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dc-Induced Optical Second-Harmonic Generation in the Inert Gases*

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We have measured dc-induced optical second-harmonic generation by a focused laser beam; we verify the predicted dependence on geometric and physical parameters, thus providing a novel method of probing the confocal parameter at the laser focus. In addition, we have deduced values of $\chi_{yyyy}(-2\omega; 0, \omega, \omega)$ for the inert gases, and we find good general agreement with various other data.

Copious generation of optical second harmonic due to electric-dipole interactions is restricted to those systems which lack a center of inversion. However, the application of a dc electric field to a centrosymmetric system removes this restriction, making possible the observation of dc-induced optical second harmonic. This process was first demonstrated in a solid by Terhune, Maker, and Savage[1] and in a number of gases by Mayer et al.[2]

We wish to report the following: the results of an analysis of dc-induced optical second-harmonic generation by a focused laser beam where the phase of the optical field near the focus is given special consideration; the experimental confirmation of this analysis; and measurements of the coefficients for the inert gas atoms.

A schematic diagram of the apparatus is shown in Fig. 1(a). The ruby laser beam (0.8 MW peak power at 6943 Å) was brought to focus near the center of a cell containing the gas under investigation. A pair of cylindrical electrodes whose geometry and dimensions are shown in Fig. 1(b) provided a dc electric field in the region of the focus. Second-harmonic light at 3471 Å was filtered from the fundamental by an aqueous copper-sulfate filter and a quartz prism monochomator (resolution ≃120 Å) and detected with a photomultiplier (1P28). This signal, proportional to the harmonic power $\mathcal{P}^{2\omega}$, was displayed on a dual-beam oscilloscope together with the signal from a photodiode monitoring the laser power $\mathcal{P}^{\omega}$. Among the gases that we have investigated so far, none has failed to give a clearly detectable signal, and the number of harmonic photons generated per laser pulse has ranged from about 6×10^2 for xenon to 4×10^3 for helium.

We wish to relate $\mathcal{P}^{2\omega}$ and $\mathcal{P}^{\omega}$ to the atomic coefficient for dc-induced second-harmonic generation, $\chi(-2\omega; 0, \omega, \omega)$ defined by

$$P_i^{2\omega} = \tfrac{3}{2}\rho L \chi_{ijkl}(-2\omega; 0, \omega, \omega) E_j^{0} E_k^{\omega} E_l^{\omega}. \qquad (1)$$

P and E are polarization and field amplitudes, respectively, at frequencies indicated by superscripts, ρ is the relative density in amagats, and L is Loschmidt's number. Local field factors[3] have been taken to be unity and the factor $\frac{3}{2}$ is in-

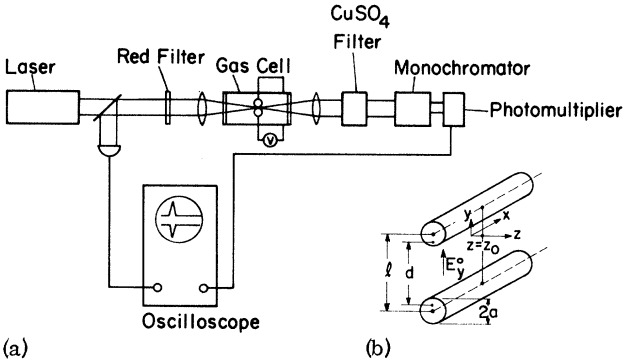

FIG. 1. (a) Schematic diagram of the apparatus. (b) Electrode geometry.

cluded in accordance with the convention

$$\lim_{\text{all }\omega\to 0} \chi(-\omega_0;\omega_1,\omega_2,\omega_3)=\chi(0;0,0,0). \tag{2}$$

