DETERMINATION OF MOLECULAR INVARIANTS ALPHA' AND GAMMA'

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By

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13. ABSTRACT

The determination of the polarizability invariants and particularly the derivatives of the invariants, the isotropic and anisotropic parts α' and γ', necessary for the prediction of the Raman scattered intensity are considered. It is shown that a simple method based on the angular dependence of the scattered Raman intensity can be utilized to obtain these invariants, provided the polarization of the incident radiation is known.

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TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF SYMBOLS

c	velocity of light $2.99793(10)^{10}$ cm/sec.
h	Planck's constant $6.62517(10)^{-27}$ erg.sec.
I	intensity
k	Boltzmann's constant $1.38044(10)^{-16}$ erg/^{o}K
N	number of molecular scatterers
T	temperature
α	isotropic part of the polarizability tensor
α'	spherical (isotropic) part of the change of the polarizability
γ	anisotropic part of the polarizability tensor
γ'	anisotropic part of the change of the polarizability
θ	angle of observation with respect to the incident
μ	reduced mass of the molecule
ν	wave number
ρ	depolarization ratio

Subscripts

h	horizontally polarized incident radiation
o	incident value
s	Stokes component
v	vertically polarized incident radiation
θ	angle between observation and irradiation
$\perp$	perpendicular
$\parallel$	parallel

I. INTRODUCTION

The Raman effect has been known and utilized for almost a half century by chemists and physicists interested in molecular structures and chemical, physical thermodynamic and crystalographic properties of matter; these range from force constants, composition, chemical bonds,isomerism, electrolytic dissociation, association to polymerization, exchange interaction, kinetics of fast reactions, structural symmetry or asymmetry, etc. In the last several years, spurned by the development of high power lasers, the application of the Raman effect, due to its unique properties, has found new fields of application[1-6]. These range from diagnostics of flow fields in fluid dynamics to the remote measurements and monitoring of air pollutants, from temperature measurements of reacting gases to concentration measurements of the products of reactions and combustion. The theory of the Raman effect and Raman spectroscopy on a laboratory level is in a very highly developed state. While the molecular polarizability invariants α' and γ' necessary for the calculation of the equivalent Raman scattering cross-sections are tabulated for a number of molecules, in particular diatomic molecules[1,7,8], there is a vast number of molecules for which these invariants are not easily available. A number of methods have been developed for the direct measurement of these

invariants[7]. Some of these methods will be discussed in the next section.

In this work it is shown that it is possible to obtain the polarizability invariants α' and γ' utilizing the angular dependence of the scattered intensity, in particular when one has available a primary illumination source of known polarization.

II. THEORETICAL BACKGROUND

As stated in the Introduction, a number of methods are available for the determination of the polarizability invariants. These are generally based on the experimental determination of the depolarization ratio ρ, defined as the ratio of the intensity of the scattered light polarized perpendicular to the xz plane $I_{\perp}$, to that polarized parallel to this plane I_{11}, when the incident light approaches along the y-axis and the scattered light is observed at right angles to the y-axis (Fig. 1),

$$\rho = \frac{I_{\perp}}{I_{11}} \tag{1}$$

or, in other words, the ratio of the scattered intensity which is polarized perpendicular to the polarization of the incident radiation to the scattered intensity which is polarized parallel to the polarization of the incident radiation, where all

measurements are made in a direction perpendicular to the propagation direction of the incident radiation. When considering the problem of measuring the state of polarization of Raman scattered radiation by a non-oriented medium such as a gas or liquid, one must perform the averaging process over all possible orientations of scattered radiation. As a result of this process, one arrives at two convenient parts of the derivatives of the polarizability tensor; the first is the isotropic part α', the other is the anisotropic part γ'. In terms of α' and γ', the depolarization ratio can be expressed as follows:

$$\rho_{Raman} = \frac{6\gamma'^2}{45\alpha'^2+7\gamma'^2} \tag{2}$$

In a similar fashion, the depolarization ratio of Rayleigh scattered radiation is given by

$$\rho_{Rayleigh} = \frac{6\gamma^2}{45\alpha^2+7\gamma^2} \tag{3}$$

From Eqs. (2) and (3) and from a measurement of the intensity ratio of I_{Ram}/I_{Ray} given by

$$\frac{I_{Ram}}{I_{Ray}} = \left(\frac{45\alpha'^2+7\gamma'^2}{45\alpha^2+7\gamma^2}\right) \frac{4}{8\pi^2\mu_\nu} , \tag{4}$$

and knowing the refractive index of the given gas which permits

the calculation of α from the relation $n-1=2\pi N\alpha$, one can obtain the polarizability invariants α' and γ'.

