Molecular Scattering of Ruby-Laser Light*

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The advent of the laser has made it possible to conduct a more complete study of Rayleigh scattering. In the present experiment the angular distribution of light scattered by gas molecules was measured from 45 to 135° from the direction of the incident beam in argon and xenon. The experiment was conducted both in the plane of polarization of the incident laser beam and in the plane perpendicular to it. Absolute values of the differential-scattering cross section are determined for neon, argon, xenon, oxygen, nitrogen, air, carbon dioxide, sulphur hexafluoride, and propane at NTP. The experimental results obtained with noble gases are compared with Rayleigh's theory. It is found that the ruby-laser light beam is not scattered isotropically either by argon or by xenon as predicted by the linear theory, in the plane perpendicular to the plane of polarization. In the plane of polarization the scattered intensity appears to be consistent with a cosine-squared distribution. The measured differential-scattering cross sections for noble gases at 60° are found to be approximately twice as large as the theoretical values.

INTRODUCTION

IT is known that when a beam of light passes through a gaseous medium, light is scattered in all directions by the gas molecules. A theory of this phenomenon was first developed by Lord Rayleigh in 1871.[1] Severe experimental difficulties made it impossible to make observations of light scattering by pure dust-free gases till 1915.[2] Since then several attempts were made pursuing the study of the phenomenon. However, light sources which could provide extremely intense monochromatic parallel beams were desirable for these studies, and mainly due to the lack of such sources these attempts were limited in scope and only partially successful. Thus, no detailed verification of the proposed theory was possible. With the advent of lasers and the development of sensitive photodetection devices in the last decade, a more complete quantitative study of the phenomenon of light scattering by gas molecules appeared to be possible. This paper describes the results of experimental studies performed using noble gases.

In view of the fact that all experimental investigations of Rayleigh scattering by gas molecules so far reported have been very incomplete due to extreme experimental difficulties, we believe it is advisable to report this study in all its essential details.

THEORY

For the sake of completeness, the classical theory of light scattering by gas molecules is briefly reviewed here. Consider a gas molecule located at the origin of a Cartesian coordinate system and let a plane wave polarized in the z direction be incident upon it along the x axis as illustrated in Fig. 1. Let the amplitude be unity and the phase be such that in complex representation the field at the origin is

$$\begin{aligned} E_x &= 0, \\ E_y &= 0, \\ E_z &= e^{i\omega t}. \end{aligned} \tag{1}$$

If the particle under consideration is isotropic, has a polarizability α, and its dimension is very small compared to the wavelength, the induced dipole moment $\mathbf{p}$ per molecule is given by

$$\mathbf{p} = (\alpha e^{i\omega t})\hat{z}, \tag{2}$$

where $\hat{z}$ is the unit vector in the z direction.

The electric field associated with this induced dipole moment at a large distance ($r \gg \lambda$) can be written as

$$\mathbf{e} = -(k^2/r)\hat{r} \times (\hat{r} \times \hat{z})\alpha e^{i(\omega t - \mathbf{k}\cdot\mathbf{r})}, \tag{3}$$

where $\hat{r}$ is the unit vector in the radial direction and $\mathbf{k}$ the wave vector. Contributions from magnetic dipole radiation can be considered negligible.

If the particle under consideration is not isotropic, the polarizability would be a tensor quantity and the induced dipole moment will not entirely be in the z direction. The radiation associated with such a dipole will have components polarized in directions other than that of the incident electromagnetic wave. In the case of a spherically symmetric molecule such as that of a

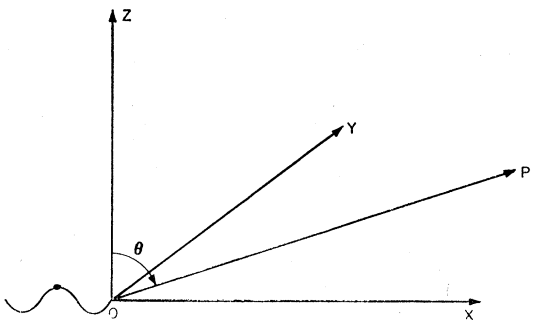

FIG. 1. The coordinate system to which the problems in scattering are referred.

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† On leave of absence from Atomic Energy Commission, Saclay, France.
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[1] J. W. Strutt, Phil. Mag., **41**, 107 (1871).
[2] J. Cabannes, Compt. Rend. **160**, 62 (1915).

noble gas, polarizability should be a scalar quantity and no such depolarization effect should be observed.

If θ is the angle between the z direction and the direction of propagation of the secondary wave, then

$$\hat{r}\times(\hat{r}\times\hat{z})=\sin\theta\hat{u}, \tag{4}$$

where $\hat{u}$ is a unit vector perpendicular to the direction of propagation. Hence

$$\mathbf{e}=-((k^2/r)\alpha\sin\theta)\hat{u}e^{i(\omega-\mathbf{k}\cdot\mathbf{r})}, \tag{5}$$

and the intensity of the scattered radiation per unit intensity of the incident beam is

$$I_i=(k^4\alpha^2/r^2)\sin^2\theta. \tag{6}$$

If the molecules of a gas do not interact and if they are randomly distributed in space, the light scattered by a large number of molecules is expected to be completely incoherent, and the total scattered intensity per unit incident intensity becomes

$$I=\sum_{i=1}^{N} I_i=\frac{Nk^4\alpha^2}{r^2}\sin^2\theta, \tag{7}$$

where N is tht total number of illuminated molecules in the field of view of the detector. If the scattered radiation is measured over an area ΔS, then P_s, the detected power per unit incident intensity, is

$$P_s=\Delta S(Nk^4\alpha^2/r^2)\sin^2\theta. \tag{8}$$

The solid angle $\Delta\Omega$ subtended by the detector at the molecule located at the origin is given by

$$\Delta\Omega=\Delta S/r^2.$$

Hence, using the definition of differential-scattering cross section per molecule as

$$\frac{d\sigma}{d\Omega}=\frac{\text{scattered energy/unit solid angle}}{\text{incident energy/unit area}},$$

Eq. (8) can be written as

$$\frac{d\sigma}{d\Omega}=\left(\frac{P_s}{N}\right)\frac{1}{\Delta\Omega}=k^4\alpha^2\sin^2\theta. \tag{9}$$

A systematic study of the scattering cross section predicted by Eq. (9) is thus necessary to ensure the validity of Rayleigh's theory of scattering of light by gas molecules.

