with this discrepancy we have obtained two Kerr constant values for each gas as reduced from their data,[8] and give a weighted average, along with miscellaneous older data at 633 nm in the last column of Table I. We obtained the first value by dividing their value for a gas by their value for helium (the values with superscript a in Table I) and then multiplying by the theoretical values for helium from BL to obtain the values (superscripted b) in the fourth column of Table I. We obtained the second values (superscripted c in Table I) directly from the values in Ref. 8 based on the dc field calibration. The averages of these two, quoted in Table I, weight the values given in Ref. 8 three times as heavily as the helium-renormalized values. This reflects our estimate of their relative errors. In addition, our final estimated error values have been increased to ±10%, which would encompass the values of the Kerr constants that one would obtain by normalizing signals to the helium signal rather than by estimating $\bar{E}_0$ absolutely.

The determination of the four-wave-mixing (ICSP and SF) coefficients for air from the Kerr constant depends to some degree ($<20\%$) on the electronic part σ. Fortunately, σ values of more than sufficient accuracy can be obtained for our gases from the second-harmonic (ESHG) data of Mizrahi and Shelton.[9] Their measurements from 700 to 450 nm show dispersion, resulting in a rise in c_{1111} values from 15% to 26% over this range, depending on the gas. We found that all of this data fits the following form (after removing helium normalization) to within experimental error:

$$c_{1111}(-2\omega,\omega,\omega,0)=(\sigma/8)(1-6\omega^2/\omega_0^2)^{-1} . \tag{22}$$

The long-wavelength limit parameters σ obtained from these fits are listed in Table II. The form of (22) will be justified in Sec. V. It is an example of the second dispersion formula B which we develop in Sec. V B, where we list the corresponding nonlinear "Sellmeier"-like dispersion frequencies ω_0 to be used in the dispersion calculations of Sec. VI.

V. ESTIMATION OF WAVELENGTH DISPERSION OF NONLINEAR COEFFICIENTS

The published nonlinear Kerr, and other nonlinear coefficients were measured at wavelengths which were clearly not in the long-wavelength limit. Calculations that use only the LWL formulas of Sec. III could easily produce predictions for ICSP coefficients at other wavelengths which are in error by anywhere from several percent to factors of 2 or larger. Therefore we develop here two independent dispersion formulas, analogous to the Sellmeier equation for the linear refractive index, in order to assess dispersion corrections for the nonlinear coefficient.

We develop two formulas for two reasons. First, because there is no single known "accurate" formula, and we can use the difference between the predictions of our two formulas to indicate the order of magnitude of the accuracy of our dispersion corrections. Secondly, we need two formulas with different capabilities. One formula (which we call A) can be applied without the existence of prior nonlinear dispersion data, with only known linear dispersion, The second, presumably more accurate formula (which we call B) can be used to extrapolate nonlinear dispersion data when they exist, for example from ESHG measurements, to all other third-order nonlinear effects (as is done in Sec. VI).

TABLE II. Value of the electronic nonlinearity parameter σ derived from ratios of the coefficient $c_{1111}(-2\omega,\omega,\omega,0)$ for various gases relative to helium, as reported in Ref. 9. This ratio was extrapolated to the long-wavelength limit, as explained in the text, and then multiplied by the value 1.76×10^{-19} esu for He (20 °C, 760 Torr), calculated in Ref. 15. Estimated errors in final digits are given in parentheses.

Gas (20 °C, 760 Torr)	σ (10^{-19} esu)
N_2	36.5(1.4)
O_2	37.8(1.1)
Ar	47.4(1.8)
H_2	27.9(0.3)[a]
He	1.76(0.05)

[a] See also Ref. 21.

TABLE III. Frequencies ω_s of the poles of the Sellmeier equation for the dispersion of the linear refractive index, taken from Ref. 20.

