

Dispersion of Nonlinear Susceptibilities of Ar, N₂, and O₂ Measured and Compared

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(Received 29 April 1985)

The dispersion of the nonlinear susceptibilities of Ar, N₂, and O₂ have been measured for wavelengths from 700.0 to 457.9 nm. A comparison is made with phenomenological models used in the literature.

PACS numbers: 42.65.Cq, 32.80.Wr, 33.80.Wz

Until recently there were few accurate measurements of the nonlinear susceptibility $\chi^{(3)}$ for gases far from resonance, and those that existed were made at the fixed wavelengths that were available, generally $\lambda = 694.3$ nm (ruby laser).¹ As a result, little if any information is available about the dispersion properties of the nonresonant $\chi^{(3)}$, and it is often necessary to make use of phenomenological models.^{2,3} By taking advantage of recent advances in the technique of electric-field-induced second-harmonic generation (ESHG) which permit accurate measurements of ratios of nonlinear susceptibilities using cw lasers,⁴ plus the availability of dye lasers tunable over a wide range, we have been able to make a systematic study of the dispersion properties of a selection of gases at wavelengths from 700.0 to 457.9 nm.

The experimental technique has been described in detail elsewhere.^{4,5} A cw laser beam from an Ar⁺-pumped rhodamine-6G or DCM dye laser, or from the Ar⁺ laser directly, is weakly focused through a sample cell containing the gas in which second-harmonic generation takes place. This is made possible by a symmetry-breaking dc field. By arranging the electrodes so that the field direction alternates in space every coherence length⁶ (adjusted by varying the gas density) periodic phase-matching results, enhancing the second-harmonic signal that is generated. The electrode spacing is 2.69 mm, resulting in optimal pressures of order 1 atm, except for He (a low dispersion medium), where phase matching occurs at the order of 100 atm. A double-prism spectrometer serves to separate the second harmonic from the fundamental, and a photomultiplier detects the signal photons which are then counted. A measurement consists of filling the cell with a high-purity gas sample and determining the count rate and precise density at which optimum signal generation occurs. By making a measurement for a sample and then repeating the process for the reference gas, without changing any other parameter, an accurate determination of $\chi^{(3)}$ for the gas sample relative to that of the reference gas is obtained. The reference gas used is helium, chosen because an accurate *ab initio* calculation of its $\chi^{(3)}$ exists.⁷ It has the further advantage of displaying relatively little dispersion, and of being far from any resonance at the wavelengths employed in this study.

The nonlinear susceptibility which describes ESHG is $\chi_{ijkl}^{(3)}(-2\omega; \omega, \omega, 0)$, which is related to the molecule-fixed components by an isotropic average.⁸ In a macroscopic measurement there exist only two independent components, and the stronger component is to a good approximation 3 times larger than the other component.⁹ In this work, we are exclusively concerned with the case of the optical-field polarization parallel to the static field, which is governed by the stronger and so more important component. In what follows, we will abbreviate this component as simply $\chi^{(3)}(\omega)$. Details of the notational convention have been given elsewhere,⁵ but in any case we shall be principally interested in ratios in this work.

For frequencies well below electronic resonance $\chi^{(3)}(\omega)$ may be expanded in even powers of ω , viz.,

$$\chi^{(3)}(\omega) = \chi^{(3)}(0)(1 + a\omega^2 + b\omega^4 + \dots). \quad (1)$$

While such an expansion of necessity ignores the contribution of low-lying vibrational overtones, these give only a small contribution to the total nonlinear susceptibility and may be ignored here. Details relating to this point are given elsewhere.^{5,9}

In Table I and Fig. 1 we present the results of $\chi^{(3)}(\omega)$ for Ar, N₂ and O₂, given as ratios to $\chi^{(3)}(\omega)$ for He, as a function of ω^2 . A weighted least-squares fit to the data has been performed by use of a truncated version of Eq. (1), yielding the parameter values given in Table II. The excellent quality of the fits (χ^2 test) indicates that terms in ω^4 and higher are unimportant at this level of accuracy. The error bars, which range from 0.3% to 1.5%, represent the total experimental uncertainty. In particular, we believe that the systematic errors in the present experiment are negligible.^{5,9} We note that the results obtained in this work are uniformly 1.5% larger than those previously reported.⁴ In the previous work the measurements were made in two stages: First, CH₄ was measured against He, and then all the other gases were measured against CH₄. The systematic error probably occurred in the CH₄-He comparison, as discussed elsewhere,⁵ which accounts for the uniform discrepancy.

