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## Method for computing the nonlinear refractive index via Keldysh theory

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## Abstract

By making use of the multiphoton limit of Keldysh theory, we show that for the case of two-photon absorption a Kramers-Kronig expansion can be used to calculate the nonlinear refractive index for different wavelengths. We apply this method to various inert gases and compare the obtained numerical values to different experimental and theoretical results for the dispersion of the Kerr nonlinearity.

Nonlinear refraction is the one of the key nonlinear optical mechanism in isotropic media such as all gases and liquids, and a large class of solids. In dielectric media, nonlinear refraction causes an intensity-dependent increase of the index of refraction  $n = n_0 + n_2 I$ , which gives rise to spectral broadening and is the basis of nearly all femtosecond pulse compression mechanisms. While nonlinear refraction in solids and liquids has been directly linked to two-photon absorption via a modified Kramers-Kronig relationship [1, 2, 3] and has been extensively explored experimentally using the  $z$ -scan technique [4], neither one of these can be used to determine the nonlinear index of refraction  $n_2$  in gases. Despite the high technical importance of this nonlinear spectral broadening mechanism in gaseous media [5, 6], therefore, all theoretical modeling of the latter depends on an indirect determination of  $n_2 = K_{1111} \gamma^{(3)}(-\omega, \omega, \omega, \omega)$  from third-harmonic generation (THG) measurements [7]  $\gamma^{(3)}(3\omega, \omega, \omega, \omega)$  or theoretical calculations [8, 9] of the dynamic hyperpolarizability  $\gamma^{(3)}(0, \omega, \omega, 2\omega)$ , which mostly refer to the scenario of electric-field induced second harmonic generation (ESHG). Even though the efficiency of second harmonic generation in an isotropic medium in the presence of a strong constant electric field is very accurately measurable, the deduced coefficients  $\gamma^{(3)}(0, \omega, \omega, 2\omega)$  show different dispersion than the coefficients  $\gamma^{(3)}(-\omega, \omega, \omega, \omega)$  governing nonlinear refraction [10], and only equal each other for the limiting case  $\omega \rightarrow 0$ , i.e., in the infrared. Probably the most accepted experimental data for  $n_2$  has been measured by Lehmeier *et al.* determining the THG efficiency in the inert gases [7]. Because this data has only been determined at one wavelengths, frequency scaling is generally considered difficult. For argon, for example, using Eq. (18) of Ref. [7] yields  $n_2 = 1.33 \times 10^{-19} \text{cm}^2/\text{W}$  at 248 nm, which disagrees with independently measured values  $n_2 = 2.9 \pm 1.0 \times 10^{-19} \text{cm}^2/\text{W}$  [11]. Both values, finally, appear to be incompatible to explain the high efficiency of a hollow fiber compressor at 248 nm, which indicates an even higher value of  $n_2$  at this wavelength [12]. This example makes it clear, that there is urgent need for improved scaling laws and more dependable theoretical estimates of the latter.

Consequently, and probably owing to the wide spread of experimental data on  $n_2$  published [7, 11, 12, 13], values used for the modeling typically varies over an order

of magnitude, even for the most commonly used inert gases. In the following, we will describe a different approach to deduce  $n_2$  in the inert gases from Keldysh theory [14, 15, 16, 17, 18] using the modified Kramers-Kronig relationship from Ref. [2]. Specifically, we utilize the description of the ionization probability  $w$  in a strong

$n_2(10^{-20}\text{cm}^2/\text{W})$	$\eta_0$	Eq. (11)	[7]	ESHG data
He	0.35	0.44	0.41	0.37
Ne	0.69	2.13	0.74	0.94
Ar	0.49	13.6	10.4	10.9
Kr	0.47	30.2	29.4	24.7
Xe	0.38	66.3	93.5	63.9