Gas (20 °C, 760 Torr)	ω_s (10^3 cm^{-1})
N_2	131
O_2	113
Ar	130
H_2	111
He	187

A. Dispersion formula A

Formula A assumes that all c-tensor elements scale by a universal "dispersion factor" $F^A(ijkl)$ which approaches unity in the long-wavelength limit. That is,

$$c_{\alpha\beta\gamma\delta}(ijkl)=c_{\alpha\beta\gamma\delta}(ijkl)_{\mathrm{LWL}}F^A(ijkl) . \tag{23}$$

We use a form for F^A that has often been used in the past, even to collate prelaser measurements such as the Kerr measurements of Szivessy.[11] Its justification was summarized in Ref. 12. We may write it as

$$F^A(ijkl)=\left[\prod_{i=1}^{4}[n^2(\omega_i)-1]\right]\Big/(n^2_{\mathrm{LWL}}-1)^4 , \tag{24}$$

where the $n(\omega_i)$ represent the linear refractive indices at each of the four frequency arguments and n^2_{LWL} is the long-wavelength limit of the refractive index. It is more than sufficiently accurate for our purposes to use the single-resonant-denominator form of the Sellmeier equation for nonpolar gases to calculate $n^2(\omega)$. We then obtain from (24) the following form of the dispersion factor

TABLE IV. Characteristic optical frequencies ω_0 of dispersion formula B for gases. These were derived from fitting the ESHG data of Ref. 9 as described in the text. The uncertainties quoted span the values which give a satisfactory fit to the data.

Gas (20 °C, 760 Torr)	ω_0 (10^3 cm^{-1})
N_2	115±10
O_2	90±5
Ar	115±10
H_2	100±10
He	158±5[a]

[a] Fit to the calculations of Ref. 15.

for method A which we will use throughout:

$$F^A(\omega_4,\omega_1,\omega_2,\omega_3)=\prod_{i=1}^{4}(1-\omega_i^2/\omega_s^2)^{-1}\ . \tag{25}$$

Here the characteristic Sellmeier frequencies ω_s are the usual ones to describe the short-wavelength dispersion of the linear refractive index (as opposed to that arising from infrared resonances). We will use the ω_s values given in the Landolt-Bornstein[20] Table 2863, and reproduced in our Table III for the gases of interest here. The Sellmeier frequency ω_s is available for hundreds of common gases and liquids, and so method A is generally applicable to any c-coefficient dispersion. The range of ω_i over which method A may be applied is not always clear. In the calculations of the c-coefficient dispersion for helium, it is found that the similar, but improved formula B, of the next section fits the BL results for He well in a range where an "effective optical frequency" ω_L defined as[9,15]

$$\omega_L=(\omega_i^2+\omega_j^2+\omega_k^2+\omega_l^2)^{1/2} \tag{26}$$

is less than two thirds of the characteristic frequency ω_0 of (22). We find that ω_0 ranges from 80% to 90% of ω_s in our gases, and so the relation (25) is useful typically for $\omega_L \lesssim \frac{1}{2}\omega_s$. A more precise limit, found in the next section, turns out to be 333 nm for air and oxygen, and a somewhat shorter wavelength for the other gases.

B. Dispersion formula *B*

The calculations by BL (Ref. 15) of c coefficients for He gas showed, as was expected, that each of the independent c-tensor element in (8) varies a little differently with frequency, and so one must, in general, develop three dispersion factors (rather than one as in formula A). In our B formulas we will call these $F^B_{1122}(ijkl)$ $F^B_{1221}(ijkl)$, and $F^B_{1212}(ijkl)$. The first independent c-tensor element will be written in terms of its long-wavelength limit as

$$c_{1122}(ijkl)=c_{1122}(ijkl)_{\mathrm{LWL}}F^B_{1122}(ijkl)\ , \tag{27}$$

and similarly for c_{1212} and c_{1122}. Again, the frequency argument set $(\omega_i,\omega_j,\omega_k,\omega_l)$ is abbreviated $(ijkl)$. We have found that the following simple one-parameter form for the F^B factors nicely fits all the values of c_{1111} and c_{1122} of helium calculated for the argument sets: $(-3\omega,\omega,\omega,\omega)$ for THG $(-2\omega,0,\omega,\omega)$ for ESHG; $(-\omega,\omega,\omega,\omega)$ for DFWM; and $(-\omega,\omega,0,0)$ for the dc Kerr effect, for ω ranging from 0 to $2\omega_0/3$. We discuss the quality of the fit