Comparison of differential scattering cross sections of two gases can be used as an indirect estimation of the validity of Eq. (9). A relation between the differential scattering cross section and the refractive index of a gas can be derived as follows. If the incident electric field is $\mathbf{E}$ and the electric displacement is $\mathbf{D}$, then they are related by the formula

$$\mathbf{D}=\epsilon_0\mathbf{E}+\mathbf{P}, \tag{10}$$

where ϵ_0 is the permittivity of free space and $\mathbf{P}$ is the polarization. We may write the electric displacement as

$$\epsilon\mathbf{D}=\epsilon\mathbf{E}, \tag{11}$$

where ϵ is the permittivity of the medium. Equating the right-hand sides,

$$\mathbf{E}=\epsilon_0\mathbf{E}+\mathbf{P}. \tag{12}$$

Dividing throughout by ϵ_0 and rearranging we obtain

$$((\epsilon/\epsilon_0)-1)\mathbf{E}=\mathbf{P}/\epsilon_0. \tag{13}$$

The refractive index of the medium is given by $n=(\epsilon/\epsilon_0)^{1/2}$, since the magnetic permeability of the gas medium can be considered to be equal to that of vacuum. Substituting this relation above, we get

$$(n^2-1)\mathbf{E}=\mathbf{P}/\epsilon_0. \tag{14}$$

Neglecting nonlinear terms in the interaction with gas molecules, the quantity $\mathbf{P}/\epsilon_0$ is proportional to $\alpha\mathbf{E}$ where α is the polarizability per molecule. Hence it follows that (n^2-1) is proportional to α. Thus the ratio between the differential-scattering cross sections of two different gases at the same pressure and temperarure for some particular angle becomes

$$(d\sigma/d\Omega)_1/(d\sigma/d\Omega)_2=\left(\frac{\alpha_1}{\alpha_2}\right)^2=\left(\frac{n_1^2-1}{n_2^2-1}\right)^2. \tag{15}$$

A more direct method of quantitatively estimating the validity of Eq. (9) would be to determine the absolute value of the differential-scattering cross section experimentally and compare it with the theoretical value calculated using α, the polarizability obtained from Clausius-Mossotti equation and known values of the refractive index of the gas. The angular dependence of the scattering cross section should also be determined experimentally and compared with that predicted by Eq. (9).

EARLIER EXPERIMENTAL INVESTIGATIONS

The first experimental observation of visible light scattering by pure dust-free gases was accomplished in 1915 by Cabannes.[2] Soon thereafter, Smoluchowski[3] and Strutt[4] (Rayleigh) reported similar results. Such investigations were pursued by Wood,[5] Raman[6], and others.[7] Rayleigh's determination of the relative scattering power of different gases[8] and Cabannes'[9] determination of the absolute scattering cross section of gases agreed satisfactorily with theoretical predictions.

The main experimental difficulties that confronted the earlier investigators could be categorized as follows: (1) source of light; (2) means of detection of feeble

[3] M. V. Smoluckowski, Bull. Acad. Soc. Cracovie, 218 (1916).
[4] R. J. Strutt, Proc. Roy. Soc. (London) **94**, 453 (1918).
[5] W. R. Wood, Phil. Mag. **39**, 423 (1920).
[6] C. V. Raman, Indian J. Phys. **2**, 387 (1928).
[7] The bibliography given by J. Cabannes, in *La Diffusion Moleculaire de la Lumiere*, (Les Presses Universitaires de France, Paris, 1929) and by K. W. F. Kohlrausch, in *Der Smekal-Raman Effekt*, (Julius Springer, Berlin, 1931) should be consulted.
[8] R. J. Strutt, Proc. Roy. Soc. (London) **95**, 171 (1918).
[9] J. Cabannes, Ann. Phys. (Paris) **15**, 5 (1921).

scattered light; and (3) the apparatus used in the experiments.

An extremely intense, monochromatic, and parallel beam of light was very desirable in order to perform such an experiment. The strongest light sources available were either the sun or arc lamps. Neither of them fulfilled all the above mentioned criteria at the same time. Sensitive photodetectors (multipliers) were needed in these experiments to measure the feeble scattered light intensities (10^{-13} to 10^{-14} times the intensity of the incident light). These devices became available only recently.

The apparatus used in the past enabled the observation of the scattered radiation in the direction perpendicular to the incident beam. However, it was not possible to observe scattered radiation in any other direction since the radiation scattered by the entrance and the exit windows completely overpowered the light scattered by gas molecules alone. So the angular dependence of the gas scattered light intensity could not be studied.

THE LASER AND THE ASSOCIATED OPTICAL DESIGN

The advent of lasers[10] has made it possible to carry out a more detailed study of Rayleigh scattering. The laser produces an intense and parallel beam of monochromatic light. It satisfies most of the requirements for a successful study of light scattering by gas molecules.

In spite of the small angular divergence of the laser beam,[11] the intensity distribution at larger angles which would cause spurious scattering of light from the walls of the apparatus had to be investigated in due detail.[12] The essential results are shown in Fig. 2. It is seen that the intensity of the laser light even at an angle of 80° was reduced only by a factor of 10^5 with respect to that of the forward parallel beam. This comparatively low intensity is still many orders of magnitude larger than the expected intensity of the light scattered by gas molecules. An optical system was designed to suppress this unwanted light.

The principle of the design is illustrated in Figs. 3 through 6. The iris 1, placed in front of the ruby, is used to produce a well-defined beam of light as shown in Fig. 3. The beam is incident on a lens having a long focal length, thereby emerging as a slowly converging beam to form a real image of the front end of the ruby at the position 0. The beam attains its smallest diameter at 0, and thereafter it slowly diverges. An iris (iris 2) is placed between the lens and 0 so that the region of observation is shadowed from the forward scattering of the lens, as shown in Fig. 3. The slowly divergent beam emerges through the exit window W. Iris 3 casts a shadow of the backward scattering of the exit window

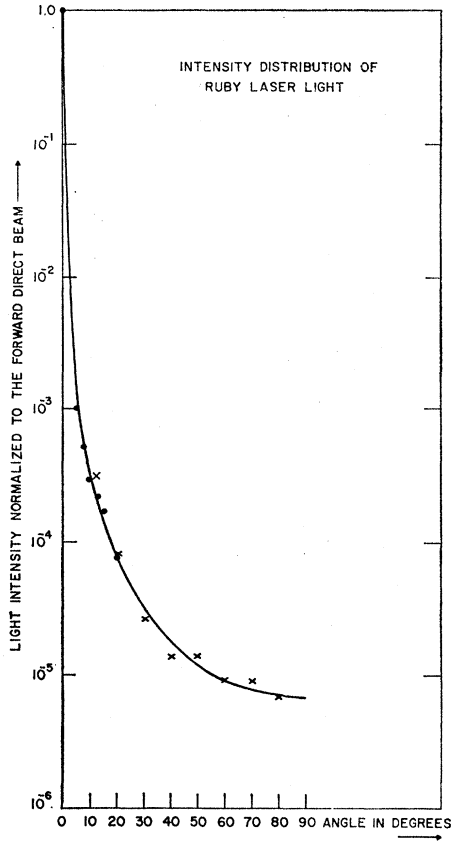

FIG. 2. The intensity distribution of the laser beam normalized to the intensity of the forward direct beam.

over the region of observation as shown in Fig. 4. The window is placed at the Brewster angle. The reflected light from this window is allowed to escape through a second window fitted with a tapered glass tube to minimize back reflection into the system as illustrated in Fig. 5.

A sketch of the complete optical design is shown in Fig. 6. The ruby holder is rigidly attached to the brass cylinder 1, which slides over one end of the brass cylinder 2, so that the ruby lies precisely on the axis of the brass cylinders. A lens of focal length 23.3 cm is cemented onto the end of the brass cylinder 2 so as to form a vacuum-tight connection. A conical transition is used to connect the brass cylinder 2 to the observation chamber. The inside of this transition is made in steps to minimize the intensity of the wall-scattered light entering the observation chamber. The holes H_1 and H_2 placed diametrically opposite each other on the walls serve as irises 1 and 2. Holes are drilled in the wall of the chamber at every 15° where metal tubes of diameter $\frac{1}{10}$-in. I.D., with glass windows cemented onto the ends, are positioned. These serve as observation windows. A conical transition similar to that described above is used to join the chamber and the brass cylinder 3, the other end of which is cut at an angle of 30° with the

[10] T. H. Maiman, Nature 187, 493 (1960).
[11] O. H. Heavens, Hilger J. 6, 63 (1961).
[12] T. V. George, L. Slama, M. Yokoyama, J. Appl. Opt. 2, 1198 (1963).