We may now consider the relative dispersion properties of several gases. This is most readily done by plotting the smoothed results for $\chi^{(3)}(\omega)/\chi^{(3)}(0)$ as a function of ω^2 as shown in Fig. 2. We have made use

TABLE I. Experimental measurements of the nonlinear susceptibility ratio $\chi^{(3)}(\omega)/\chi_{\text{He}}^{(3)}(\omega)$ for the gases Ar, N₂, and O₂ in the visible. The uncertainty of the last digits is indicated in parenthesis for each measured ratio.

| λ_{air} (nm) | ν_{vac} (cm ⁻¹) | $\chi^{(3)}(\omega)/\chi_{\text{He}}^{(3)}(\omega)$ | | |
|--------------------------------|---|---|----------------|-----------------------------|
| | | Ar | N ₂ | O ₂ ^a |
| 700.0 | 14 282 | 29.67(25) | 23.04(15) | 25.27(30) |
| 694.3 | 14 399 | 29.59(27) ^a | 23.17(14) | 25.52(28) |
| 690.0 | 14 489 | 29.76(25) ^a | 23.01(12) | 25.38(28) |
| 680.0 | 14 702 | 30.03(17) | 23.08(12) | 25.65(27) |
| 670.0 | 14 921 | 29.56(26) ^a | 23.16(12) | 25.91(22) |
| 660.0 | 15 147 | 29.94(28) ^a | 23.24(11) | 26.04(21) |
| 650.0 | 15 380 | 30.40(18) | 23.50(11) | 26.31(23) |
| 640.0 | 15 620 | 30.19(14) | 23.62(9) | 26.30(23) |
| 632.8 | 15 798 | 30.21(17) | 23.72(10) | 26.29(20) |
| 620.0 | 16 124 | 30.75(21) | 23.76(13) | 26.68(21) |
| 610.0 | 16 389 | 30.88(20) | 23.67(11) | 26.74(22) |
| 600.0 | 16 662 | 20.99(16) | 23.99(9) | 26.94(22) |
| 590.0 | 16 944 | 31.25(16) | 24.25(9) | 27.23(23) |
| 580.0 | 17 236 | 31.28(19) | 24.30(9) | 27.57(26) |
| 514.5 | 19 430 | 32.52(17) | 25.24(11) | 29.93(26) |
| 496.5 | 20 135 | 33.26(32) | 25.47(13) | 30.96(35) |
| 488.0 | 20 487 | 33.50(22) | 25.86(13) | 31.16(31) |
| 476.5 | 20 981 | 34.33(22) | 26.20(20) | 31.83(48) |
| 457.9 | 21 831 | 34.41(46) | 26.95(29) | ... |

^aThese values were obtained by first measuring against N₂ used as a transfer standard, and then using the smoothed values for $\chi_{\text{N}_2}^{(3)}(\omega)/\chi_{\text{He}}^{(3)}(\omega)$.

of

$$\chi_{\text{He}}^{(3)}(\omega)/\chi_{\text{He}}^{(3)}(0) = 1 + [\omega/(58\,300\text{ cm}^{-1})]^2, \quad (2)$$

which adequately represents the *ab initio* results of Sitz and Yaris,⁷ to calibrate the data. By way of comparison

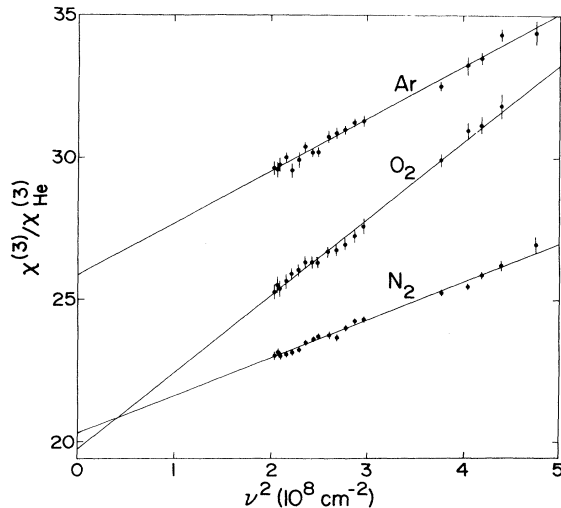


FIG. 1. Experimental results for $\chi^{(3)}(\omega)/\chi_{\text{He}}^{(3)}(\omega)$ plotted vs ω^2 , for Ar, N₂, and O₂. The straight lines are the results of weighted least-squares fits to the data, presented in Table II.

