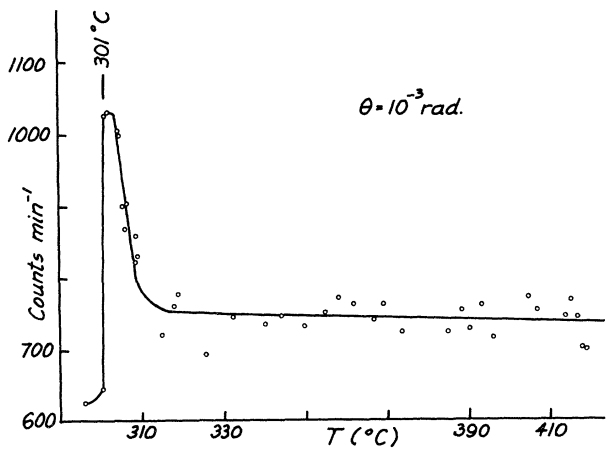

FIG. 1. Plot of intensity (uncorrected for slit smearing or background) versus temperature for a scattering angle of 0.001 rad. Background is nearly constant with T above T_c and therefore does not affect the shape of this curve.

temperature range over which the intensity increases compares roughly with the range reported by Münster and Sagel for the opalescence of the solid solution Al-Zn.[10]

Calculations using the phase diagram and density data of Ref. 9 and the known geometry of the sample cell have convinced us that it is not possible to account for the observations above 301°C on the basis of changes in x-ray absorption occurring in the neighborhood of the phase-separation temperature because of the formation of two liquid layers whose volumes vary with T.

Detailed data and an analysis of our results on the basis of existing theories will be reported in a future, more extensive publication.

We gratefully acknowledge the support furnished in part by the U. S. Office of Naval Research and in part by the National Science Foundation. The assistance of Mr. J. Fisher and Mr. J. Leskoske in the construction of the apparatus was invaluable.

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OPTICAL THIRD-HARMONIC GENERATION IN GASES

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(Received 12 June 1967)

Experimental optical third-harmonic coefficients for inert gases are presented and compared with experimental Kerr coefficients and theoretical dc hyperpolarizabilities.

We wish to report the observation of optical third-harmonic generation (THG) in gases, particularly helium, neon, argon, krypton, and xenon. THG in crystals, glasses, and liquids has been reported previously by Maker, Terhune, and Savage.[1] The motive for studying these gases is that the nonlinear susceptibilities are relatively amenable to quantum-mechanical calculation. Interesting features of the propagation of third-harmonic radiation have also become apparent.

A schematic diagram of the apparatus is shown in Fig. 1. A Q-switched ruby laser (Lear-Siegler LS 100) provided a fundamental light pulse (6943 Å) of 50-nsec duration and about 2-MW peak power. The signal from a photocell monitoring the fundamental light was displayed on one beam of a dual-beam oscilloscope (Tektronix Type 551). The laser beam passed through a red filter to attenuate stray flash-tube light and was focused in front of the glass entrance window of the gas cell. All succeeding optical components were made of quartz to pass the ultraviolet third-harmonic radiation (2314 Å).

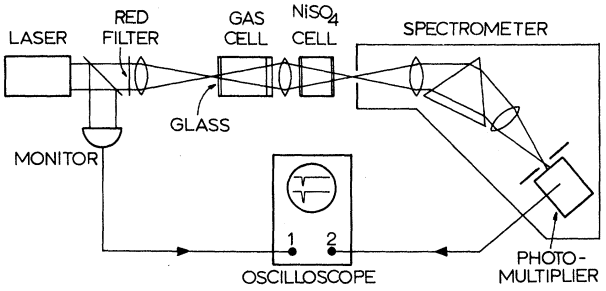

FIG. 1. Schematic diagram of apparatus.

Almost all the fundamental light was absorbed in a cell containing saturated aqueous $NiSO_4$ solution, and further wavelength discrimination was effected with a prism spectrometer. The signal from the photomultiplier detector (Mazda 27M3), corresponding typically to 50 photoelectrons at the photocathode or about 10^4 third-harmonic photons originally generated, was displayed on the other beam of the oscilloscope and photographed together with the trace from the monitor photocell. The trace heights were proportional to $\mathcal{P}^{3\omega}$ and $\mathcal{P}^{\omega}$, the third-harmonic and fundamental peak powers, respectively. The wavelength of the signal and its power dependence—$\mathcal{P}^{3\omega}$ proportional to $(\mathcal{P}^{\omega})^3$—were determined experimentally and taken as evidence of the genuine third-harmonic generation.