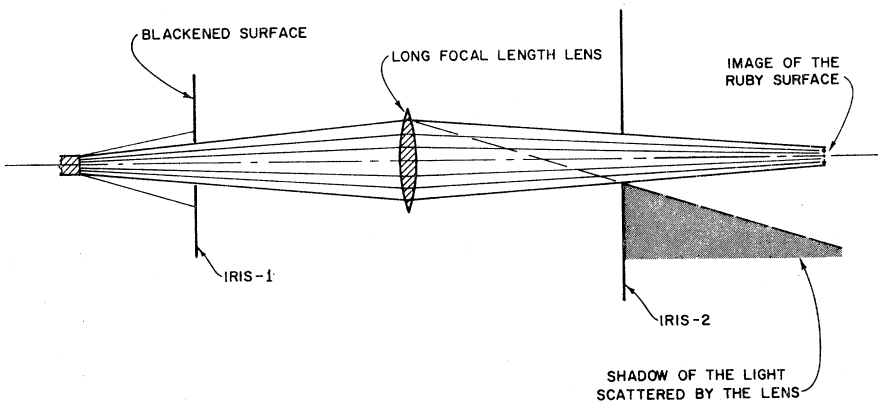

FIG. 3. Diagram showing the formation of the shadow due to the forward scattering of the lens.

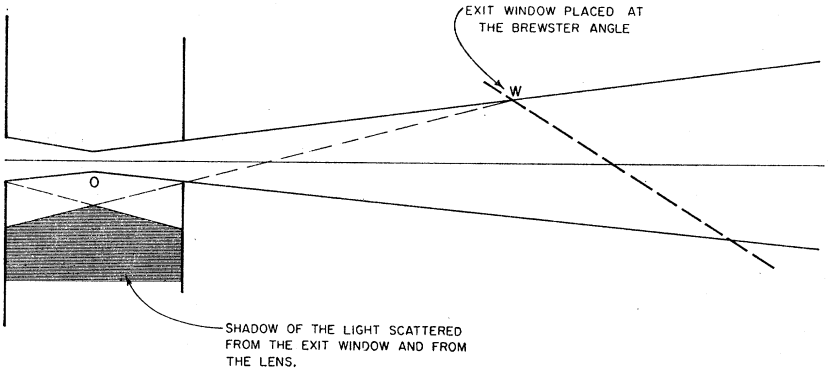

FIG. 4. Diagram showing the formation of the shadow due to the backward scattering of the exit window.

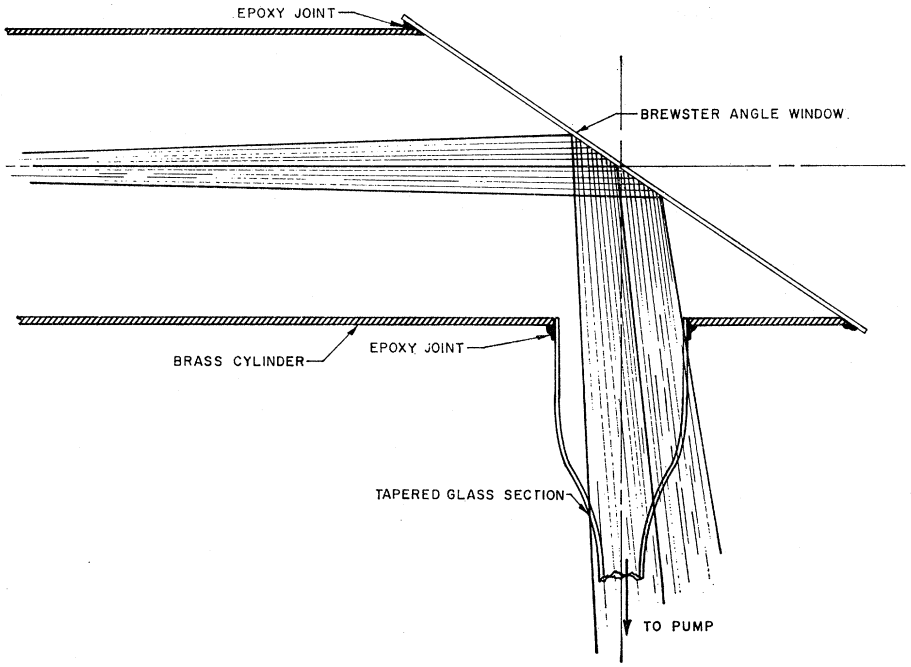

FIG. 5. Illustration of the function of the tapered glass section.

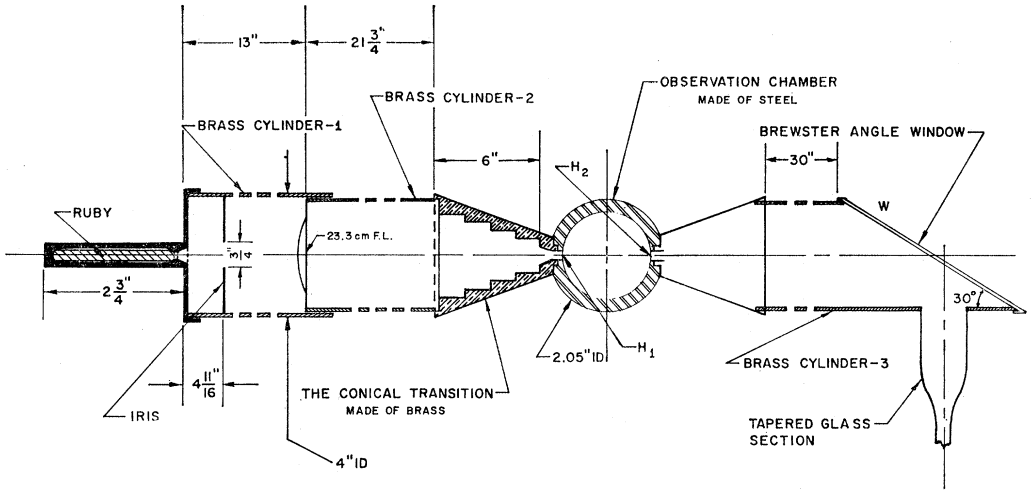

FIG. 6. Explanatory diagram showing the design of the experimental apparatus.

axis. A glass window is epoxied on the end and a tapered glass is cemented onto the hole. The tapered section is in turn connected to the vacuum pump and containers of the various gases under investigation. The tube from the lens to the exit window having a total volume of approximately 10.5 liters can be evacuated.

The successful design of the optical system incorporating the laser as an intense light source provided a previously unrealizable tool for the study of the light scattering by gas molecules.[13]

DESCRIPTION OF THE APPARATUS AND EXPERIMENTAL PROCEDURE

The optical system was rigidly fixed on top of a circular aluminum table of 84 cm in diameter. Corresponding to each observation window, a set of two slots was provided in the table for positioning a photomultiplier (PM_1). Scattered radiation was detected as a function of the angle of scattering by moving this photomultiplier in the horizontal plane.

The intensity of the incident laser beam was monitored by means of a photomultiplier (PM_2) by detecting a part of the beam transmitted through a partially transparent mirror. The photomultipliers were provided with interference filters (50–60 Å wide) centered around 6943 Å and red filters (Corning 2–64) to eliminate light originating in the xenon flash tubes. The capacitors for the xenon flash tubes were charged to an energy corresponding to twice the input energy at the threshold of lasering, and it was triggered manually at a repetition rate of once per minute.