TABLE V. Extrapolation of Kerr data to the long-wavelength limit (LWL) using the dispersion factor $F^A(-\omega,\omega,0,0)$ in dispersion formula A. The Kerr coefficients are taken from Table I and the "Sellmeier" frequencies ω_s are taken from Table III.

Gas (20 °C, 760 Torr)	λ (nm)	F^A[a]	$10^{19}(\sigma+B_0)$esu[b] (esu)	$10^{19}(\sigma+B_0)$[c] (esu, average)
N_2	515	1.046	241(9)	
	633	1.030	244(4)	
				242
O_2	515	1.062	517	
				517
Ar	515	1.046	47.6(10)	
	633	1.030	38.8(6)	
				44.4 (47.4)[f]
H_2	515	1.064	59.2(5)	
	633	1.042	50.4(3)	
				55.8
He	515	1.022	1.95(2)[d]	
	633	1.014	2.18(1)[e]	
				1.76[g]

[a] Dispersion factor which equals $(1-\omega^2/\omega_s^2)^{-2}$.

[b] Computed by dividing the experimental Kerr coefficients from last column of Table I by the value of F^A. Relative weights for computing the averages in the next column are given in parentheses. These are proportional to the inverse of errors quoted by sources.

[c] Average computed using relative weights assigned in previous column. For reasons given in the text we believe that, except as noted, the uncertainties in these values are at least $\sim\pm 10\%$ (i.e., greater than quoted by the data sources). This quantity is equivalent to $c_{1221}(-\omega,\omega,0,0)_{\mathrm{LWL}}$.

[d] From Ref. 8.

[e] From Ref. 18.

[f] Value which will be used in calculation. It comes directly from σ of Table II and has ±5% uncertainty.

[g] Precise value from theoretical calculation of Ref. 15. Experimental values shown only for comparison purposes.

in more detail below. Our formulas are

$$F^{B}_{1122}(ijkl)=(1-\omega^2_{1122}/\omega_0^2)^{-1} \ , \tag{28}$$

where

$$\omega^2_{1122}\equiv[13\omega_L^2+6(\omega_i\omega_j+\omega_k\omega_l)]/12 \ , \tag{29}$$

with the same formula for F^{B}_{1221}, but with

$$\omega^2_{1221}\equiv[13\omega_L^2+6(\omega_i\omega_l+\omega_j\omega_k)]/12 \ , \tag{30}$$

and similarly for F^{B}_{1212}, with

$$\omega^2_{1212}\equiv[13\omega_L^2+6(\omega_i\omega_k+\omega_j\omega_l)]/12 \ . \tag{31}$$

In each case the factor multiplying 6 is made up of frequency arguments paired in the same way the space subscripts are paired. (Recall that 1 and 2 represent any orthogonal space directions).

We note that, as in the results of BL for He, (29)–(31) give

TABLE VI. Some degenerate four-wave mixing (DFWM) c coefficients obtained from formula A. All frequency argument sets here are $(-\omega,-\omega,\omega,\omega)$ and $\omega(\text{cm}^{-1})\equiv\lambda^{-1}$. These coefficients were obtained using the dispersion factor F^A calculated from Eq. (24) with the dispersion frequencies ω_s of Table III. The uncertainties in these c-coefficient values are at least ±10%, arising from the uncertainties in the Kerr constants, plus uncertainties from the errors in F^A discussed in the text.