The laser beam is taken to be a lowest order Gaussian mode with wave vector $\hat{z}k^{\omega}$, confocal parameter b, and beam waist located at the coordinate origin. All of the gases studied exhibit normal dispersion throughout the wavelength region 6943-3471 Å so that the wave vector mismatch Δk defined by

$$\Delta k = 2k^{\omega}-k^{2\omega} \tag{3}$$

is negative and small compared to k^{ω}. Δk_0 will be used to indicate the wave vector mismatch at STP. The transverse dc electric field $E_y{}^0(z)$ in the region of the beam is given, to a good approximation, by

$$E_y{}^0(z)=\frac{2V}{d\cosh^{-1}(l/2a)}\frac{1}{1+[2(z-z_0)/d]^2}, \tag{4}$$

where

$$d^2=l^2-4a^2. \tag{5}$$

The approximation depends on the optical beam-waist diameter being small compared to d and its far-field diffraction angle δ being small. In Eq. (4), V is the applied dc voltage, a is the electrode radius, l is the distance between the electrode axes, and z_0 is the z coordinate of the electrode axes [see Fig. 1(b)]. The distance between equivalent thin electrodes, d, is also a measure of the extent of the field in the z direction. An analysis similar to that applied by Kleinman, Ashkin, and Boyd[4] and by Ward and New[5] to related problems yields

$$\mathcal{P}^{2\omega}=(\mathcal{P}^{\omega})^2[E_y{}^0(z_0)]^2\frac{36\pi^4L^2\omega^3}{e^2c^4}\left|\frac{\chi}{\Delta k_0}\right|^2 \times\frac{1}{d}\,\Gamma(\rho)B(b)Z(z_0), \tag{6}$$

where χ is the relevant element of $\chi(-2\omega;0,\omega,\omega)$ and e is the base of natural logarithms. Γ, B, and Z are dimensionless factors which can be optimized to unity by choice of experimental parameters and are given by the following:

$$\Gamma(\rho)=\left\{\frac{\rho}{\rho_0}\exp\left(\frac{\rho_0-\rho}{\rho_0}\right)\right\}^2 \tag{7}$$

where the optimum relative density,

$$\rho_0=2/[d|\Delta k_0|], \tag{8}$$

is that which makes the coherence length in the gas equal to $\pi d/2$;

$$B(b)=4[(b/d)^{1/2}+(d/b)^{1/2}]^{-2} \tag{9}$$

which is optimized by setting the beam confocal parameter b equal to d; and

$$Z(z_0)=\{1+[2z_0/(b+d)]^2\}^{-1} \tag{10}$$

which is optimized when the plane of the electrode axes is located at the beam waist. A detailed derivation of this analysis will be presented elsewhere.

The dependence of $\mathcal{P}^{2\omega}$ on various parameters predicted by Eq. (6) has been studied experimentally. The expected dependence on optical power and dc electric field has been verified. That is

$$\mathcal{P}^{2\omega}\propto(\mathcal{P}^{\omega})^n[E_y{}^0(z_0)]^m,$$

where (for harmonic generation in helium) it is found that $n=2.00\pm0.06$ for $\mathcal{P}^{\omega}<0.8$ MW and $m=2.06\pm0.06$ with $E^0<75$ esu. Figure 2(a) shows an example (for nitrogen) of the dependence of optical harmonic power on gas density. The power has been normalized to unity at the maximum but the abscissa is fixed by gas density, electrode geometry, and a value for Δk_0 taken from the literature.[6] The theoretical curve is $\Gamma(\rho)$ from Eq. (7) and the fit is seen to be good. Figure 2(b) shows the variation of optical harmonic power (in this case for air) as the electrodes are moved along the optical beam. A curve of the form $Z(z_0)$ given by Eq. (10) has been fitted to the data. The width of the curve yields a value for b, an effective beam confocal parameter, which is about thirteen times larger than the value estimated from the far-field diffraction angle of the beam, δ, using

$$b=4/(k^{\omega}\delta^2). \tag{11}$$

This lack of quantitative agreement is not surprising since Eq. (6) has been constructed for a single, lowest-order, Gaussian-mode laser beam while the laser used here exhibits complicated multimode structure. However, the effective b derived from plots similar to Fig. 2(b) does remain in the range 8-18 times the value of $4/(k^{\omega}\delta^2)$ as the focusing optics are modified to change δ over a range 0.0054-0.036. This scanning procedure constitutes a novel method for probing the form of the laser beam near the focus. Figure 2(c) shows the effect on harmonic power of changing b by changing the focusing optics. For each optical arrangement, b was determined from the width of a plot similar to Fig. 2(c). Data for two electrode pairs of different sizes are includ-