The experimental procedure essentially consisted of first evacuating the system and observing the spurious signal level, followed by the introduction of the gas under investigation and observing the increase in signal level. This increase in signal level would be proportional to the amount of light scattered by molecules in the field of view of the photomultiplier. The scattered light signal in every case is to be normalized with respect to the output of the photomultiplier monitoring the laser beam intensity.

The laser light consists of a large number of random light pulses of random duration with random amplitude distribution. The normalization of the scattered signal with respect to the intensity of the incident beam can be performed on each one of the individual pulses by taking the ratio of their respective amplitudes. This procedure has an added advantage of eliminating the error due to noise pulses which are present in the output of the sensitive photomultipliers. Since the laser light falling on the cathode of the reference photomultiplier (PM_2) is sufficiently strong, it can be operated at lower voltages making it noise free. But in order to detect the feeble scattered light intensity, the other photomultiplier (PM_1) should be operated at the maximum allowable voltage. This, however, causes a number of noise pulses to occur. Oscilloscopically displayed, they resemble the individual laser pulses. But by comparing the amplitudes of only those pulses which are coincident in time, the contribution of the noise pulses can be eliminated. Cooling the photomultiplier by means of dry ice was found to be very effective in substantially minimizing the noise pulses. However, it was found that the amplitude ratios of the time-coincident noise-free pulses even in a single shot were fluctuating randomly up to 25% of the mean value. But the average of the ratios over a large number of pulses for different experiments varied by only a few percent. The use of electronic integrators to average the photomultiplier outputs over the entire duration of laser action and subsequent determination of the amplitudes ratio of the photomultiplier outputs showed similar fluctuations. The results of the experiment, here described, have been obtained using electronic integration of the photodetector outputs.

[13] T. V. George, L. Slama, M. Yokoyama, and L. Goldstein, Phys. Rev. Letters **11**, 403 (1964). This was a preliminary publication of the present work.

TABLE I. The relative transmission of light through observation windows.

Position	45°	60°	75°	90°	105°	120°	135°
Relative transmission through windows	1.11	1.08	1.12	1.00	1.09	0.88	0.99

STUDY OF THE APPARATUS

In order to ascertain the validity of the results of the experiment, it is necessary to study in great detail the performance of the apparatus itself. It was found that the efficiency of transmission of light through each one of the observation windows varied slightly. A quantitative study of the transmission characteristics was performed by means of a uniformly luminous source having an appropriate intensity located at the center of the observation chamber. By placing the photodetector (PM_1) successively at each observation window, the relative light transmission efficiencies of the observation ports were determined. Table I shows the relative photomultiplier response at each observation window normalized to the value for the scattering angle corresponding to 90°.

The alignment of the observation ports of the chamber was checked by observing the angular variation of light scattered from a glass rod placed in the observation chamber. An *L*-shaped glass rod of 4 mm diam was placed in the chamber so that its horizontal portion would be collinear with the laser beam inside the scattering chamber. The rod was illuminated through the top end and the angular distribution of light scattered from the rod when light was directed in the same direction as the laser beam was first determined. The glass rod was then reversed so that the incident light was directed in the opposite direction. The angular distribution of the scattered light was again determined. The corrections associated with variation in transmission through the windows was applied and the curves were plotted as a function of the angle. These were found to be mirror images of each other with respect to $\chi=90°$, where χ is the scattering angle. This result ensures the proper alignment of the observation windows.

From geometrical considerations, it can be shown that the volume of interaction between the laser beam and the gas molecules seen by the photomultiplier is a function of the scattering angle. Hence for the precise determination of the angular distribution of the scattered intensity per unit volume, it is necessary to know the ratios of the interaction volume seen at different angles. This was experimentally determined as follows. A discharge tube of 4-mm I.D. was placed in the observation chamber, such that it occupied the same volume as the laser beam illuminated gas column. The uniform discharge plasma filling the tube was excited by a dc source. The relative values of the light intensity observed at the observation windows are proportional to the volumes of the uniformly luminous gaseous discharge seen at each window. It should be noted that the output of the photomultiplier (PM_1) yields the corrections due to the differences in transmission through each window and those associated with the variation of the interaction volume. The relative response of the photomultiplier at different observation windows with the discharge operated as described is shown in Table II.

PHOTOMULTIPLIER SENSITIVITY

During the course of the experiments it was found that the sensitivity of the photomultiplier (PM_1) used in detecting the scattered light varied substantially. Therefore, it was necessary to monitor its sensitivity. To this end a set of neon lamps (GE, NE-51) were fixed rigidly at the windows of the observation posts on one side of the chamber. These were pulsed on for 200 μsec, approximately 300 msec before and after the laser was triggered. Filters were used to reduce the intensity of the "standard" neon light reaching the photomultiplier which was placed at the observation window diametrically opposite to the neon lamp. The light intensity was thus adjusted so that the response of the photomultiplier to this standard light source would approximately be of the same order as that due to the laser light scattered signal. Finer adjustments on the light intensity were made by varying the resistance in series with the neon bulbs. The average of the responses of the photomultiplier (PM_1) to the standard light sources was taken to be a measure of the sensitivity of the photomultiplier (PM_1). The conditions of operation of the standard light sources were left undisturbed throughout the entire experiment on molecular scattering and the photomultiplier's sensitivity was monitored.

EXPERIMENTAL PROCEDURE

The scattering chamber was evacuated to a pressure of about one micron and the intensity level of the laser light (scattered by the entrance and exit windows and rescattered by the walls of the apparatus) observed at each window was determined. Due to its nature, it is referred to as the spurious scattering. The output of the reference photomultiplier (PM_2), which samples part of the incident laser beam, and that of the photomultiplier (PM_1) placed successively at the respective windows were displayed on an oscilloscope. A typical oscilloscope pattern is shown in Fig. 7. There are three traces associated with the output of photomultiplier (PM_1). Two of them correspond to the standard light

TABLE II. The relative response of the photomultiplier (PM_1).

Position	45°	60°	75°	90°	105°	120°	135°
Relative response of the photomultiplier	1.38	1.29	1.13	1.00	1.23	1.11	1.52

source which is pulsed 300 msec before and after the laser is triggered; and the third corresponds to the observed level of scattered laser light. There is only one trace associated with the output of the reference photomultiplier (PM_2). The oscilloscope pattern was photographed by means of a standard 35-mm camera and the image was projected on a screen. Measurements were made on all the four traces and the peak values attained in each case was recorded. If the average of the measured values of the standard light source is designated by "(Std. Light)"$_1$ and the other two are designated respectively by "(Spurious)" and "(Laser Ref)"$_1$, then the ratio R_v (the subscript v refers ro experiments with no gas in the system), given by

$$R_v=\frac{\text{(Spurious)}}{\text{(Laser Ref)}_v\text{(Std. Light)}_v},$$

should be constant and be a measure of the spuriously scattered laser light observed at each observation window. This ratio was determined for every observation port corresponding to scattering angles between 45 and 135°. Then gas at known temperature and pressure was introduced and the experiment was repeated in the same manner. If the response of the photomultiplier (PM_1) to the scattered laser light is designated by "(Gas Scatt)" and the other two measured quantities as "(Laser Ref)"$_g$ and "(Std. Light)$_g$" in the same manner as above, then the ratio R_g (the subscript g refers to experiments with gas), given by

$$R_g=\frac{\text{(Gas Scatt)}}{\text{(Laser Ref)}_g\text{(Std. Light)}_g},$$

should also be constant for each scattering angle. This ratio will correspond to the sum of the intensities due to scattering by gas molecules and spurious scattering. However, if the response of the photomultiplier (PM_1) to the standard light sources differs in the two experiments [i.e., $(\text{Std. Light})_v \neq (\text{Std. Light})_g$], the variation of the photomultiplier sensitivity is to be accounted for