Gas (20 °C, 760 Torr)	λ^{a} (nm)	$F^{A\,b}$	$10^{19}c_{1122}{}^{c}$ (esu)	$10^{19}c_{1111}{}^{d}$ (esu)
N_2				
	261	1.43	26.7	39.2
	333	1.241	23.1	34.0
	522	1.090	20.3	29.9
	694	1.050	19.6	28.8
	1053	1.021	19.0	28.0
	LWL	1	18.6	27.4
O_2				
	333	1.34	55.6	77.7
	522	1.124	46.7	65.2
	694	1.068	44.3	61.9
	1053	1.028	42.7	59.6
	LWL	1	41.5	58.0
Ar				
	261	1.43	2.83	8.47
	522	1.090	2.15	6.46
	694	1.050	2.07	6.22
	1053	1.021	2.02	6.05
	LWL	1	1.98	5.93
H_2				
	300	1.46	5.09	9.62
	522	1.129	3.94	7.44
	694	1.070	3.73	7.05
	1053	1.030	3.59	6.79
	LWL	1	3.49	6.59
Air[e]				
	333		29.7	42.8
	522		25.6	37.0
	694		24.6	35.5
	1053		23.8	34.4
	LWL		23.3	33.6

[a] The shortest wavelengths tabulated are those below which formula B is known to have larger than 10% error.

[b] This dispersion factor equals $(1-\omega^2/\omega_s^2)^{-4}$ by Eq. (24).

[c] Calculted by subtracting σ values from Table II from twice the $\sigma+B_0$ from Table V, and multiplying by $F^A/24$. See Eq. (17).

[d] Calculated by adding $(\sigma+B_0)/9$ from Table V to $\sigma/72$ from Table II, and multiplying by F^A.

[e] Coefficients by adding 0.78 times the N_2 value to 0.21 times the O_2 value.

$$\omega_{1122}^2+\omega_{1221}^2+\omega_{1212}^2=3\omega_L^2 \ .$$

That is, in the B formulas, the "effective" frequency ω_L equals the rms value of the effective "tensor" frequencies defined in (29)–(31).

For the arguments calculated by BL, $\omega_k=\omega_l$, in which cases $F_{1212}^B=F_{1221}^B$ [see Eq. (10)]. In these cases, the c_{1111} calculated by BL must, by (8), equal $c_{1122}(ijkk)+2c_{1212}(ijkk)$. Furthermore, for Ar and He, A_0 and B_0 are negligibly small; thus the long-wavelength limits of the c_{1122}, c_{1212}, and c_{1221} in (8) are all $\sigma/24$. In the case of He, the choice $\omega_0=161\,146\ \mathrm{cm}^{-1}$ reproduced all the BL, results to better than 10% at $\omega_L=2\omega_0/3$, and to better than 3% at $\omega_L=\omega_0/2$. Some coefficients were reproduced much better than others. This percentage decreased to less than 0.2% as ω_L approached zero. In the limit of low frequencies, the asymptotic data were fit even better (in fact, within the estimated 0.1% accuracy), by $\omega_0=153\,009\ \mathrm{cm}^{-1}$. This gives an estimate of the uncertainty in the best value of ω_0 to use for He. From (27)–(30) one may verify that $F_{1122}^B(-\omega,-\omega,\omega,\omega)$ is by far the most sensitive of the three coefficients up to ω near $2\omega_0/3$ where it changed by -4.4% for a 1% increase in ω_0.