From the definition of the depolarization ratio, it is evident that at least two measurements are necessary to obtain the same. Here one can distinguish between two basic experimental techniques. One takes cognizance of the polarization of the scattered radiation; the other does not. In order to take account of the polarization of the scattered radiation, one may proceed as follows:

a) One may use unpolarized incident radiation and measure the scattered radiation polarized once in one direction and then polarized perpendicular to the direction of the first measurement.

b) One may use incident radiation which is polarized perpendicular to the direction of observation, and measure scattered radiation polarized parallel to the incident radiation and perpendicular to the incident light polarization.

Since Raman scattered radiation is not polarized, in both the above cases, it is necessary to utilize polarizers for the observation of the scattered radiation. This, of course, complicates the experimental procedure, and it is therefore not the best one could hope for.

The other experimental method for the depolarization ratio measurement does not provide for the measurement of

the polarization of the scattered radiation. Here, too, two procedures are possible. One utilizes incident light polarized parallel and perpendicular to the observation direction and measures the intensity of the scattered radiation, the ratio of which is the depolarization ratio given by Eq. (2). In the other case, one uses incident radiation polarized parallel to the observation direction, and nonpolarized incident light. The ratio of both intensities again provides the polarization ratio. In this case, however, ρ is given by

$$\rho = \frac{6\gamma'^2}{45\alpha'^2+13\gamma'^2} \tag{5}$$

While the above procedures provide the required information necessary to obtain the equivalent scattering cross-sections, it is possible to obtain the latter in a much simpler way. One could, for example, obtain the equivalent scattering cross-section of an unknown gaseous or liquid specie by comparing the scattered intensity to the scattered intensity of a specie for which the equivalent scattering cross-section is known, this procedure being followed under the same conditions of illuminating intensity, frequency, pressure, temperature, etc. This procedure can provide information which is sufficient for a great number of applications. However, the polarizability invariants, and the depolarization ratio provide additional

information as to the symmetry of the given molecular structure, the equivalent scattering cross-section, cannot provide.

The Raman scattered intensity as a function of the observation angle θ may be represented for unpolarized primary illumination by

$$I_\theta = \frac{kI_o N(\nu_o-\nu)^4}{\nu[1-\exp(-h\nu/kT)]}\left\{[45\alpha'^2+7\gamma'^2](1+\cos^2\theta)+6\gamma'^2\sin^2\theta\right\} \quad (6)$$

which reduces for vertically polarized light and normal observation, i.e., normal to the plane formed by the polarization direction and direction of propagation to

$$I_{11} = \frac{kI_o N(\nu_o-\nu)^4}{\nu[1-\exp(-h\nu/\alpha T)]}[45\alpha'^2+7\gamma'^2] \quad (7)$$

and for horizontally polarized light to

$$I_\perp = \frac{kI_o N(\nu_o-\nu)^4}{\nu[1-\exp(-h\nu/kT)]}[(45\alpha'^2+7\gamma'^2)\cos^2\theta+6\gamma'^2\sin^2\theta]. \quad (8)$$

The depolarization ratio,

$$\rho = \frac{I_\perp}{I_{11}} = \frac{(45\alpha'^2+7\gamma'^2)}{(45\alpha'^2+7\gamma'^2)}\cos^2\theta+6\gamma'^2\sin^2\theta \quad (9)$$

When the angle of observation is equal to $\pi/2$ with respect to the direction of the incident radiation, Eq. (9)

becomes

$$\rho = \frac{6/7}{45/7 \frac{\alpha'^2}{\gamma'^2} + 1} \qquad (10)$$

Since the symmetrical part of the polarizability invariant α' changes only when the molecule is distorted in a totally symmetrical manner, α' will be zero for all vibrations which are not in a totally symmetric specie and the depolarization ratio from Eq. (10) becomes 6/7. On the other hand, all unsymmetrical species will have $\rho<6/7$ since α' will not vanish. This feature is of importance in identifying totally symmetric vibrations.

