Measurement of the hyperpolarizability ratio $X_{yyyy}(-2\omega;0,\omega,\omega)/X_{yyxx}(-2\omega;0,\omega,\omega)$ for the inert gases*

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The ratio of dc electric-field-induced optical second-harmonic coefficients $R \equiv X_{yyyy}(-2\omega;0,\omega,\omega)/X_{yyxx}(-2\omega;0,\omega,\omega)$ has been measured for each of the inert gases. The results at $\omega = 0.066$ a.u. (the ruby-laser frequency) are: helium, 2.97 ± 0.03; neon, 3.01 ± 0.05; argon, 2.99 ± 0.04; krypton, 2.96 ± 0.04; and xenon, 3.03 ± 0.04. In the limit $\omega = 0$, symmetry considerations require $R = 3$. A theoretical estimate of R at $\omega = 0.066$ a.u. predicts deviations from 3 which are significantly larger than those observed experimentally.

I. INTRODUCTION

We wish to report a measurement of the ratio of the two independent coefficients for dc electric-field-induced second-harmonic generation in helium and other inert gases.

A centrosymmetric system does not usually generate second harmonic. However, when subjected to a dc electric field $\vec{E}^0$, and an optical field $\vec{E}^\omega$ at frequency ω, a system, even if centrosymmetric, develops a dipole moment $\vec{p}^{2\omega}$ at the second-harmonic frequency which subsequently radiates. This process is known as dc electric-field-induced second-harmonic generation and has been studied by Mayer *et al.*[1] and by Finn and Ward.[2,3] If $\vec{E}^0$ is chosen to be in the y direction and $\vec{E}^\omega$ in the x-y plane, $p_y^{2\omega}$ for a spherically symmetric system, such as an inert-gas atom, can be written

$$p_y^{2\omega} = \tfrac{3}{2} X_{yyyy}(-2\omega; 0, \omega, \omega) E_y^0 E_y^\omega E_y^\omega + \tfrac{3}{2} X_{yyxx}(-2\omega; 0, \omega, \omega,) E_y^0 E_x^\omega E_x^\omega \ . \quad (1)$$

There are only two independent coefficients and these may be chosen to be $X_{yyyy}(-2\omega; 0, \omega, \omega)$ and $X_{yyxx}(-2\omega; 0, \omega, \omega)$ which appear in Eq. (1). We have measured the ratio R of these coefficients for each of the inert gases:

$$R \equiv \frac{X_{yyyy}(-2\omega; 0, \omega, \omega)}{X_{yyxx}(-2\omega; 0, \omega, \omega)} \ . \quad (2)$$

It may be noted, for comparison, that third-harmonic generation in an inert-gas atom is described by only one independent coefficient, and the same is true of the dc hyperpolarizability, while the Kerr effect has, in principle, two independent coefficients, but only one particular combination is usually measured. The nonlinear coefficients are defined[4,5] so that, in general

$$\lim_{\text{all } \omega \to 0} X(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = X(0; 0, 0, 0) \ . \quad (3)$$

In this limit any process of this order has only *one* independent coefficient since $X(0; 0, 0, 0)$ has only one. In the case of dc electric-field-induced second harmonic, an additional numerical relationship is then imposed by symmetry:

$$\lim_{\omega \to 0} R = 3 \ . \quad (4)$$

It is the deviation of R from 3 at a given nonzero ω which is characteristic of a particular atomic species.

The usefulness of a measured value of R for helium can best be indicated by reviewing, briefly, the previously available, related data. The best quantum-mechanical calculations of nonlinear susceptibilities for helium[6,7] are thought to be good to 1%. Kerr coefficients for the inert gases[8] have been measured to 7%, but the result for helium is about 20% larger than the calculated value.[6] Clearly, additional accurate experimental data for helium are desirable. Absolute measurements for helium of the dc electric-field-induced second-harmonic coefficient[3] and third-harmonic coefficient[4] are uncertain to within a factor 3 and are not a stringent test of the theory. Improvement of the experimental uncertainties to the 10% region does not seem to be attainable at present. R, however, can be measured with small uncertainty (±1%) since a *relative* measurement is involved.