Table 1: Correction factor  $\eta_0$  and values for the nonlinear refractive index  $n_2$  at 800 nm. ESHG data has been compiled from Refs. [8, 9, 10] and corrected for the dispersion of the DFWM process [Eq. (16)]. Data from [7] was scaled from 1064 nm using Eq. (12) with  $\nu = 3/2$ .

electric field  $E$  at angular frequency  $\omega$  from Ref. [19, 16, 20]

$$w(E) = \frac{\omega_p 2^{2n} A_{n^*}(\gamma)}{n^* \Gamma(n^*) \Gamma(n^* + 1)} \left( \frac{\Theta}{E \sqrt{1 - \gamma^2}} \right)^{2n^* - 1} \times \exp \left[ -\frac{\Theta}{3E} g(\gamma) \right] \quad (1)$$

where  $\omega_p$  is the angular frequency corresponding to the ionization energy of the gas,  $n^{*2} = Z^2 \omega_p / \omega_H$  describes scaling relative to the hydrogen atom, and  $E = (I/2\epsilon_0 c)^{1/2}$  the electric field. Here  $c$  is the speed of light,  $\epsilonpsilon_0$  the dielectric constant, and  $I$  the intensity. The parameter  $\Theta$  is defined as

$$\Theta = \frac{4}{q_e} \omega_p^{3/2} \sqrt{2m_e \hbar}, \quad (2)$$

with  $q_e$  and  $m_e$  the electron charge and mass, respectively. The function  $g(\gamma)$  is defined as

$$g(\gamma) = \frac{3}{2\gamma} \left[ \left( 1 + \frac{1}{2\gamma^2} \right) \sinh^{-1}(\gamma) - \frac{\sqrt{1 + \gamma^2}}{2\gamma} \right], \quad (3)$$

with the Keldysh parameter [14]

$$\gamma = \frac{\omega \sqrt{2\hbar \omega_p m_e}}{E q_e}. \quad (4)$$

Calculation of the factor  $A_{n^*}(\gamma)$  typically involves computation of an infinite series [20, 19]. As we will only consider the perturbative case  $\gamma \rightarrow \text{inf}$  of multiphoton ionization, we can greatly simplify the description of the ionization rate  $w = \sigma_m I^m$ . In this case,

$$A_n(\gamma) \approx \frac{10}{9} \frac{1}{\Gamma(n^* + 1)} \quad (5)$$

and

$$g(\gamma) \approx 3 \frac{2 \log(2\gamma) - 1}{4\gamma}. \quad (6)$$

Considering two-photon absorption, i.e.,  $m = 2$ , the PPT theory [16] allows for estimation of two-photon absorption coefficients, which simplifies  $w$  to

$$w_{\text{MPI}} = \frac{5}{\Gamma^3(n^* + 1)} \left[ \frac{\exp(2) q_e 2^{4n^*}}{3m_e c \epsilon_0 \hbar} \right]^2 \omega_p^5 I^2 = \sigma_2 I^2. \quad (7)$$

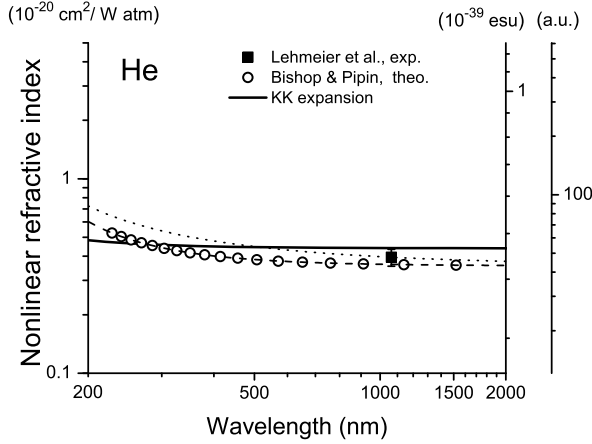


Figure 1: Nonlinear refractive index of helium. Solid line: Kramers-Kronig expansion of PPT theory, Eq. (11), including correction by factor  $\eta_0$ , Eq. (12). Circles: computed values for the DFWM efficiency [10]. Square: measured value of the THG efficiency [7]. Dashed and dotted lines: extrapolations using Eq. (15) with  $\nu = 3/2$  and a fit to the series expansion  $n_2 = n_{20} + n_{22}\omega^2 + n_{24}\omega^4$  [9], respectively.