From the ratio $\mathcal{P}^{3\omega}/(\mathcal{P}^{\omega})^3$ the third-harmonic coefficient can be deduced. The calculation is straightforward if the fundamental beam is a plane wave,[2] but this is not a convenient configuration for the observation of THG in gases. The analysis for focused beams has been treated previously for second-harmonic generation by various authors,[3] and we have used the same analysis extended albegraically to cover THG, where interesting new features emerge. For example, if the mismatch Δk is defined in terms of the magnitudes of the fundamental and third-harmonic propagation vectors k_1 and k_3 by

$$\Delta k = 3k_1 - k_3,$$

it is found that for normal dispersion ($\Delta k < 0$) or for nominal index matching ($\Delta k = 0$), no net THG results from focusing into a homogeneous medium of infinite extent. The extension of the analysis to THG (which will be described in detail elsewhere) has led to the choice of fundamental beam configuration in the gas cell (Fig. 1) and may be used to compute the third-harmonic signal as a function of gas pressure. In the present experiment, the glass entrance window to the gas cell is absorbing to radiation at 2314 Å and the fundamental beam expands through the cell so that there is no significant generation in the quartz exit window or in any gas adjacent to it. Under these conditions it can be shown that, with the cell evacuated, the third-harmonic field at the detector is equivalent to half that generated in the final coherence length ($\pi/|\Delta k|_{\text{glass}}$) of the glass window. A plane-wave analysis[2] then suffices to show that

$$[\mathcal{P}^{3\omega}/(\mathcal{P}^{\omega})^3]_0 = K|\eta(X/\Delta k)_{\text{glass}}|^2. \quad (1a)$$

The third-harmonic coefficient X, shorthand for $X_{zzzz}(-3\omega;\omega,\omega,\omega)$, relates the polarization amplitude $p^{3\omega}$ to the fundamental electric field amplitude[4] E^{ω}:

$$p_z^{3\omega} = \tfrac{1}{4}X_{zzzz}(-3\omega;\omega,\omega,\omega)E_z^{\omega}E_z^{\omega}E_z^{\omega}.$$

The factor η, a function of refractive indices, is of order unity, and an approximate expression for K will be given below. For a gas, both X and Δk are proportional to density; so the coherence length ($\pi/|\Delta k|_{\text{gas}}$) becomes small when the pressure in the cell is high. It is convenient to consider harmonic generation in the high-pressure limit when the fundamental beam area and hence its efficiency for THG do not change significantly in the first coherence length of gas adjacent to the glass window. Under these conditions it can be shown that the third-harmonic field at the detector due to the gas is equivalent to half that generated in the first coherence length and that this is in antiphase with the contribution from the glass. The plane-wave analysis[2] can again be used to calculate the total THG:

$$[\mathcal{P}^{3\omega}/(\mathcal{P}^{\omega})^3]_{\infty} = K|\eta(X/\Delta k)_{\text{glass}} - (X/\Delta k)_{\text{gas}}|^2. \quad (1b)$$

It should be noted that the ratio $(X/\Delta k)_{\text{gas}}$ is independent of pressure.

Experimental results for the third-harmonic signal as a function of gas pressure are shown in Fig. 2. Numerical analysis at intermediate pressures has been carried out for the case of a single-mode Gaussian beam whose envelope approximates that of the experimental beam. This has yielded theoretical curves which have been used to extrapolate from the high-pres-

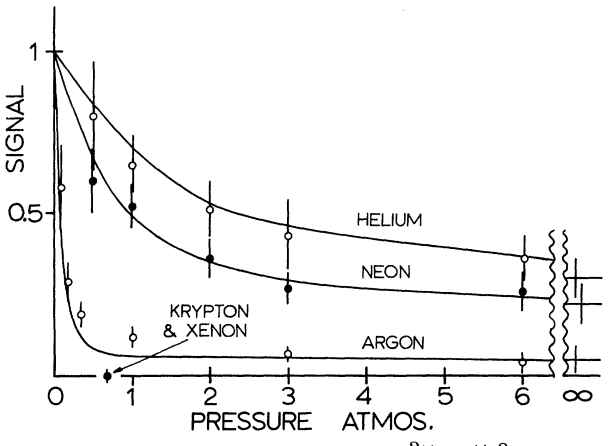

FIG. 2. Third harmonic signal, $[\mathcal{P}^{3\omega}/(\mathcal{P}^{\omega})^3]$ as a function of gas pressure. Theoretical curves used to obtain the asymptotic signals at infinite pressure are shown for helium, neon, and argon. For krypton and xenon the experimental point shown at $\frac{2}{3}$ atm is effectively at infinite pressure since $|\Delta k|$ is large.

sure data to the asymptotic signals at infinite pressure. The curves are drawn in Fig. 2 for helium, neon, and argon at intermediate pressures and give a better fit than might be expected for our elliptical cross-section multimode beam. The asymptotic signals are in any case insensitive to the form of the theoretical curves. For krypton and xenon the experimental points at $\frac{2}{3}$ atm are effectively at infinite pressure since $|\Delta k|$ is large.