For the inert gases other than helium there are measurements of Kerr coefficients[8] (±7%), and measurements relative to helium of dc electric-field-induced second-harmonic coefficients[3] (±3.5 – 7%) and third-harmonic coefficients[4] (±8 – 20%). Several *ab initio* calculations[9] are available for neon and argon, but they are inconsistent with each other by as much as a factor 2. The only type of calculation applicable to all these gases is a method used by Dawes[10] which gives a variation of third-harmonic coefficient from gas to gas

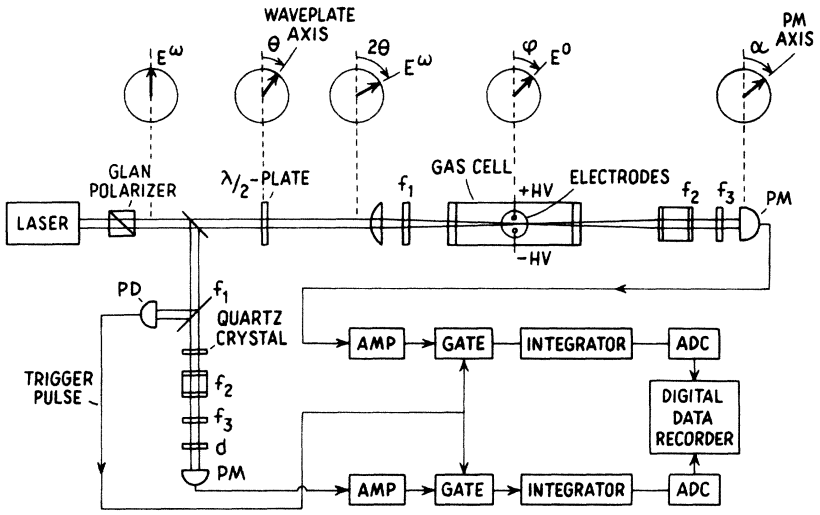

FIG. 1. Schematic diagram of the apparatus: d, diffuser; f_1, red filter; f_2, aqueous $CuSO_4$ filter; f_3, 2ω interference filter; PM, photomultiplier RCA type 4818; PD, photodiode RCA type 922.

in good agreement with experiment. The method starts from a time-dependent perturbation-theory expression, collapsing the sum over intermediate states to a single term and using linear polarizabilities as input data. We will use an extension of the Dawes method in Sec. III to make estimates of R for comparison with experiment.

The measurement of R is described in Sec. II and the results are discussed in Sec. III.

II. EXPERIMENTAL

A schematic diagram of the apparatus is shown in Fig. 1. The plane of polarization of a 1-MW TEM_{00} ruby-laser beam (initially vertically polarized) is controlled by a rotatable half-wave plate (with one of the axes at an angle θ to the vertical). The beam is focused into the gas under observation, between electrodes which provide a dc field $\vec{E}^0$ transverse to the beam and at an angle φ to the vertical. The dc electric-field-induced second-harmonic radiation generated in the gas is detected with a photomultiplier, integrated during the laser pulse and recorded (V_s). The laser-beam intensity is monitored via the second harmonic generated in a quartz crystal, and this information is also recorded (V_m). Defining the harmonic signal S in terms of V_s, V_m, and the dc-interelectrode voltage V_0 by

$$S \equiv V_s / V_m V_0^2 , \tag{5}$$

it can be shown that the variation of S with the angular orientations of the wave plate and dc electric field is given in terms of the ratio R defined in Eq. (2) by

$$S = \text{const} \times [R^2 \cos^2(2\theta - \varphi) + \sin^2(2\theta - \varphi)] . \tag{6}$$