Coefficients for  $\sigma_2$  can be found in Table I. Note that we deliberately keep the entire formalism in SI-units to simplify comparison with experimental data. For the calculation of intensity dependent index changes, we insert the above results into the modified Kramers-Kronig relations [2]

$$\Delta n(\omega) = n_2 I = \frac{c}{\pi} \int_0^{\infty} \frac{\Delta \alpha(\omega')}{\omega^2 - \omega'^2} d\omega'. \quad (8)$$

The intensity-dependent change of absorption at half ionization energy can then be written as

$$\Delta \alpha \left( \frac{\omega_p}{2} \right) = \hbar \frac{\omega_p}{2} \rho \frac{\partial w}{\partial I} = \hbar \omega_p \rho \sigma_2 I. \quad (9)$$

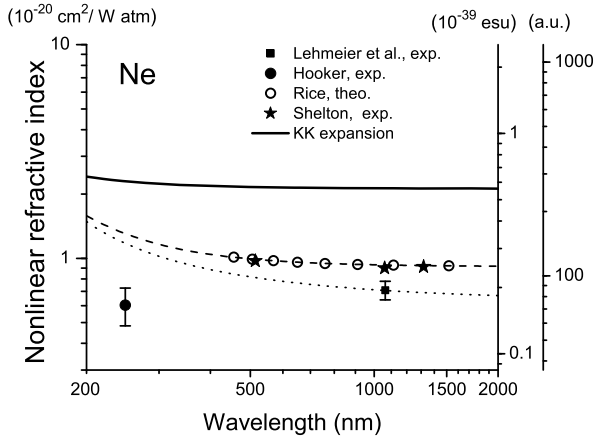


Figure 2: Nonlinear refractive index of neon. Circles: computed values for the ESHG efficiency (second-order perturbation theory (MP2),  $\gamma_{\parallel}$  in [9]). Stars: measured ESHG efficiency. ESHG data dispersion was rescaled for DFWM according to Eq. (16). Filled circle: Experimental  $n_2$  data [11]. Other symbols and lines as described in the caption of Fig. 1.

Neglecting any frequency dependence of absorption above ionization energy, we can use Eq. (9) as an estimate for computing the nonlinear refractive index

$$n_2(\omega) \approx \eta \frac{c\rho\sigma_2\hbar\omega_p}{\pi} \int_{\omega_p/2}^{\infty} \frac{1}{\omega^2 - \omega'^2} d\omega' \quad (10)$$

$$= \eta \frac{c\rho\sigma_2}{\pi} \frac{\hbar\omega_p}{\omega} \tanh^{-1} \frac{2\omega}{\omega_p}, \quad (11)$$

where  $\eta$  is a correction factor to account for the exact spectral dependence of absorption above the ionization edge. It is quite clear from the spectral behavior of linear absorption above  $\omega_p$  that  $\eta = 1$  will give rise to an overestimation of  $n_2$  as it surmises a frequency-independent  $\Delta\alpha$ . Using linear absorption data  $\alpha(\omega)$  [21, 22, 23], one can derive a correction

$$\eta(\omega) = \int_{\omega_p}^{\infty} \frac{\alpha(\omega')}{\omega^2 - \omega'^2} d\omega' / \int_{\omega_p}^{\infty} \frac{\alpha_{\max}}{\omega^2 - \omega'^2} d\omega' \quad (12)$$

to remove this systematic error of Eq. (11). Alternatively, one could also use directly computed data of the two-photon absorption cross sections [24, 25], which, however, are only available for a much smaller spectral range and the elements helium, neon, and argon. For the wavelengths under consideration, it is found sufficient to consider the limiting case  $\eta_0 = \eta(\omega \rightarrow 0)$ , because  $\eta$  only deviates from  $\eta_0$  by about 5% for 200 nm wavelength. Based on the data of Refs. [21, 22, 23] we compute the