$X/\Delta k$ is real for all the gases investigated since they all exhibit negligible absorption in the range 6943-2314 Å. $(X/\Delta k)_{\text{glass}}$ is also real to a good approximation, since it is found experimentally to be essentially equal to $(X/\Delta k)$ for krypton or xenon. Combining Eqs. (1a) and (1b) yields

$$(X/\Delta k)_{\text{gas}}/\eta(X/\Delta k)_{\text{glass}} = 1 \pm \{[(\mathcal{P}^{3\omega}/(\mathcal{P}^{\omega})^3]_{\infty}/[(\mathcal{P}^{3\omega}/(\mathcal{P}^{\omega})^3]_{0}\}^{\frac{1}{2}}. \quad (2)$$

Therefore, for each gas there is a choice of two values for $(X/\Delta k)_{\text{gas}}/\eta(X/\Delta k)_{\text{glass}}$. Experiments with mixed gases have reduced the possible combinations to the two alternative sets labeled (i) and (ii) in Table I.

We have carried out a preliminary time-dependent perturbation calculation for helium using matrix elements from the literature[5] which has yielded the value $\chi_{zzzz}(-3\omega;\omega,\omega,\omega) = 10^{-38}$ esu per atom. This is not expected to be good to better than a factor of 3, since only a limited number of singly excited, discrete, intermediate states have been included. For the inert gases the frequency of the transition from the ground state to the first excited state ω_η exceeds 3ω. In fact, the ratio $(3\omega/\omega_\eta)^2$ is 0.06 for helium and increases progressive-

Table I. Comparison of measured third-harmonic coefficients with experimental Kerr coefficients and theoretical dc hyperpolarizibilities. The two sets of third-harmonic data (i) and (ii) are alternative interpretations of the experiments and are discussed in the text. The third-harmonic coefficients are measured relative to glass and have been scaled to $\chi_{zzzz}(-3\omega;\omega,\omega,\omega) = 4.5\times10^{-39}$ esu per atom for helium to facilitate comparison with the Kerr coefficients.

	Δk at 0°C (cm^{-1})	$(X/\Delta k)$ relative to glass		χ ($\times10^{-39}$ esu per atom) Third-harmonic scaled to helium		Kerr effect	dc
		(i)	(ii)	(i)	(ii)		
Helium	0.38[a]	0.45 ± 0.06	1.55 ± 0.06	4.5 ± 0.6	4.5 ± 0.2	4.5 ± 0.5[d,e]	4.33[f] 2.62[d]
Neon	0.72[a]	0.53 ± 0.06	1.47 ± 0.06	10.0 ± 1.1	8.1 ± 0.4	11.0 ± 2.5[e]	10.4[f]
Argon	7.0[b]	0.77 ± 0.07	1.23 ± 0.07	142 ± 14	66 ± 4	100 ± 7[e]	194[f]
Krypton	16.5[c]	1 ± 0.15	1 ± 0.15	434 ± 65	126 ± 19	250 ± 25[e]	
Xenon	42[c]	1 ± 0.15	1 ± 0.15	1100 ± 170	321 ± 48	680 ± 70[e]	
Glass	...	$1/\eta$	$1/\eta$	...	...	...	...

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ly to 0.4 for xenon. The perturbation expressions for the coefficients indicate that if this ratio is sufficiently small compared with unity, the third-harmonic coefficients for a particular gas should be equal to the dc hyperpolarizibility $\chi_{zzzz}(0;0,0,0)$ and the Kerr-effect coefficient $\chi_{zzzz}(-\omega;0,0,\omega)$. It is also qualitatively predicted that as the ratio increases, the third-harmonic coefficient should become larger than the other two coefficients. The Kerr coefficient has been measured for all these gases[6,7] to about ±10%, and the dc hyperpolarizibility has been calculated for helium,[6,8] neon,[8] and argon[8] by a variational method. We therefore compare these data in Table I with relative values for third-harmonic coefficients corresponding to the experimental data of sets (i) and (ii) scaled to $\chi_{zzzz}(-3\omega;\omega,\omega,\omega)=4.5\times10^{-39}$ esu per atom for helium. It will be seen that the third-harmonic coefficients of set (i) are in good over-all agreement with the predictions from the Kerr-effect coefficients.

It should be noted that all the values of $(X/\Delta k)$ measured here, including the value for glass, are the same to within a factor of 4, whereas the coefficients χ for the gases alone range over more than an order of magnitude. This is not surprising, since $X/\Delta k$ is independent of density and can also be shown on the basis of time-dependent perturbation theory to be insensitive to the characteristic frequencies of the medium.

A crude estimate of the absolute THG coefficient can be made on the assumption that the fundamental field is monochromatic and of constant amplitude and phase over the estimated beam area A. In this case, the constant of proportionality in Eqs. (1a) and (1b) is

$$K=2^8\pi^4(3\omega)^2/A^2c^4.$$

This yields for helium $\chi_{zzzz}(-3\omega;\omega,\omega,\omega)=10^{-38}$ esu per atom with an estimated uncertainty of a factor of 5 arising from the complex but unknown mode structure of the fundamental beam. This is in satisfactory agreement with values shown in Table I for the measured Kerr coefficient and the dc hyperpolarizibility.

We are most grateful to A. D. Buckingham and D. A. Dunmur for the communication of their Kerr-effect data before publication.

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