Returning now to Eqs. (7) and (8), it is evident that two ratios can be formed. The first, as given in Eq. (9), permits the evaluation of the depolarization ratio ρ, and from it the ratio α'/γ'. The second ratio can be formed by utilizing Eq. (8) above and performing the measurements at two different angles. Thus one may obtain

$$\frac{I_1}{I_2} = \frac{I_{o1}}{I_{o2}} \frac{[(45\alpha'^2+7\gamma'^2)\cos^2\theta_1+6\gamma'^2\sin^2\theta_1]}{[(45\alpha'^2+7\gamma'^2)\cos^2\theta_2+6\gamma'^2\sin^2\theta_2]} \qquad (11)$$

It is evident from Eq. (11) that knowing the angles of observation and measuring the scattered radiation intensity I_1 and I_2, the ratio α'/γ' can be evaluated. This method is quite simple and requires only a simple radiation intensity measurement.

III. EXPERIMENTAL APPARATUS

In order to perform the measurements as indicated above, an apparatus as shown in Fig. 2 was utilized. The apparatus was essentially that of Ref. 3, except that several viewing ports were utilized. These were at $\theta=45^{\circ}$, 90°, 225° and 270°, as indicated in the figure. A photographic view of the experimental arrangement is shown in Fig. 3. The chamber could be evacuated and pressurized to several atmospheres of pressure. Pressure and vacuum monitoring instrumentation was incorporated in the apparatus. For a complete description, Ref. 3 should be consulted.

A Q-switched ruby laser of 100 megawatt peak power was utilized. Since the chamber was filled with a known gas, and therefore the expected Raman lines were known and no interference or overlapping of frequencies was expected, narrow bandpass filters could be used for these measurements.

IV. EXPERIMENTAL PROCEDURES AND RESULTS

As pointed out above, it is possible to obtain the ratio of α'^2/γ'^2 by simply measuring the intensity of the scattered radiation at two different angles of observation, provided the incident illumination is polarized in the plane of observation (horizontally) and utilizing Eq. (11).

To demonstrate the capability of this method, tests were conducted utilizing gases whose polarizability invariants are well-known and available in the literature. These gases are nitrogen and oxygen. Before, however, attempting to determine the polarizability invariants, a test of the apparatus and the polarization of the lasers was conducted. Since with the laser polarized normal to the plane of observation, no angular dependence is predicted (Eq. (7)), tests were conducted for both N_2 and O_2 in that mode. The results are shown in Fig. 4, wehre the intensity ratio is plotted as a function of observation angle normalized to the intensity at 90^o observation. It is evident from this figure that the experimental results are in good agreement with the theoretical predictions, thus verifying the experimental apparatus and the polarization of the laser.

Having confirmed the operation of the apparatus and the polarization of the laser, tests were conducted for both O_2 and N_2 with the laser polarized in the plane of observation. The scattered intensity as a function of angle of observation was obtained for both species. The results for O_2 and N_2 are shown in Figs. 5 and 6, respectively. The data are presented normalized to the scattered intensity at 90^o. In the same figures are also shown the results as given in Refs. 7 and 8.

As can be noted from these figures, the data obtained in this work appear to agree reasonably well with those of Ref. 7. Some scatter of the data is to be expected in view of the single pulse operation of the laser and some minor difficulties in monitoring accurately the primary pulse power during these experiments.

In Table I, the ratio of $(\frac{\alpha'}{\gamma})^2$ as obtained in this work and in Refs. 7 and 8 are shown.

V. CONCLUSIONS

In view of the above experimental results, it may be concluded that the method of obtaining the polarizability invariants utilizing the angular dependence is capable of providing reasonably reliable data quickly, easily and economically, without the need of complicated experimental apparatus and complicated procedures.