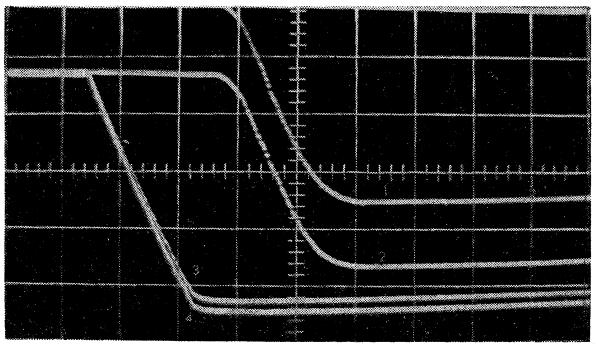

FIG. 7. Oscilloscope traces of the photomultiplier outputs. Trace 1: PM_2 output corresponding to the total power in the laser beam. Trace 2: PM_1 output corresponding to the detected power of the scattered light. Traces 3 and 4: PM_1 output corresponding to the "standard" light source.

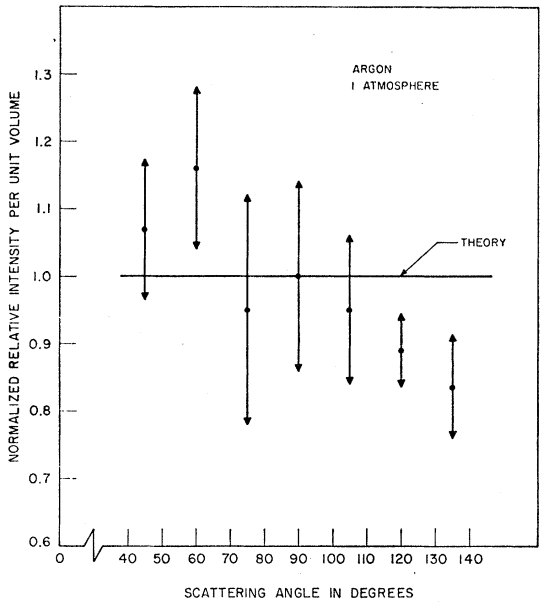

FIG. 8. Angular distribution of the intensity of scattered light for vertically polarized incident beam in argon at 1 atm.

in the calculation. Further, the "(Std. Light)" values for different scattering angles may be different. Both these aspects can be taken care of by evaluating S according to the relation

$$S=\langle(\text{Std. Light})_v\rangle\left[\frac{\text{Gas Scatt}}{\text{(Laser Ref)}_g\text{(Std. Light)}_g}\times\frac{\langle(\text{Std. Light})_g\rangle}{\langle(\text{Std. Light})_v\rangle}-\frac{\text{Spurious Scatt}}{\text{(Laser Ref)}_v\text{(Std. Light)}_v}\right],$$

where the $\langle\ \rangle$ refers to the average over a large number of experiments. S would be truly a relative measure of the light scattered by gas molecules alone. Now, by applying the corrections based on Table II to S, which compensate for the variation of the scattering volume and window transmission for different scattering angle, the angular dependence of the scattered intensity per unit volume can be calculated.

According to the elementary theory outlined in the introduction, $(d\sigma/d\Omega)=B\sin^2\theta$, where B is a constant for a given gas at a constant temperature and pressure and for a given wavelength of light. Here θ is the angle between the direction of the E vector of the linearly polarized incident beam and the direction of propagation of the secondary ray. If the observation is made in the *horizontal* plane, and if the incident light beam is *vertically polarized*, then $\theta=90°$ for all scattering angles. If the incident beam is horizontally polarized, $\sin^2\theta=\cos^2\chi$, where χ is the scattering angle. Hence the experiment on the angular dependence of the scattered intensity per unit volume was performed for these two cases. Figure 8 shows the results for argon at one

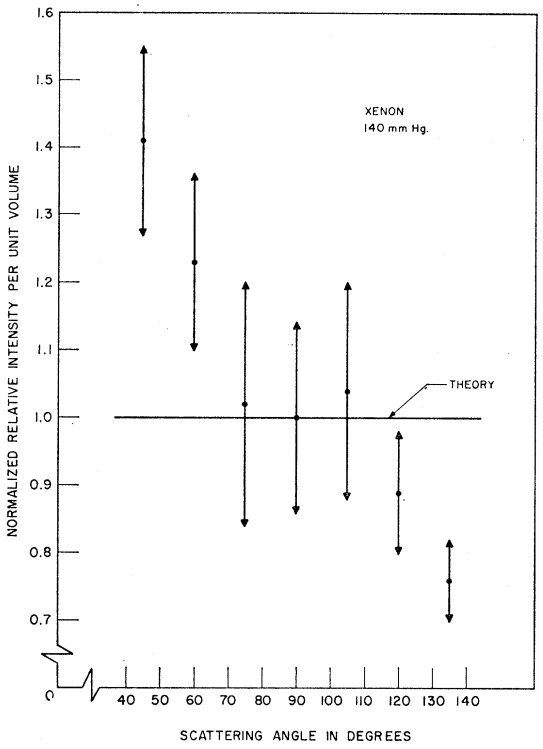

FIG. 9. Angular distribution of the intensity of scattered light for vertically polarized incident beam in xenon at 140 mm Hg.

atmosphere pressure and room temperature when the laser beam was polarized in the plane perpendicular to the plane of observation. Experiments using xenon (at 140 mm Hg of pressure) under identical conditions,

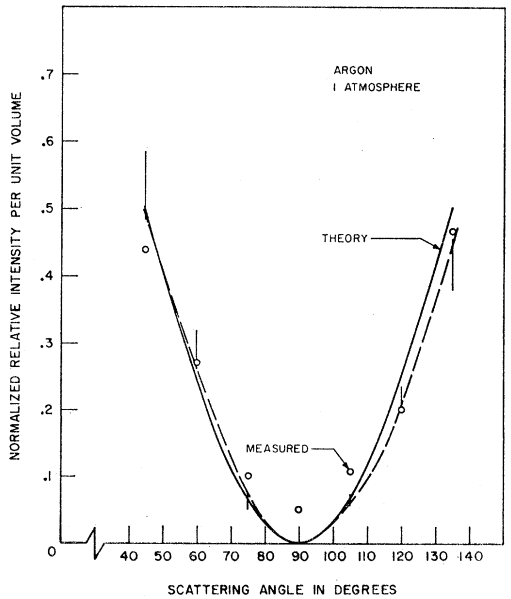

FIG. 10. Angular distribution of the intensity of scattered light for horizontally polarized beam in argon at 1 atm.

yielded the results shown in Fig. 9. Both curves are arbitrarily normalized to their values at $\chi=90°$. Since, as already mentioned, the sensitivity of the photomultiplier (PM_1) was randomly fluctuating to a certain extent, it was necessary to take the average of a series of values. The 95% confidence margins are shown with each averaging value. The results from Figs. 8 and 9 imply that when the laser beam *is polarized in the plane perpendicular to the plane of observation*, the intense ruby laser light is *not* scattered isotropically in argon and xenon which is in apparent contradiction with theory.