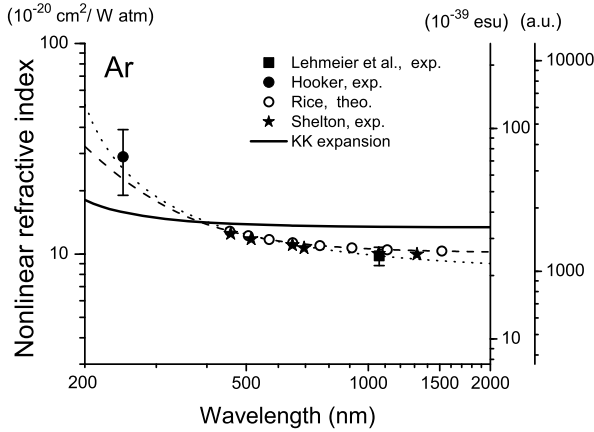


Figure 3: Nonlinear refractive index of argon. Symbols and lines as described in the caption of Fig. 2.

correction factor  $\eta_0$  in Table 1. All the above consideration can be carried together for the following completely analytic estimation

$$n_2 \approx \frac{\rho \omega_p^5}{\hbar c \pi \Gamma^3 (n^* + 1)} \left( \frac{\exp(2) q_e 2^{4n^*}}{m_e \epsilon_0} \right)^2 \quad (13)$$

in the long wavelength limit. Finally, the Kramers-Kronig transformation approach can be further generalized to compute higher-order nonlinearities, e.g.,

$$n_4(\omega) = \frac{\eta c \rho \sigma_3 \hbar \omega_p}{3\pi \omega} \tanh^{-1} \frac{3\omega}{\omega_p}, \quad (14)$$

which has found some mentioning in early literature [13].

Calculations for the 5 inert gases in comparison to experimental and theoretical data is shown in Figs. 1 - 5. Experimental data has been mainly extracted from measurements of the third-harmonic efficiency by Lehmeier *et al.* [7], which is probably the most accepted reference on experimental data for  $n_2$  of the inert gases. As all data has been acquired at a wavelength of 1064 nm, we have extrapolated the data to indicate the dispersion of  $n_2$  with wavelength. Using an adapted version of the relation

$$n_2(\omega) = \frac{\nu \omega - \omega_p}{\nu \omega' - \omega_p} \quad (15)$$

originally suggested to scale THG data using  $\nu = 2$ , we find excellent agreement with published theoretical data [10] and published experimental work [11] letting  $\nu = 3/2$ . We augmented the data by theoretical calculations [9, 10] and measurements [8] of the hyperpolarizability of the gases under considerations. With the noted exception of the data provided by Bishop and Pipin, however, the hyperpolarizability data only provide ESHG efficiencies, which unfortunately exhibit a different dispersion behavior. Without further processing, this data can therefore only be sensibly used

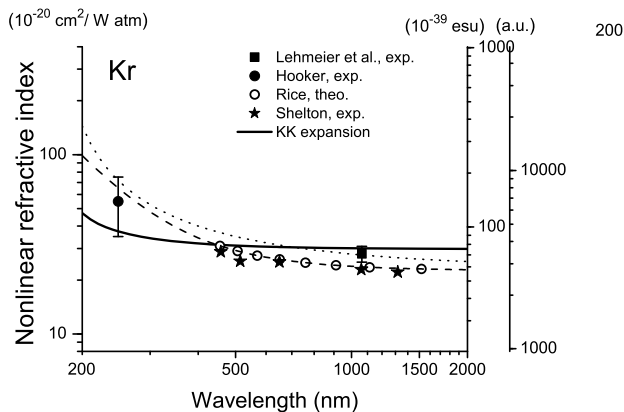


Figure 4: Nonlinear refractive index of krypton. Symbols and lines as described in the caption of Fig. 2.