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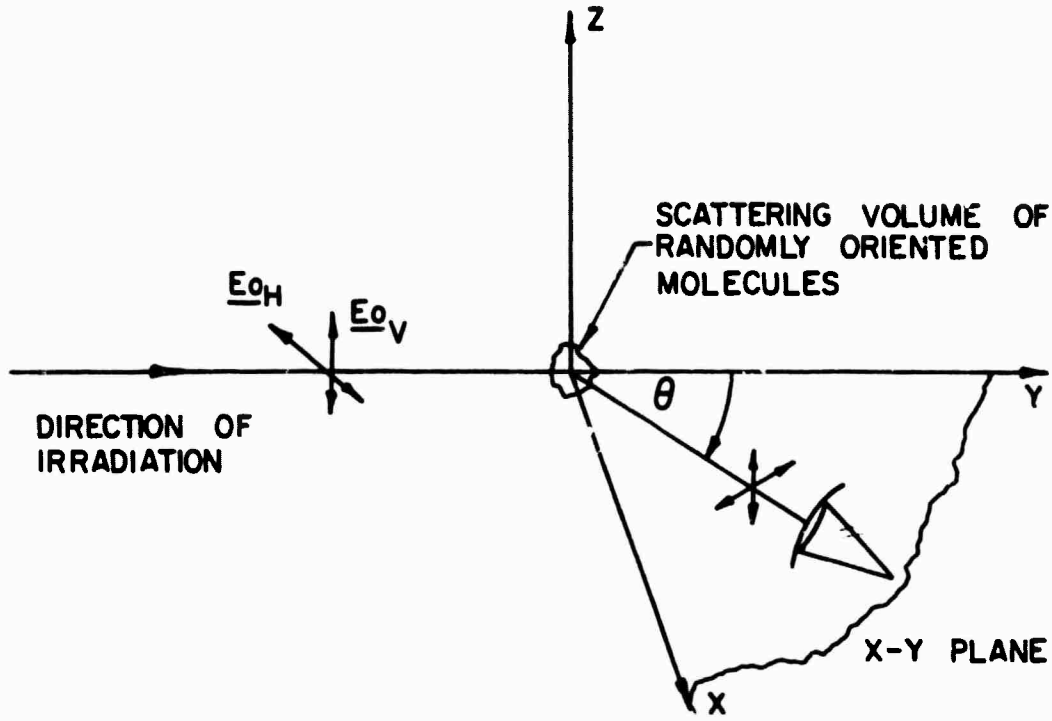


$(\ )_V$ - VERTICALLY POLARIZED RADIATION (Y-Z PLANE)

$(\ )_H$ - HORIZONTALLY POLARIZED RADIATION (X-Y PLANE)