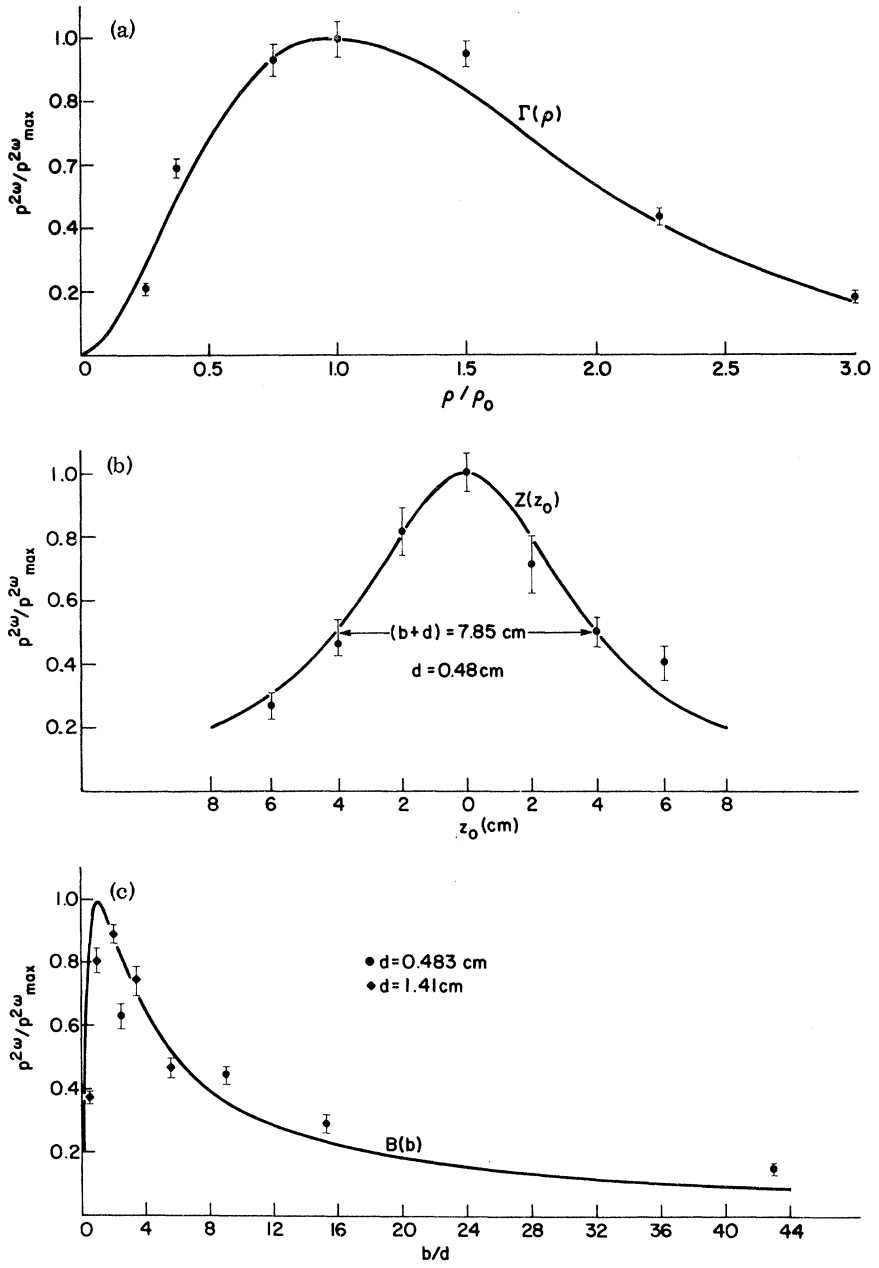

FIG. 2. (a) Normalized harmonic intensity as a function of gas density compared with the theoretical curve from Eq. (7). (b) Normalized harmonic intensity as a function of electrode position z_0 compared with the theoretical curve from Eq. (10). The width of the curve yields an effective value for b. (c) Normalized harmonic intensity as a function of b as derived from plots like that shown in (b). Data are shown for two electrode sizes subject to the same intensity normalization. The theoretical curve is from Eq. (9).

ed, both sets of data having been subjected to the same harmonic-intensity normalizing factor. The fit to the curve $B(b)$ given by Eq. (9) is surprisingly good bearing in mind the multimode structure of the laser beam. We intend to repeat these experiments with a single-mode laser.