to estimate the long wavelength limit  $n_2(\omega \rightarrow 0)$ . Based on the extensive work of Ref. [10], we corrected the dispersion the ESHG data using the relation

$$\gamma_{\text{DFWM}}(\omega) \approx \gamma_{\text{ESHG}}(\omega) \left[ \frac{\gamma_{\text{ESHG}}(0)}{\gamma_{\text{ESHG}}(\omega)} \right]^{2/3}. \quad (16)$$

Again, this adjustment provides a much better agreement with the experimental data for gases like krypton and argon at 248 nm wavelength [11] but fails to explain the values reported for neon and the large negative  $n_2$  of xenon, which is, however, attributed to a local coincidence with a two-photon resonance. The main reason for including the ESHG data is their much higher reliability. Typically, a precision of about 2% or better is claimed for ESHG data, whereas values of 10% are already considered as extremely reliable for all methods of determining hyperpolarizabilities with three optical fields, i.e., DFWM or THG measurements. Conversion between the different units used throughout has been accomplished with the relation

$$n_2 \left( \frac{\text{cm}^2}{\text{W}} \right) = 3.95 \times 10^{14} n_2 (\text{esu}) = 8.28 \times 10^{-23} \gamma (\text{a.u.}) \quad (17)$$

suggested in Refs. [7, 5].

Inspecting the data in Figs. 1 - 5, one finds that in the long wavelength limit all different methods of estimating  $n_2$  agree with each other within 20-30% with the exception of the neon data (Fig. 2), where the Kramers-Kronig expansion yields more than double the value of an interpolation of the data in Ref. [7] and also markedly deviates from theoretically predicted hyperpolarizability data. It has been remarked before, however, that correct computation of this data is particularly sensitive to the choice of basis functions for neon [8], and experimental ESHG data showed unexplainable oddities such as an anomalous dispersion of the hyperpolarizability [9]. Otherwise, Eq. (11) delivers excellent results for the wavelength range down



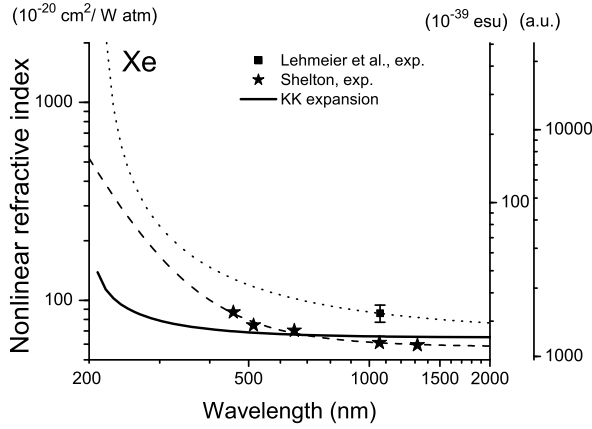


Figure 5: Nonlinear refractive index of xenon. Symbols and lines as described in the caption of Fig. 2.

to 500 nm, with deviations from other methods that are widely compatible with the error margins of these methods. Below 500 nm it becomes noticeable that the Kramers-Kronig expansion does not appear to predict the correct dispersion behavior of  $n_2$ , which is most likely to be attributed to the omission of Stark shift effects and other terms that have been discussed extensively for the computation of  $n_2$  in solids. Table II lists a compilation of  $n_2$  values for 800 nm, which is currently probably the most important wavelength for pulse compression experiments.