The variation of the scattered intensity per unit volume observed in argon and xenon for *horizontally polarized incident beam* is shown in Figs. 10 and 11. These results are found to be consistent with those obtained with the vertically polarized beam. That is, the values obtained with the vertically polarized beam

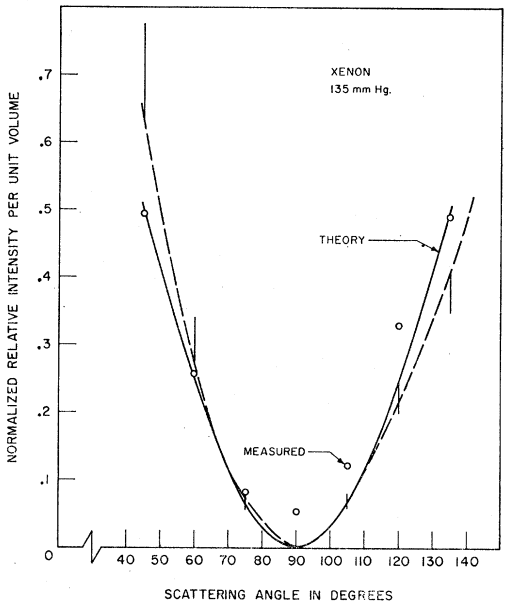

FIG. 11. Angular distribution of the intensity of scattered light for horizontally polarized incident beam in xenon at 135 mm Hg.

multiplied by the square of the cosine of the respective scattering angles (shown as vertical bars in the figures) yield within experimental accuracy the measured intensities in this case. Quantitative experimental studies of the field of view of the photomultiplier and the polarization state of the incident laser beam showed that the observed intensity at $\chi=90°$ can be fully accounted for by the vertically polarized component present in the incident beam (1.56%) and the finite aperture of the detector.

DETERMINATION OF THE ABSOLUTE VALUE OF THE DIFFERENTIAL SCATTERING CROSS SECTION

For the determination of the differential-scattering cross section of gas molecules, it was necessary to

calibrate the photomultiplier (PM_1) which was used to measure the scattered light intensity. This was accomplished by appropriately attenuating the laser beam by a large but known factor and measuring the attenuated beam intensity with the same photomultiplier. The experimental arrangement used for the calibration is shown in Fig. 12. The laser beam was deflected vertically downwards by a mirror M into a glass beaker containing a copper sulfate solution of known thickness. The attenuated beam was focused by a condensing lens at the photocathode of the photomultiplier (PM_1) operated under the same conditions as in the measurement of the scattered light intensities. If P_0 is the power of the incident beam, and P that of the beam emerging from the copper sulfate solution, then

$$P=P_0e^{-\beta h}, \tag{16}$$

where β is the attenuation coefficient and h is the thickness of the copper sulfate solution.

If V_1 and V_2 are the outputs of photomultipliers (PM_1) and (PM_2), respectively, as observed on the

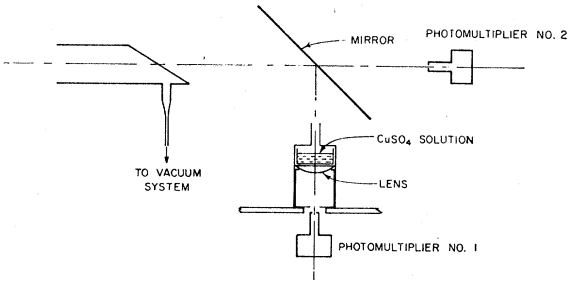

FIG. 12. Experimental setup for the calibration of the photomultiplier.

oscilloscope, then

$$V_1=K_1P$$

and (17)

$$V_2=K_2P_0,$$

where K_1 and K_2 are constants. Therefore

$$V_1/V_2=(K_1/K_2)(P/P_0). \tag{18}$$

It follows that

$$V_1/V_2=K_0e^{-\beta h}$$

with (19)

$$K_0=K_1/K_2.$$

The experiment was performed by varying the thickness (h) of the solution.[14] The plot of V_1/V_2 against h on a semilog scale is shown in Fig. 13. The value of V_1/V_2 for $h=0$ gives the constant K_0, the most probable value of which is calculated by the method of least mean square error. The reflection coefficients at the interfaces between air and copper sulfate solution ρ_{as}, copper

[14] h is obtained from measurements of volume of the solution (to 0.01-cc precision) and the area of cross section of the beaker (113 cm²).

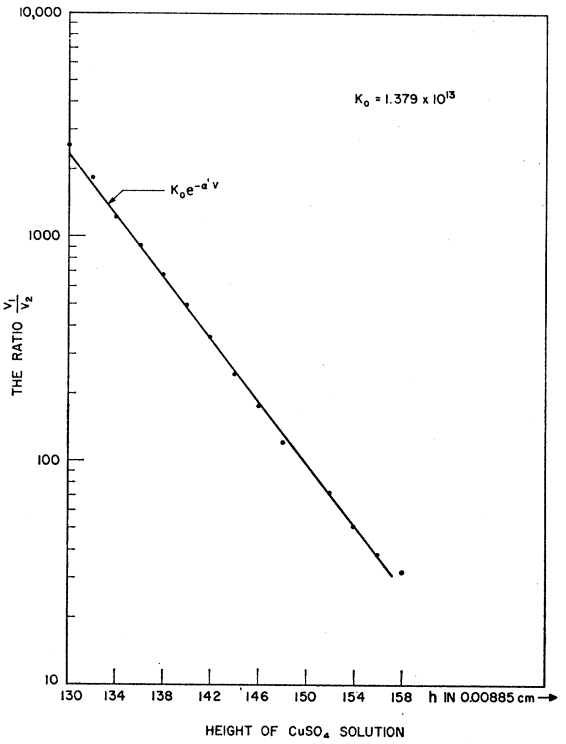

FIG. 13. Calibration curve of the photomultiplier.

sulfate solution and glass ρ_{sg}, and glass and air ρ_{ga} are determined. The losses due to these reflections are compensated by modifying K_0 as

$$K_T=\frac{K_0}{(1-\rho_{as})(1-\rho_{sg})(1-\rho_{ga})}.$$

With K_T thus determined one obtains the ratio of the

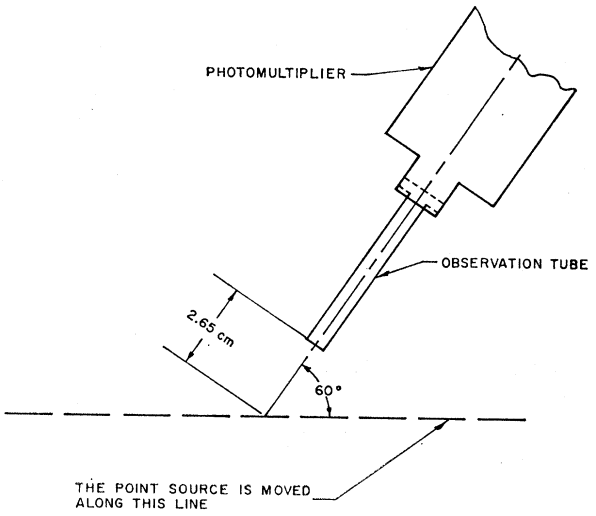

FIG. 14. Experimental arrangement for the determination of the field of view of the photomultiplier.