Equation (6) has been used to obtain values of $\chi(-2\omega; 0, \omega, \omega)$ for the inert gases from measurements of $\mathcal{P}^{2\omega}/(\mathcal{P}^{\omega})^2$. For spherically symmetric atoms there are two independent nonzero coefficients, say χ_{yyyy} and χ_{yyxx} (dropping the frequency labels for brevity). In the present experiments these two coefficients are measured independently with the optical field linearly polarized either parallel ($\vec{E}^{\omega} = \hat{y}E_y{}^{\omega}$) or perpendicular ($\vec{E}^{\omega} = \hat{x}E_x{}^{\omega}$) to the dc electric field [$\vec{E}^{0} = \hat{y}E_y{}^{0}$, see

Fig. 1(b)]. In each case the harmonic field was found to be linearly polarized in the y direction as expected. It can be shown that

$$\lim_{\omega^2/\omega_0^2\to 0} \chi_{yyyy} = 3 \lim_{\omega^2/\omega_0^2\to 0} \chi_{yyxx}, \quad (12)$$

where ω_0 is a characteristic excitation frequency for the atom. This relation should be less well satisfied for krypton ($\omega^2/\omega_0^2 \sim 0.15$) than for helium ($\omega^2/\omega_0^2 \sim 0.005$). However, we find

$$\frac{\chi_{yyyy}(\mathrm{Kr})3\chi_{yyxx}(\mathrm{He})}{3\chi_{yyxx}(\mathrm{Kr})\chi_{yyyy}(\mathrm{He})} = 0.98 \pm 0.12,$$

suggesting that $\chi_{yyyy}(\mathrm{Kr})$ and $3\chi_{yyxx}(\mathrm{Kr})$ are equal to within 14%. Other measurements reported here are confined to χ_{yyyy}. For helium the absolute value is found to be

$$\chi_{yyyy}(\mathrm{He}) = 3.8 \times 10^{-39} \text{ esu/atom (experimental)},$$

with an estimated factor-of-three uncertainty. This may be compared with the result of a time-dependent perturbation-variation calculation by Sitz and Yaris[7] which is thought to be good to 1%,

$$\chi_{yyyy}(\mathrm{He}) = 3.79 \times 10^{-39} \text{ esu/atom (theoretical)}.$$

The close agreement is very satisfactory but limited in significance by the large experimental uncertainty which arises largely from the uncertainty in b and from a lack of detailed knowledge about the multimode structure of the laser beam.

Ratios of coefficients can be determined experimentally with much smaller uncertainties (3-7%). These ratios for the inert gases scaled to the Sitz and Yaris value[7] for helium are shown in Table I together with values of Δk_0 from the literature and typical experimental values for the density ρ and the dc electric field $E_y^0(z_0)$. Each ratio represents data from three different runs involving a total of about 400 laser shots. Also shown in Table I are (i) χ_{yyyy} calculated using a simple theory due to Dawes[8] and normalized to the value for helium calculated by Sitz and Yaris,[7] (ii) various theoretical dc hyperpolarizabilities χ^0, (iii) experimental Kerr coefficients χ^K (accurate to better than ±10%), and (iv) experimental third-harmonic coefficients (accurate to ±20%) normalized to the value for helium calculated by Sitz and Yaris.[7] Coefficients for these different processes in the same atom are ex-

Table I. Experimental values for $\chi_{yyyy}(-2\omega;0,\omega,\omega)$ in units of 10^{-39}esu/atom; the absolute result for helium is shown and relative values scaled to the value for helium calculated by Sitz and Yaris (Ref. 7). Columns (i)-(iv) show other nonlinear coefficients for comparison as discussed in the text. Also shown are Δk_0 from the literature and typical experimental gas densities and dc electric fields.