FIG. 1 COORDINATE SYSTEM SHOWING THE DIRECTION OF LASER IRRADIATION AND THE ORIENTATION OF THE VIEWING SYSTEM

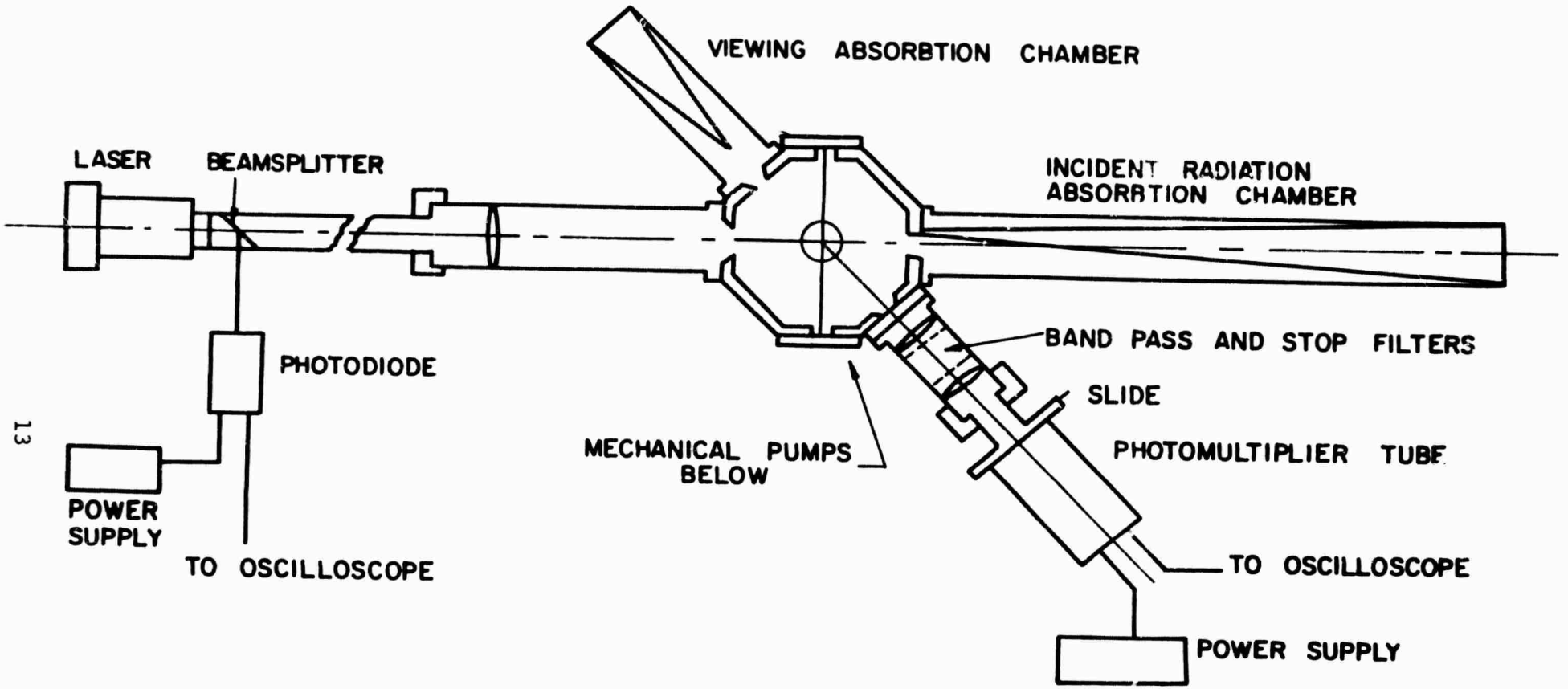
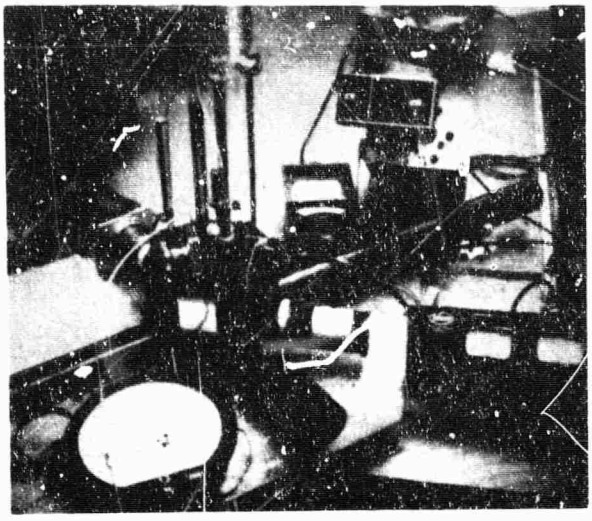
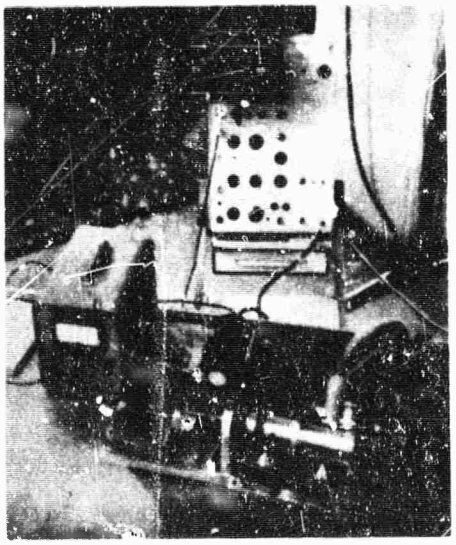