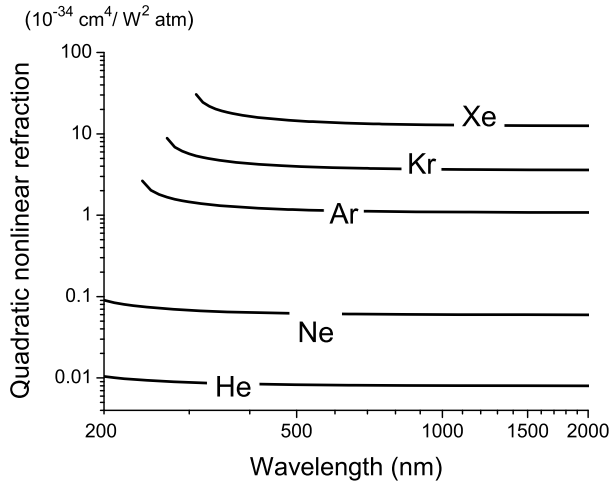


Figure 6: Quadratic nonlinear refractive index  $n_4$  of the inert gases as predicted by Eq. (14).

Figure 6 depicts values of the quadratic nonlinear refraction coefficient  $n_4$  for all inert gases, extending the perturbative expansion  $n(I) = n_0 + n_2 I + n_4 I^2$ . De-

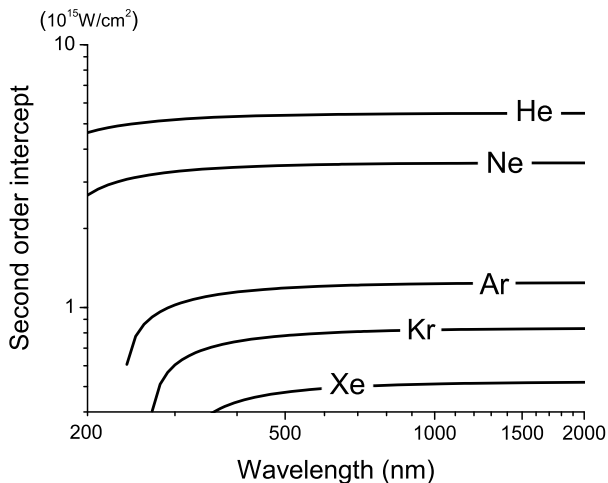


Figure 7: Second order intercept intensity  $I_{IP2} = n_4/n_2$  for the inert gases as predicted by Kramers-Kronig expansion of the PPT theory. Beyond these intensities,  $\chi^{(5)}$  effects are expected to overrule the regular  $\chi^{(3)}$ -based nonlinear refraction.

pending on the gas, values of  $n_4$  are estimated to lie in the range from  $10^{-36}$  to  $10^{-33} \text{ cm}^4$ . Most notably, the Kramers-Kronig theory clearly predicts a positive sign of  $n_4$ , which appears to be in contradiction with some early work [13], where  $\chi^{(5)}$ -type nonlinearities had been suggested to explain saturation of nonlinear refraction effects. Today, it is rather undisputed that multiphoton-induced plasma generation causes saturation of nonlinear refraction. From the computed  $n_4$  values, we can compute the second-order intercept intensity  $I_{IP2} = n_4/n_2$ , which is shown in Fig. 7. Quite independent of wavelength, this intercept intensity amounts to  $5 \times 10^{14} \text{ W/cm}^2$  for xenon and is about 10 times higher for helium. Quite clearly, these values have little practical relevance because the ionization rate  $w$  exceeds  $10^{15} \text{ s}^{-1}$  directly at the intercept, i.e., the gas is completely ionized within a single cycle of the electric field. Therefore, it is only imaginable that  $n_4$  has a weak modifying influence in the range about one order of magnitude below the intercept for very short pulses while a plasma-induced reduction of the nonlinear phase will practically always dominate.

In conclusion, we have established an alternative route for estimating the nonlinear refraction of inert gases from a Kramers-Kronig transformation of the PPT theory.

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