we have also indicated the range of the dispersion of the linear polarizability $\alpha(\omega)$ for the molecules considered.¹⁰ It is immediately apparent from this figure that the nonlinear dispersion is much larger than the linear dispersion. Further, over the range of frequencies illustrated, the differences in the degree of dispersion for the different gases is far more pronounced in the nonlinear case.

In the literature¹¹ attempts have been made to calculate the dispersion properties of $\chi^{(3)}$ in terms of the

TABLE II. Results of weighted least-squares fits to the data for $\chi^{(3)}/\chi_{\text{He}}^{(3)}$ presented in Table I and Fig. 1. The fitting function has the form $f(\omega) = A(1 + B\omega^2)$. The results may be put on an absolute basis by the use of the *ab initio* result of Sitz and Yaris (Ref. 7): $\chi_{\text{He}}^{(3)}(\omega) = 42.6(1 + B_{\text{He}}\omega^2)$, in atomic units (1 a.u. = $6.2353 \times 10^{-65} \text{ C}^4 \text{m}^4 \text{J}^{-3}$). The value of B_{He} is $2.94 \times 10^{-10} \text{ cm}^2$ with ω in inverse centimeters.

| Gas | A | B (10^{-10} cm^2) |
|-----------------------------|------------------|------------------------------------|
| Ar | 25.85 ± 0.19 | 7.11 ± 0.26 |
| H ₂ ^a | 14.72 ± 0.09 | 9.01 ± 0.22 |
| D ₂ ^a | 14.54 ± 0.11 | 8.54 ± 0.26 |
| N ₂ | 20.30 ± 0.11 | 6.55 ± 0.20 |
| O ₂ | 19.73 ± 0.27 | 13.64 ± 0.54 |

^aData for H₂ and D₂ come from Ref. 5.

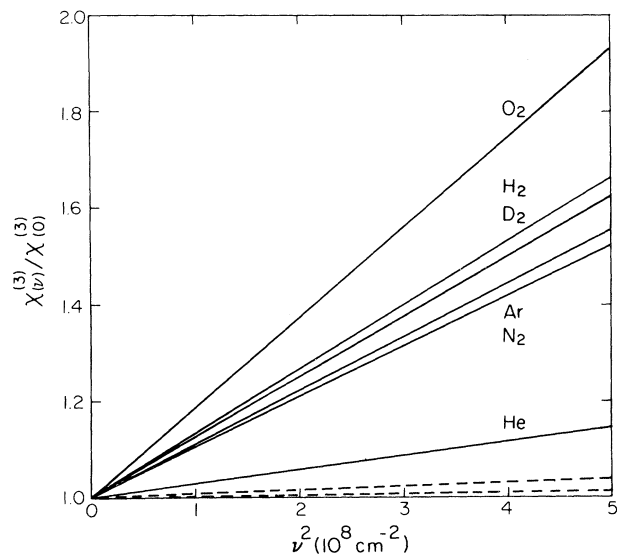


FIG. 2. The dispersion of $\chi^{(3)}(\omega)$, illustrated by plotting $\chi^{(3)}(\omega)/\chi^{(3)}(0)$ vs ω^2 , for He, Ar, H₂, D₂, N₂, and O₂ (solid lines). The fitted functions presented in Table II, calibrated by use of the *ab initio* result for $\chi_{\text{He}}^{(3)}(\omega)$, have been used to draw these curves. For comparison, the dispersion of $\alpha(\omega)$ (Ref. 10) has also been indicated by plotting $\alpha(\omega)/\alpha(0)$ vs ω^2 for the two extreme cases (H₂, upper dashed line; and He, lower dashed line).