FIG. 2 SCHEMATIC OF THE EXPERIMENTAL APPARATUS



SCATTERING CHAMBER, PHOTOMULTIPLIER TUBE WITH SUPPORTING EQUIPMENT



LASER SYSTEM

FIG. 3 PHOTOGRAPHIC VIEWS OF THE EXPERIMENTAL APPARATUS

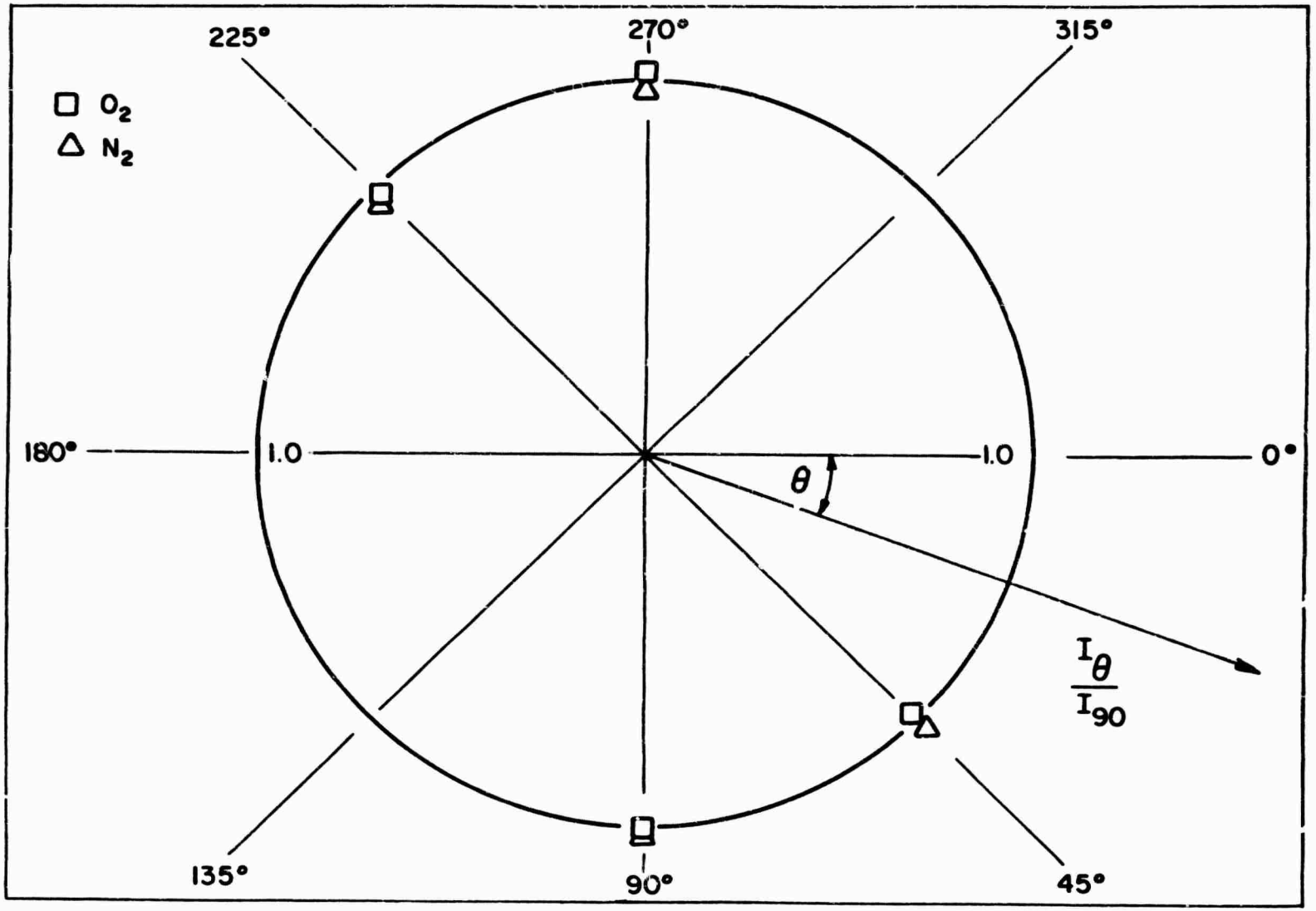