A typical plot of S against $\cos^2(2\theta - \varphi)$ as φ is

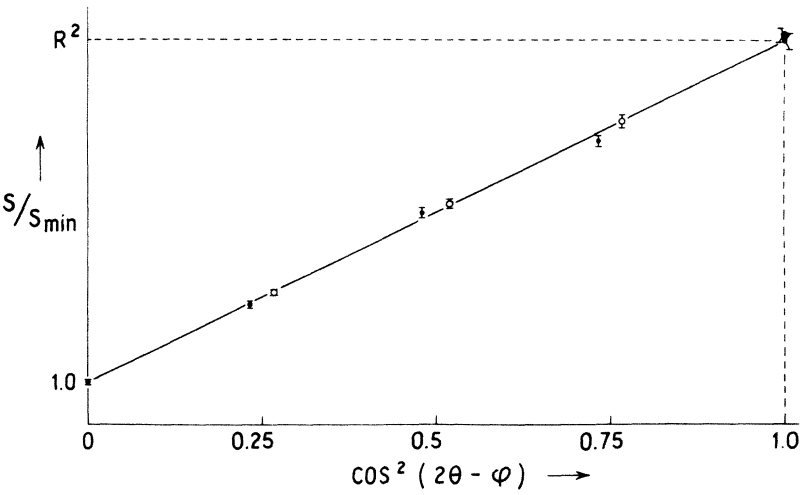

FIG. 2. Variation of second-harmonic signal with angular orientation of the wave plate (θ) for fixed dc electric field orientation ($\varphi = 90°$). ● indicates data for $0 < (2\theta - \varphi) \leq 90°$, and ○ for $90° < (2\theta - \varphi) < 180°$. A 0.6° correction to $(2\Theta - \varphi)$ has been applied for best fit to the straight line. The error flags indicate standard deviations attributable largely to photon statistics, and the intercept of the line at $\cos^2(2\Theta - \varphi) = 0$ is normalized to unity.

TABLE I. Experimental results and standard deviations for R [defined in Eq. (2)] for the inert gases. The ω_0 are characteristic frequencies obtained by fitting refractive indices to a single-oscillator model.

	No. of runs	ω_0 (a.u.) [a]	R
He	3	0.94	2.97 ± 0.03
Ne	1	0.95	3.01 ± 0.05
Ar	1	0.63	2.99 ± 0.04
Kr	1	0.54	2.96 ± 0.04
Xe	2	0.46	3.03 ± 0.04

[a] C. Cuthbertson and M. Cuthbertson, Proc. Roy. Soc. (Lond.) A135, 40 (1932).

held fixed and θ is varied in the range 0–90° is shown in Fig. 2.

In practice, no attempt is made to locate the zeros of θ or φ to better than 2°. This uncertainty causes the raw data corresponding to Fig. 2 to lie on an ellipse rather than a straight line since the points at θ and $90° - \theta$ do not, in general, coincide. A zero correction to $2\theta - \varphi$ to give best fit to a straight line has been applied to the data shown in Fig. 2, but the resultant value for R is insensitive to the magnitude of this correction.

Each point in Fig. 2 typically involves an average of 30 laser pulses, and the error flags indicate standard deviations attributable largely to photon statistics. The largest second-harmonic signals generated in helium produce about 300 photoelectrons at the photomultiplier cathode, corresponding to 10 000 photons generated in the helium.

We have considered a number of possible optical effects which could lead to systematic errors in the value of R and have found each of them to be negligible. Variations of the polarization state of the laser beam near threshold were eliminated by a Glan polarizer placed outside the laser cavity (see Fig. 1). Deviations from linear polarization of the fundamental beam at the electrodes could still arise as a result of incorrect wave-plate retardance or residual birefringence in other optical elements. The degree of linear polarization was checked after each optical element by measuring the minimum-to-maximum transmission ratio through a second polarizer for various wave-plate angles and with and without gas in the cell. The largest measured ratio was 5×10^{-4} and the resulting fractional error in R is of the same order and therefore negligible. The measured value of R is insensitive to a slight polarization sensitivity of the detector since the harmonic polarization is the same for the points at each end of the graph in Fig. 2. If such an effect were present, its sign would reverse when the angle between dc electric field and photomultiplier-tube axis ($\varphi - \alpha$, see Fig. 1) is changed by 90°. In preliminary measurements, a significant dependence of the wave-plate transmission on its angular position was noted. This was due to the combined effects of the interferometric dependence of reflectivity on thickness, the slight wedge of the wave plate, and its rotation axis not being quite coincident with the beam axis. Antireflection coatings reduced this effect to an acceptable level. The variation of transmission through the wave plate was then 0.4% peak-to-peak and the effect on R is not greater than this. Also the effect would change sign on rotating the dc electric-field orientation (φ) by 90°. The sensitivity of the photomultiplier changes from point to point on the photocathode by as much as 10%/mm as measured with a focused beam. Rotation of a wedged