One sees that, according to the above rule B, the ESHG measurements of Mizrahi and Shelton[9,21] (MS) should be imitated well (as they are in fact) by

$$c_{1111}(2\omega,\omega,\omega,0)=\frac{\sigma}{24}\left[\frac{1}{1-7\omega^2/\omega_0^2}+\frac{2}{1-11\omega^2/2\omega_0^2}\right] . \tag{32}$$

The data of MS fall in the range $0.12\omega_0<\omega<0.35\omega_0$, where (32) is seen to differ from (22) by less than 0.2%. Hence we fitted their data by the simpler (22) to obtain the σ values of Table II and the values of ω_0 given in Table IV. The errors in ω_0 quoted in Table IV ($\sim 10\%$), give the range of values which fit the data of MS to within experimental error. These errors contribute an uncertainty to c values calculated by formula B that is between 10% and 40% of the difference between the predictions of formulas A and B.

VI. CALCULATIONS OF c COEFFICIENTS WITH DISPERSION

Using the two dispersion formulas A and B, we will now make two estimates of the long-wavelength limit for the Kerr coefficient $(\sigma+B_0)$ from the data. With the values of σ from ESHG measurements in Table II and the assumption of (16), we may deduce the coefficients for any any of the five effects reviewed in Sec. II at any "effective" wavelength (ω_L^{-1}) down to the ultraviolet region. To illustrate this we will tabulate some numerical examples for ICSP and self-focusing for the gases we have considered, as these coefficients are of most immediate concern in high-power laser applications.

The application of the A formulas, Eqs. (23) and (24), to extrapolate Kerr data to the long-wavelength limit results in values of $24c_{1221}(-\omega,-\omega,0,0)_{\mathrm{LWL}}=\sigma+B_0$ given in Table V. In Table VI we list the two independent c tensor elements for the degenerate four-wave mixing argument set $(-\omega,-\omega,\omega,\omega)$ that we derived from Table V with the aid of relation (16) and the electronic nonlinear parameters σ of Table II. The sample optical frequencies chosen were at the fundamental (1053 nm) and harmonic (522 nm) of large glass lasers, at the ruby laser frequency (694 nm), and at $\omega_L=2\omega_0/3$ (which the comparison with the calculations for helium showed to be a probable limit of accuracy of formula B). The dispersion factors were calculated using (24) with the "Sellmeier" parameters of

TABLE VII. Extrapolation of Kerr data to the long-wavelength limit of Eq. (21), made using the dispersion factor F_{1221}^B defined as in Eq. (28) with the characteristic argument ω_{1221}^2 which, for our argument set, equals $13\omega^2/6$ from Eq. (30). The expected uncertainty in these values is $\sim\pm 10\%$ for reasons explained in the text.

Gas	λ		$10^{19}(\sigma+B_0)$ esu	
(20°, 760 Torr)	(nm)	F_{1221}^B	From data[a]	Average
N_2	515	1.066	240(9)	240
	633	1.043	241(4)	
O_2	515	1.112	494	494
Ar	515	1.066	45.6(10)	42.9
	633	1.043	38.4(6)	(47.4)[b]
H_2	515	1.089	57.9(5)	54.8
			49.7(3)	
He	515	1.036		1.83[c]
	633	1.024		1.80[c]
	∞	1		1.76

[a] Parentheses contain weights used to compute average. Weights are inversely proportional to estimated errors.

[b] Value which will be used in calculation. It comes directly from σ of Table II and has ±5% uncertainty.

[c] These values, obtained by multiplying 1.76 by the F_{1221}^B factor, agree with the values calculated in BL (see Table I) to within 0.5%.

Table III. It would be difficult to assess the accuracy and useful wavelength range of method *A* without the following treatment of the same coefficients by method *B*.

The results of extrapolating Kerr data to the long-wavelength limit with the aid of the *B* formulas (27)–(31) are given in Table VII. These are then used to obtain the *c* coefficients for DFWM displayed in Table VIII. These results are presumably more accurate than those of Table VI because they are based on the experimentally measured dispersion in $c_{1111}(-2\omega,0,\omega,\omega)$, rather than on the measured dispersion in the linear refractive index *n*.