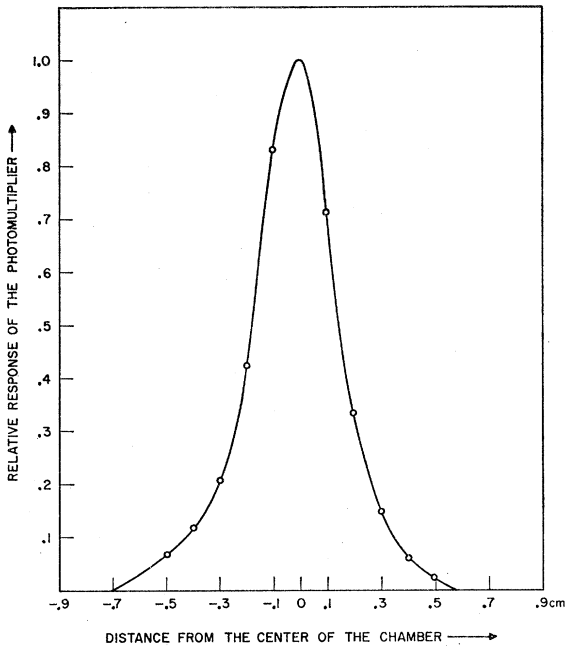

FIG. 15. The relative response of the photomultiplier as a point source is moved in its field of view.

scattered power detected by PM_1 to the incident power

$$P/P_0=(1/K_T)(V_1/V_2). \tag{20}$$

Taking extreme care not to disturb the operating conditions of both photomultipliers and in particular the position of photomultiplier (PM_2), the measurement of the differential scattering cross sections at an angle of $\chi=60°$ for various gases was carried out. Since the Brewster angle window was positioned such that the spurious scattering was minimized when the laser beam was horizontally polarized, the experiment was performed under this condition. The ratio (V_1/V_2) was measured for various gases at atmospheric pressure and room temperature and (P/P_0) was calculated according to Eq. (19). In xenon, the experiment was performed at 135-mm Hg pressure.

For the precise evaluation of the scattering cross section, it was necessary to determine directly the field of view of photomultiplier (PM_1) and the effective solid angle that each molecule in the field of view subtends at the cathode of the photomultiplier. In order to determine the field of view ideally, a point source should be moved across the scattering chamber along the path of the laser beam. Practical difficulties associated with such an experiment suggested constructing a similar system consisting of an identical observation tube and a photomultiplier as shown in Fig. 14. A hole of $\frac{1}{3}$ mm diam was drilled in a brass plate and was illuminated from one side using a mercury arc lamp. The hole was covered with a piece of white paper so that scattering occurred rather uniformly in all directions. The point source thus produced was moved along the dashed line shown in Fig. 14. The response of the photomultiplier as a function of the distance normalized to its own maximum value is shown in Fig. 15.

The solid angle subtended at the photocathode by a point source placed at the center of the observation chamber was calculated from geometrical considerations. The increase in the transmission of light due to reflections within the tube was experimentally determined using the same experimental arrangement as shown in Fig. 14. Thus the effective solid angle that a molecule located at the center of the chamber would subtend at the photodetector was determined to be 2.04×10^{-3} sr.

In the experiment, measurement of the scattering cross section was made by observing the scattered light at $\chi=60°$, with the incident beam horizontally polarized. The variation of the response of the photomultiplier when a point source is moved in its field of view and the fact that the molecules located away from the center of the chamber would be scattering light at angles other than 60° were taken into consideration in the calculation.

Consider a slab of thickness dl at a distance l from the center of the chamber in the cylindrical column of the gas medium through which the laser beam passes. The total number of scatterers in this volume element is given by

$$dN=n_0A\,dl, \tag{21}$$

where n_0 is the number of molecules/cm^3 and A the area of cross section of the cylindrical column.

If P_0 is the power of the incident laser beam and dP is the detected power radiated from this slab, the scattered power per unit incident intensity is

$$P_s=\frac{dP}{(P_0/A)}. \tag{22}$$

Substituting Eqs. (21) and (22) in Eq. (9) and rearranging terms, one obtains

$$dP=P_0n_0\Delta\Omega(d\sigma/d\Omega)dl. \tag{23}$$

Since the intensity variation of the scattered light in the plane of polarization of the incident beam was found to be approximately proportional to $\cos^2\chi$, where χ is the scattering angle, one may write

$$(d\sigma/d\Omega)=(d\sigma/d\Omega)_{60°\perp}\cos^2\chi, \tag{24}$$

where $(d\sigma/d\Omega)_{60°\perp}$ is a constant, which would be the differential scattering cross section at 60° for the case of vertical polarization. Let W be the response of the photomultiplier shown in Fig. 15. Modifying Eq. (23) accordingly one obtains

$$dP=WP_0n_0\Delta\Omega(d\sigma/d\Omega)_{60°\perp}\cos^2\chi dl. \tag{25}$$

Thus the total power measured by the photodetector would be

$$P=P_0n_0\Delta\Omega\left(\frac{d\sigma}{d\Omega}\right)_{60°\perp}\int W\cos^2\chi dl. \tag{26}$$

TABLE III. Differential scattering cross section for various gases.

Gases	Ne	Ar	Xe	O_2	N_2	Air	CO_2	SF_6	C_3H_8
Experimental values in 10^{-28} cm^2	0.048	0.843	5.71	0.90	1.04	1.03	2.76	6.08	19.6
Theoretical values in 10^{-28} cm^2	0.027	0.47	2.88						

The dependence of χ on l can be evaluated from the geometry. $\int W \cos^2\chi dl$ is obtained by graphical integration. Substituting the value of n_0 (for 23.3°C and normal pressure) and the experimentally determined value of $\Delta\Omega$ in Eq. (26), one obtains

$$(d\sigma/d\Omega)_{60°\perp} = (P/P_0)2.07\times10^{-16}. \quad (27)$$

Thus, the differential scattering cross section at the angle of 60° in the plane of polarization is

$$(d\sigma/d\Omega)_{60°} = 5.17\times10^{-17}(P/P_0). \quad (28)$$

Using the measured value of (P/P_0) one obtains $(d\sigma/d\Omega)$.

The polarizability α is calculated from known values of refractive index of the gas using the Clausius-Mossotti equation. This value of α and the wavelength in the medium are used in Eq. (9) to calculate the theoretical value of the differential scattering cross section. The experimental and the theoretical values are shown in Table III. The measured values are approximately twice as large as those predicted by the classical theory. It is to be pointed out, however, that the values of the polarizability α, obtained from Clausius-Mossotti relation were not directly checked in these experiments. Great care was exercised to keep the laser beam power density in the scattering chamber orders of magnitude below that for which gas breakdown could occur.[15] Conservative estimates of the errors involved in the cross section measurements show that the experimental results should not deviate more than 35% from the true values. Hence the discrepancy between the theoretical and experimental values are beyond experimental errors and cannot be explained on the basis of the linear theory outlined in this article.

POSSIBLE CAUSES FOR DISCREPANCIES

On the basis of these observations, it appears necessary to search for possible causes for the deviation of the experimental results from theory. We have investigated the following possibilities: (1) presence of dust in the gas; (2) multiple scattering effect may not be negligible; (3) nonlinear scattering might be taking place; (4) depolarization effects; (5) shift in wavelength of laser light due to heating of ruby crystal; and (6) broadening of the spectrum of the scattered light.