better known linear susceptibility $\chi^{(1)}$. We may now evaluate these procedures quantitatively. Two models are common. The first, used by Ward and co-workers,^{2,3} is based on a means of estimating the dispersion in $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$ due to Dawes,¹² who applied an effective resonant-frequency approximation coupled with some exact sum rules to the formal expression for $\chi^{(3)}$. Their result for ESHG may be writ-

$$\chi_{ijkl}^{(3)}(-\omega_\sigma; \omega_1, \omega_2, \omega_3) \propto \chi^{(1)}(\omega_\sigma) \chi^{(1)}(\omega_1) \chi^{(1)}(\omega_2) \chi^{(1)}(\omega_3) \{ \delta_{ij} \delta_{kl} + \delta_{il} \delta_{jk} + \delta_{ik} \delta_{jl} \}, \quad (5)$$

is in fact the $\chi^{(3)}$ analog of the popular Miller's rule,¹⁵ used to describe crystals.^{11,16} For ESHG this may be written, with use of Eq. (4), as

$$\chi^{(3)}(\omega) = \chi^{(3)}(0) [1 + 6(\omega/\omega_0)]^2. \quad (6)$$

For purposes of comparison we have rewritten our smoothed results in the form $\chi^{(3)}(\omega) = \chi^{(3)}(0) [1 + C(\omega/\omega_0)^2]$, with use of the ω_0 values obtained from available linear-dispersion data.¹⁰ The comparison is made in Table III, where we have once again made use of Eq. (2) in calibrating the results. What can be clearly seen is that there is no particular correlation between the linear and the nonlinear dispersion. Both models underestimate the dispersion and neither can consistently order the molecules as to magnitude of nonlinear dispersion. In absolute terms, if the level of accuracy required is not high, then such models may

TABLE III. Test of phenomenological and approximate models of nonlinear dispersion. We write $\chi^{(3)}(\omega)/\chi^{(3)}(0) = [1 + C(\omega/\omega_0)^2]$, where ω_0 is chosen so that $\chi^{(1)}(\omega)/\chi^{(1)}(0) = [1 + (\omega/\omega_0)^2]$ gives the best fit to linear-dispersion data (Ref. 10). The model of Owyong (Ref. 14) predicts $C=6$ and that of Ward and co-workers (Refs. 2 and 3), $C=10$. The experimental results give the values listed below.

| Gas | ω_0 (10^{13} cm^{-1}) | C^a |
|----------------|--|-------|
| He | 206 | 13 |
| Ar | 138 | 19 |
| H ₂ | 113 | 15 |
| D ₂ | 115 | 15 |
| N ₂ | 126 | 15 |
| O ₂ | 119 | 23 |

(a) We assume (see Ref. 7) $\chi_{\text{He}}^{(3)}(\omega)/\chi_{\text{He}}^{(3)}(0) = 1 + [\omega/(58300 \text{ cm}^{-1})]^2$ in calibrating the experimental results. The uncertainty in C due to the combined uncertainties of the fit and the calibration is about ± 0.6 . Subtracting out the vibrational contribution to $\chi^{(3)}$ for H₂ and D₂ will reduce C by 1, with the corrections likely to be smaller for the other molecules.

ten as

$$\chi^{(3)}(\omega) = \chi^{(3)}(0) [1 + 10(\omega/\omega_0)^2], \quad (3)$$

where ω_0 is the effective frequency which gives the best fit to the linear dispersion, viz.,

$$\chi^{(1)}(\omega) = \chi^{(1)}(0) [1 + (\omega/\omega_0)^2], \quad (4)$$

a form which adequately describes linear dispersion well below resonance.¹³

A second model due to Owyong¹⁴ comes from calculating $\chi^{(3)}$ for an isotropic anharmonic oscillator. His result,

give some idea of $\chi^{(3)}(\omega)/\chi^{(3)}(0)$, but largely because there is less than a factor of 2 variation in $\chi^{(3)}(\omega)/\chi^{(3)}(0)$ anyway (over the range of frequencies considered). Some improvement may be realized by simply replacing the C value of these models by a value such as $C=18$, which more closely typifies the present results. This is in contrast to the total inadequacy of such an approach, as first pointed out by Bigio and Ward, in predicting deviations from Kleinman symmetry.^{3,9}

In conclusion, we can but recommend that caution be used in estimating the dispersion of $\chi^{(3)}(\omega)$ for ESHG, and we feel that this must similarly apply to other nonlinear processes to which simple models such as those given here have also been applied.

This work was supported by grants from the Natural

Sciences and Engineering Research Council of Canada and from the Research Corporation (New York).

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