	Δk_0	ρ	$E_y^0(z_0)$	$\chi_{yyyy}(-2\omega;0,\omega,\omega)$		χ^0	χ^K	$\chi^{3\omega}$
	cm^{-1}	amagats	esu	experiment	theory (i)	(ii)	(iii)[j]	(iv)[k]
				absolute				
He	0.0946[a]	32	76	$3.8 \times 3^{\pm 1}$	0.88	3.59[f] (4.3[g], 3.0[h])	4.5	
				relative to $\chi(\mathrm{He}) = 3.79$[e]				
He				3.79	3.79			4.0
Ne	0.177[b]	24	19	10.5 ± 0.34	7.05	10.4[g], 3.5[h]	8.5	8.9
Ar	1.754[c]	2.5	23	119 ± 3.8	110	194[g], 85[h]	98	126
Kr	3.64[d]	1.2	15	291 ± 14	265	-	233	386
Xe	8.71[d]	0.5	11	805 ± 57	757	-	650	979

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pected to differ since $(\omega/\omega_0)^2$ is not negligible. The differences exhibited by the data in Table I are close to estimates which we have made on the basis of Dawes'[8] theory. We conclude that the experimental dc-induced optical second-harmonic coefficients are consistent with the data presented, to within 1.5 times the combined uncertainty.

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Precision Infrared Zeeman Spectra of CH_4 Studied by Laser-Saturated Absorption*

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Zeeman splitting of the methane 2947.912-cm^{-1} $F_1^{(2)}$ line was studied. The g factor of the rotational magnetic moment of methane was measured to be $g_J = +0.311 \pm 0.006$ and it was found that $g_J(\nu_3 = 1)$ is equal to $g_J(\nu_3 = 0)$. A Doppler-generated "level-crossing" saturated absorption signal was observed and is described.

There have been a number of studies exploiting the very narrow linewidths obtained through a variety of nonlinear optical processes.[1-5] In this Letter we report an investigation of the Zeeman splitting of the $F_1^{(2)}$ component of the methane $P(7)$ ν_3 line.[6] Some aspects of the Zeeman structure of this transition have already been investigated by Luntz and Brewer[4] using a level-crossing method. Exploiting the particularly good precision capability of methane saturated absorption and frequency-offset locking, we have been able to resolve the magnetic splitting of the methane infrared line despite the smallness of the methane rotational magnetic moment.

Nonlinear absorption of 3.39-μm He-Ne laser radiation by methane has been thoroughly described in Ref. 1. We departed in this experiment from the standard arrangement described there by using an absorption cell external to the laser cavity, thereby making it possible to change readily the type of light polarization and its orientation as well as the orientation of the magnetic field. Frequency-offset locking, an eminently satisfactory way of obtaining precision line shapes and line-center shifts, was again a central feature of the measurement technique. Because a particular laser frequency can be offset from a reference laser with almost the same precision as contained in the reference, we are able, with either digital or analog procedures, to program a frequency scan of excellent reproducibility. The fluctuations of the absolute frequency of the controlled laser are about 150 Hz for a 1-sec averaging time.

We briefly consider the experimental details. (1) A reference laser is locked to the center of the methane absorption signal. (2) The beat-frequency signal between this reference and a second laser, the local oscillator, is obtained and is frequency-locked to a convenient value, 4500 kHz. (3) Finally, a beat is obtained between the local oscillator and the powerful laser oscillator that illuminates the external absorption-cell system. The external cell system is either locked to its absorption-line center (the beat frequency being monitored as the magnetic field is changed) or to a programmed frequency offset from the local oscillator source. The desired line shapes of the external cell absorption are then extracted by multiple-pass signal-averaging methods.

A 1-m-long He^3-Ne^{22} laser with about 7mW of output power is the radiation source for the external cell. After passing through a Rochon polarizing prism, about 8% of this output is steered into one detector. This signal is used to dynamically control the laser excitation, thus producing