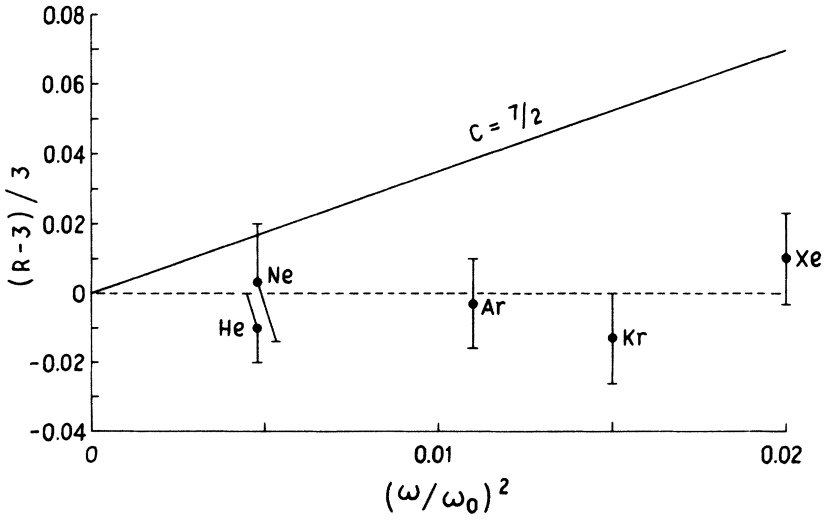

FIG. 3. R [defined in Eq. (2)] for the inert gases as a function of $(\omega/\omega_0)^2$ where $\omega = 0.066$ a.u. is the ruby-laser frequency and ω_0 is a characteristic frequency which varies from atom to atom. The solid line shown is predicted by Eq. (11′). Error flags on the data indicate standard deviations.

wave plate could move the beam over the photocathode and thus give a spurious variation of photomultiplier output. However the effect on R estimated from the wave-plate wedge and typical photocathode sensitivity gradient is less than $\frac{1}{2}\%$; it would change sign when the dc electric-field orientation (φ) is rotated by 90° and change randomly when the photomultiplier is moved.

To check for any of the orientation-dependent systematic effects discussed above, a run for a particular gas was divided into four experiments each yielding a graph like Fig. 2, differing only in the horizontal and vertical orientation of the dc electric field and of the photomultiplier tube. Considering the data from all gases as a whole, the apparent variation of R with dc electric-field and photomultiplier-tube orientations was less than $\frac{1}{2}\%$ and statistically insignificant, thus showing the orientation-dependent systematic effects to be insignificant also.

Mean values of R for each gas are given in Table I together with standard deviations which arise from three sources: statistical fluctuations attributable largely to photon statistics ($\lesssim \frac{1}{2}\%$); uncertainty in the digital zero level of the data-acquisition system ($\lesssim \frac{1}{2}\%$), and nonlinearity of the photomultipliers and electronics ($\lesssim 1\%$).

III. DISCUSSION

It can be seen from Table I that R for each of the inert gases is within 2% of the value 3 and the difference from 3 is not significant. Theoretical estimates of R will now be derived for comparison with these experimental results.