Consider the values of Tables VI and VIII for the ICSP coefficient $c_{1122}(-\omega,-\omega,\omega,\omega)$. This was recently measured in air at ω^{-1} equal to 1053 nm.[7] The formula *A* and formula *B* values are 23.86 and 23.8 (10^{-19} esu), respectively, within 0.3% of each other, and in good agreement with the measured value 20±5.[7] Since the formula *A* and formula *B* values are based on the same data num-

TABLE VIII. Some degenerate four-wave mixing *c* coefficients obtained from formula *B*, and all having frequency argument sets $(-\omega,-\omega,\omega,\omega)$ with $\omega(\mathrm{cm}^{-1})$ being equal to λ^{-1}. These coefficients were obtained from Eq. (27) using the long-wavelength coefficients of Table VII, multiplied by the dispersion factors F^B_{1122} and F^B_{1212} of Eqs. (28) and (31), with the dispersion parameters of Table IV. The errors carried over from Kerr measurements are ~±10% except for argon, which is ±5%, being based on more accurate ESHG data (normalized to helium). The shortest wavelength in each list is $3/[\omega_0(\mathrm{cm}^{-1})]$, which we estimate to be the limit of usefulness of the *B* dispersion formulas, Eqs. (26)–(30).

Gas (20 °C, 760 Torr)	λ (nm)	$10^{19}c_{1122}$[a] (esu)	$10^{19}c_{1212}$[b] (esu)	$10^{19}c_{1111}$[c] (esu)
N_2				
	261	45.3	6.90	59.1
	333	29.0	5.63	40.3
	522	21.7	4.79	31.3
	694	20.2	4.59	29.3
	1053	19.2	4.45	28.1
	LWL	18.5	4.35	27.2
O_2				
	333	97.4	12.6	123
	522	52.2	9.32	70.8
	694	45.9	8.65	63.2
	1053	42.1	8.22	58.2
	LWL	39.6	7.91	55.4
Ar				
	261	4.84	2.45	9.74
	522	2.32	2.18	6.67
	694	2.16	2.08	6.33
	1053	2.05	2.02	6.09
	LWL	1.98	1.98	5.93
H_2				
	300	8.36	2.44	13.2
	522	4.23	1.75	7.73
	694	3.83	1.65	7.13
	1053	3.58	1.58	6.74
	LWL	3.40	1.54	6.48
Air[d]				
	333	43.1	7.04	104
	522	27.9	5.69	61.8
	694	25.4	5.40	36.1
	1053	23.8	5.20	34.1
	LWL	22.7	5.05	32.9

[a] Calculated by subtracting σ values from Table II from twice the $\sigma+B_0$ from Table VIII, and multiplying by $F^B_{1122}/24$ from Eq. (28).

[b] Calculated by adding $(\sigma+B_0)/72$ from Table VIII to $\sigma/36$ from Table II and multiplying by F^B_{1212} from Eq. (31).

[c] Equals $c_{1122}+2c_{1212}$. See Eqs. (8) and (10).

[d] Coefficients calculated by adding 0.78 times the N_2 value to 0.21 times the O_2 value.

bers, the value 0.3% is a reasonable estimate of the error arising from the dispersion correction. This error is independent of the ±10% limit on the Kerr-experimental uncertainty, and so we are led to a state that, for air at 20 °C, 1 atm, and at 1053 nm,

$$c_{1122}(-\omega,-\omega,\omega,\omega)=(24\pm 3)\times 10^{-19} \tag{33}$$

in esu, with the stated limit being absolute. We feel from the foregoing discussion that the probable limit of uncertainty is smaller, perhaps $\sim\pm 2$ (rather than ± 3) around the most probable value of 23.8×10^{-19} esu.