(1) To study the effect of dust on the intensity of the scattered light, dust was produced artificially in the scattering chamber and observation was made over a period of 25 h. Two electrodes of 2 cm in diameter were placed in the chamber approximately 2 cm apart, one above and the other below the laser beam. A high-voltage power supply was connected to the electrodes producing an electric field between them. In order to liberate dust from the electrodes, the voltage was increased until an arc of short duration was formed. Simultaneously, an increase in the scattered laser light was observed. The voltage was immediately reduced to zero and then increased to a "safe" value, so that the charged dust particles were swept by the electric field. The intensity of the scattered light was found to decrease steadily with time. The gases used for these investigations were air and SF_6. With 1500 V across the electrodes, it was found that the influence of dust became negligible within a few hours. The gases under investigation were introduced into the scattering chamber through filters. The dust particles which escaped capture by the filter may have reached the chamber uncharged. In order that these be acted upon by the electric field, a strong source of radioactive material was placed directly below the scattering chamber and observations were performed upon the scattered light over extended periods of time. No change in the intensity of scattered light was observed. Thus, it should be concluded that the contribution of dust to the scattered radiation is negligible. It would have been possible to arrive at this result indirectly by comparing the ratios of the scattering cross sections determined experimentally with the corresponding theoretical values given by Eq. (15). Table IV shows the experimental and theoretical values. The agreement between the two sets

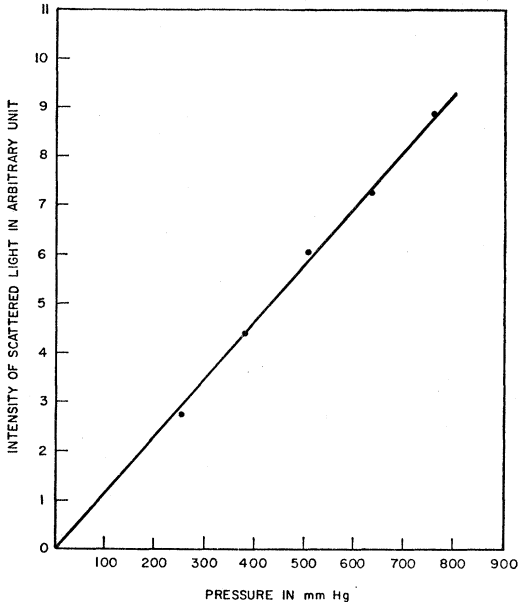

FIG. 16. Pressure dependence of the intensity of scattered light at 135° with the incident beam in argon at room temperature.

[15] R. G. Meyerand and A. F. Haught, Phys. Rev. Letters **11**, 401 (1963).

TABLE IV. Experimental and theoretical ratios of the differential scattering cross sections of the noble gases.

Gas 1	Gas 2	$\left(\frac{d\sigma}{d\Omega}\right)_1 \Big/ \left(\frac{d\sigma}{d\Omega}\right)_2$ Experimental	$\left(\frac{n_1^2-1}{n_2^2-1}\right)^2$
Argon	Neon	17.6	17.5
Xenon	Neon	119	107.9

of ratios assures the absence of dust in the gases under investigation.

(2) Rayleigh's theory of light scattering is developed under the hypothesis that the interaction between molecules (dipoles) is negligible. This hypothesis can be verified by studying the dependence of the intensity of scattered light upon molecular density. The number of molecules in the field of view of the photodetector is directly proportional to the molecular density. However, the average intermolecular distance decreases as the inverse cube root of the molecular density. The interaction between molecules, which is dependent upon the intermolecular distance, is thus directly related to molecular density. Since molecular density is proportional to gas pressure at a constant temperature, if this interaction is negligible, scattering would be linearly related to pressure; if not, deviation from linearity would be expected. Figure 16 shows the variation of the intensity of the scattered light at an angle $\chi=135°$ as a function of pressure in argon at room temperature. The linear relationship experimentally determined substantiates the hypothesis that in argon up to one atmosphere of pressure (at room temperature) intermolecular interaction is negligible.

(3) Study of the possible nonlinearity in scattering was performed by determining the amplitude ratios of the individual time-coincident pulses in the scattered and incident laser light as described earlier. A sevenfold increase in the amplitude of the incident laser pulses did not alter this ratio. Hence in these experiments no nonlinear scattering was observed.

(4) Depolarization in the scattered signal, if any, was found to be too small to be detected. If the scattered signal were depolarized, substantially large signals would have been observed in the direction perpendicular to the beam in the plane of polarization of the incident light. The finite aperture of the photomultiplier and the imperfection in the polarization of the incident beam fully accounted for the observed signal in this direction. Thus depolarization effects in the scattering of light by noble gas molecules can be considered to be negligible.

(5) Care was taken to keep the temperature of the ruby crystal unchanged during the entire experiment. The crystal and the flash tubes were cooled by circulating air at a constant rate. Moreover, the rate at which the laser was fired was kept at exactly once every sixty seconds. To further assure the frequency stability of the laser output, the cooling was cut off and the laser was fired once every 60 sec for half an hour and the wavelength of the laser light was measured by means of a monochromator having 0.8 Å resolution. No change in wavelength was observed.

(6) The scattered light was detected by means of a photomultiplier equipped with an interference filter with 50 Å bandwidth. If the spectrum of the scattered light was broadened by more than this amount, there could be an error in the determination of the angular dependence of the differential-scattering cross section. Therefore, the experiment was repeated without any interference filters. The results were the same showing that the spectral broadening, if there was any, was far less than 50 Å.

CONCLUSION

In spite of the availability of lasers producing intense parallel beams of light and sensitive photomultipliers, severe problems were encountered in suppressing light scattered from the walls of the apparatus over a wide angular range. A systematic study of the laser showed that the beam divergence was beyond tolerable limits. The optical system designed to suppress the ill effects brought the level of the spuriously scattered light intensity to approximately 10^{-14} times the intensity of the incident beam over an angular range of 45 through 135°.

The relative variation of the differential scattering cross section for argon and xenon was carried out over the indicated angular range. The scattered radiation was always observed in the horizontal plane. The experiments were performed with the incident beam both vertically and horizontally polarized. It is found that when the ruby-laser light beam (of about 0.1 J) is vertically polarized, it is not scattered isotropically either by argon or by xenon as predicted by the linear theory. And when the beam is horizontally polarized, the angular variation of the scattered intensity appears to be consistent with a cosine square distribution.

The precise determination of the differential-scattering cross section for various gases was carried out at a scattering angle of 60° in the plane of polarization of the incident light. The measured values were found to be approximately twice the theoretical values. The discrepancy between the two sets of values are beyond experimental errors and cannot be adequately explained on the basis of the presently available linear theory.

Note added in proof. The variation of the effective scattering volume of the gas seen at different angles and the losses due to various interface reflections which have been taken into consideration in this paper were neglected in Ref. 13.

ACKNOWLEDGMENTS

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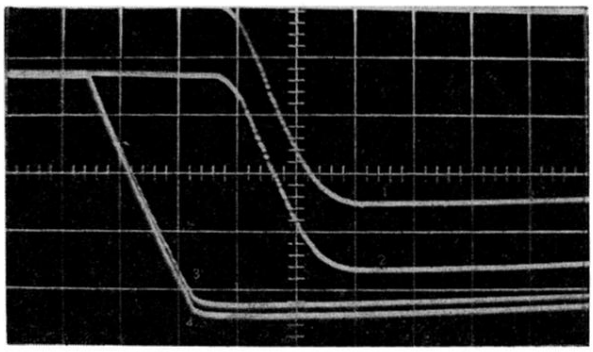

FIG. 7. Oscilloscope traces of the photomultiplier outputs. Trace 1: PM_2 output corresponding to the total power in the laser beam. Trace 2: PM_1 output corresponding to the detected power of the scattered light. Traces 3 and 4: PM_1 output corresponding to the "standard" light source.