The nonlinear coefficients as used in this paper are defined so that

$$X^*(2\omega; 0, -\omega, -\omega) \equiv X(-2\omega; 0, \omega, \omega) . \tag{7}$$

In addition, ω is much smaller than the frequency of any transition from the ground state, so that X may be taken to be real and Eq. (7) becomes

$$X(2\omega; 0, -\omega, -\omega) = X(-2\omega; 0, \omega, \omega) . \tag{8}$$

Equation (3) suggests an expansion of the coefficients in a power series in ω about $\omega = 0$, and Eq. (8) indicates that only even powers of ω should be included. For ω small and using Eq. (4),

$$X_{yyyy}(-2\omega; 0, \omega, \omega) = X_{yyyy}(0; 0, 0, 0)\left(1 + \frac{C_1}{\omega_0^2}\omega^2 \cdots\right) , \tag{9}$$

$$X_{yyzz}(-2\omega; 0, \omega, \omega) = \tfrac{1}{3}X_{yyyy}(0; 0, 0, 0)\left(1 + \frac{C_2}{\omega_0^2}\omega^2 \cdots\right) , \tag{10}$$

and therefore from Eq. (2)

$$R = 3\left(1 + \frac{C}{\omega_0^2}\omega^2 \cdots\right) , \tag{11}$$

where

$$C = C_1 - C_2 . \tag{12}$$

The expressions have been written, for convenience, in terms of numerical coefficients C_1, C_2, and C, and a frequency ω_0.

The values of C_1, C_2, and ω_0 may be estimated using the method due to Dawes[10] discussed in Sec. I. We have extended the method to dc electric-field-induced second-harmonic generation and the results, cast in the form of Eqs. (9)–(11), are

$$X_{yyyy}(-2\omega; 0, \omega, \omega) = X_{yyyy}(0; 0, 0, 0)(1 + 10\ \omega^2/\omega_0^2 \cdots) , \tag{9'}$$

$$X_{yyzz}(-2\omega; 0, \omega, \omega) = \tfrac{1}{3}X_{yyyy}(0; 0, 0, 0)(1 + \tfrac{13}{2}\ \omega^2/\omega_0^2 \cdots) , \tag{10'}$$

and

$$R = 3(1 + \tfrac{7}{2}\ \omega^2/\omega_0^2 \cdots) . \tag{11'}$$

In the Dawes method, ω_0 is the frequency of the single oscillator best fitting the refractive-index dispersion of the particular atom, whereas the numerical coefficients are assumed independent of the atom involved. The characteristic frequencies ω_0 for the inert gases are shown in Table I. An indication of the reliability of the results using the Dawes method can be obtained by comparing them with a calculation by Sitz and Yaris[6] of $X_{yyyy}(-2\omega; 0, \omega, \omega)$ for helium, which is thought to be good to 1%. Cast in the form of Eq. (9) this result becomes, for ω small,

$$X_{yyyy}(-2\omega; 0, \omega, \omega) = X_{yyyy}(0; 0, 0, 0)[1 + 12\ \omega^2/(0.94)^2 \cdots] , \tag{9''}$$

where ω is in a.u. (the ruby-laser frequency is 0.066 a.u.) and the value $\omega_0 = 0.94$ a.u. for helium has been used. Equation (9'') reproduces the variation with ω of $X_{yyyy}(-2\omega; 0, \omega, \omega)$ calculated by Sitz and Yaris to within 10% for $\omega < 0.13$ a.u. Comparing Eqs. (9') and (9'') shows that the Dawes-method estimate for C_1 is 10, whereas the more rigorous calculation gives 12, and we would hope that the numerical coefficient $\frac{7}{2}$ in Eq. (11') is equally satisfactory.

The experimental data is shown in Fig. 3 where

$(R-3)/3$ is plotted against $(\omega/\omega_0)^2$ for the inert gases, ω being the same for each (0.066 a.u.) and ω_0 varying from gas to gas as shown in Table I. A line representing Eq. (11′) with the numerical coefficient $\frac{7}{2}$ is also shown and is clearly a very poor fit to the data. We find this discrepancy surprising. The reliability of the theory could be improved considerably by extending to $X_{yyxx}(-2\omega; 0, \omega, \omega)$ for helium the procedure applied by Sitz and Yaris to $X_{yyyy}(-2\omega; 0, \omega, \omega)$, and we hope that this will be done.

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