Similarly, A and B versions of the self-focusing c coefficients for air under the same conditions are listed as 34.31 and 32.55 (10^{-19} esu), respectively. This 5% difference is well below the 10% Kerr experimental uncertainty. Using the B value as the more probably correct value and a 15% absolute limit of uncertainty, we obtain the following value for the common self-focusing coefficient or "nonlinear index" (12) of air at 20 °C, 760 Torr, and 1053 nm, in esu:

$$n_2=(1.2\pm 0.2)\times 10^{-16}\ . \tag{34}$$

This value is two order of magnitude less than for common laser glasses. The n_2 for argon under the same conditions is seen to be less by 5.4 and its ICSP coefficient less by a factor of 11. From these argon values, one can calculate the advantage gained by substituting argon for air in the path of a 1053-nm laser, an advantage that was seen in the experiments of Ref. 7.

Of course, for any comparison of our calculated coefficients with experimental ones to be valid in molecular gases, the experimental laser pulses must have a power spectrum much narrower than the Raman linewidths in the gas. In air these linewidths are around 3 GHz.[22] This is about five times the spectral width of the Nova laser used in Ref. 7. To estimate the error from this source, we see from our Tables I and II that the electronic term in formula (17) for the ICSP coefficient (33) is 7% of the total. The nuclear term derived from (13) is seen to decline for shorter (or spectrally broader) laser pulses by the ratio of laser-to-Raman linewidths, in this case 20%. Therefore the experiment might be expected to indicate a value for this coefficient that is about 20% lower than in (33). Similar considerations apply to other coefficients to the extent that they are not entirely electronic in origin.

At the second harmonic (522 nm) of the glass laser wavelength, we see that the self-focusing coefficient predicted by method A is 40% less than that predicted by method B. As we explained above, we prefer the value predicted by method B, but think that ±40% is a reasonable estimate of its uncertainty. The difference between the predictions of the two methods is less for all the other coefficients, being, for example, only 8% for the ICSP coefficient at 522 nm. We would also expect a comparison between methods A and B to give meaningful ranges of predicted values for other c coefficients, such as those which govern the stimulated Raman effect, that we have not discussed in this paper.

A useful pattern can be seen in a comparison of the two dispersion parameters ω_s and ω_0 for the six gases studied here. The values of ω_0 range between 80% and 90% of their corresponding ω_s values. If, instead of Table IV, we had used $\omega_0=0.85\omega_s$ everywhere, the predictions of the B formulas would not have been significantly changed. Therefore both A and B methods can be meaningfully compared to estimate dispersion of any third-order optical effect in any isotropic material (for $\omega_L \lesssim 2\omega_0/3$) by using the universally available Sellmeier frequencies ω_s only.

Whole beam self-focusing of a 308-nm beam in pressurized air has been studied recently by Shimoji *et al.*[23] From these studies they estimate a value of $n_2 \sim 2.9\times 10^{-16}$ esu per atmosphere of air at 300 K.[24] Formula A (Table VI) predicts a value of 1.6×10^{-16} esu and formula B (Table VIII) predicts 3.9×10^{-16} esu, at 333 nm. The average value of the two formulas is 2.8×10^{-16} esu, which is surprisingly close to the measurement. The possible sources of error in their measurements have not yet been evaluated by Shimoji *et al.*,[24] but such measurements at longer wavelengths are typically uncertain by ±50%.[4,12]

In summary, we have developed a general method for calculating third-order nonlinear optical susceptibilities describing a particular effect at one wavelength from the susceptibilities of other effects measured at other wavelengths. We have used this method to calculate the susceptibilities for five effects (self-focusing, intensity-induced change in polarization), dc Kerr effect, electric field-induced second-harmonic generation, and third-harmonic generation) throughout the visible in N_2, O_2, Ar, H_2, and air. The method is most accurate when some nonlinear dispersion data is available, but can be used with only linear dispersion data (in which case the advantage of an independent check is lost). Dispersion corrections can exceed factors of 2 or 3 at the violet limit of the usefulness of the method. A recent measurement of the ICSP index in air at 1053 nm is consistent with the calculation here based on Kerr data at 515 nm.

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