FIG. 4 PLOT OF θ VS. I_θ / I_{90} FOR N_2 AND O_2 WITH VERTICALLY POLARIZED LASER

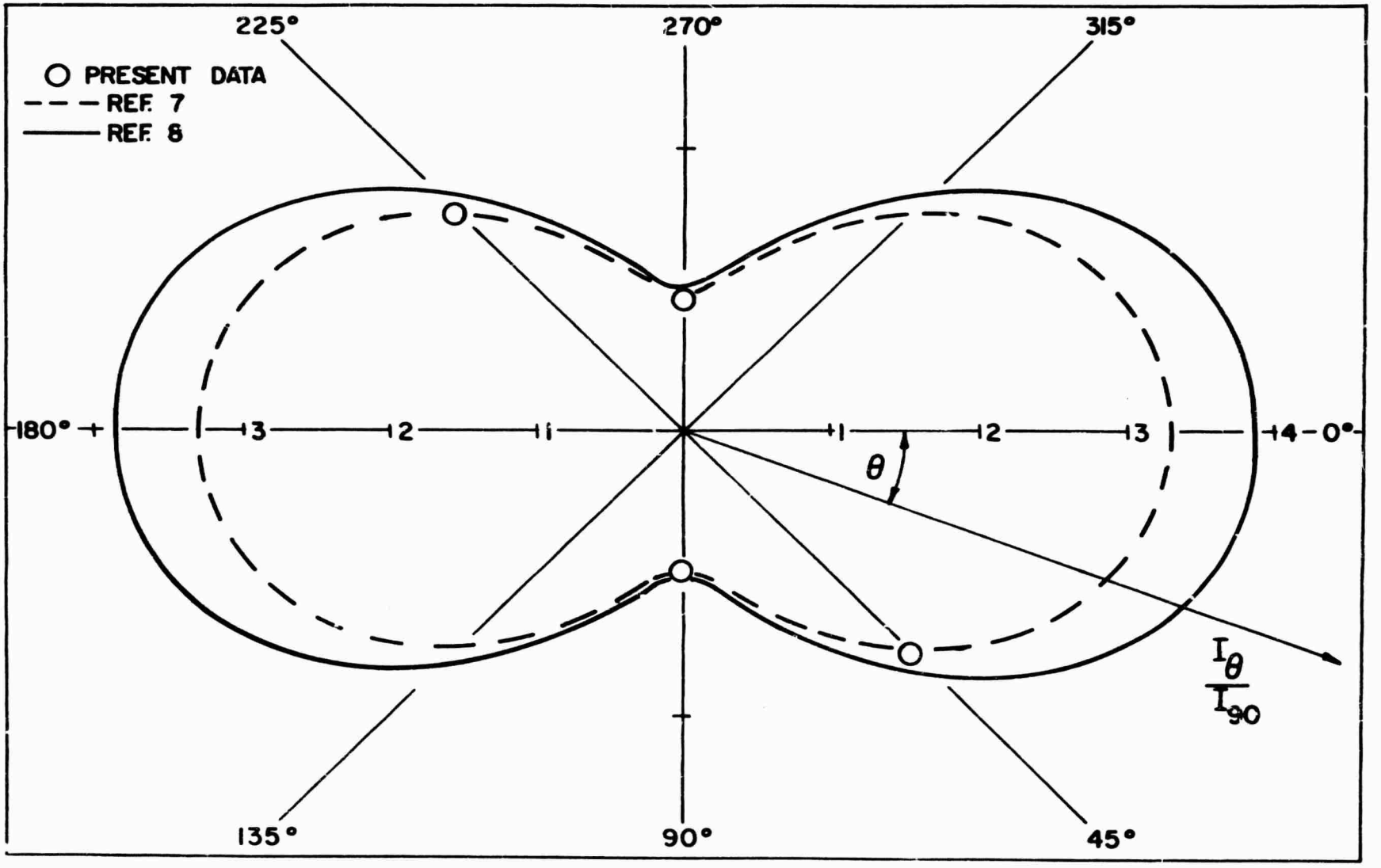


FIG. 5 PLOT OF θ VS. I_θ / I_{90} FOR OXYGEN WITH HORIZONTALLY POLARIZED LASER

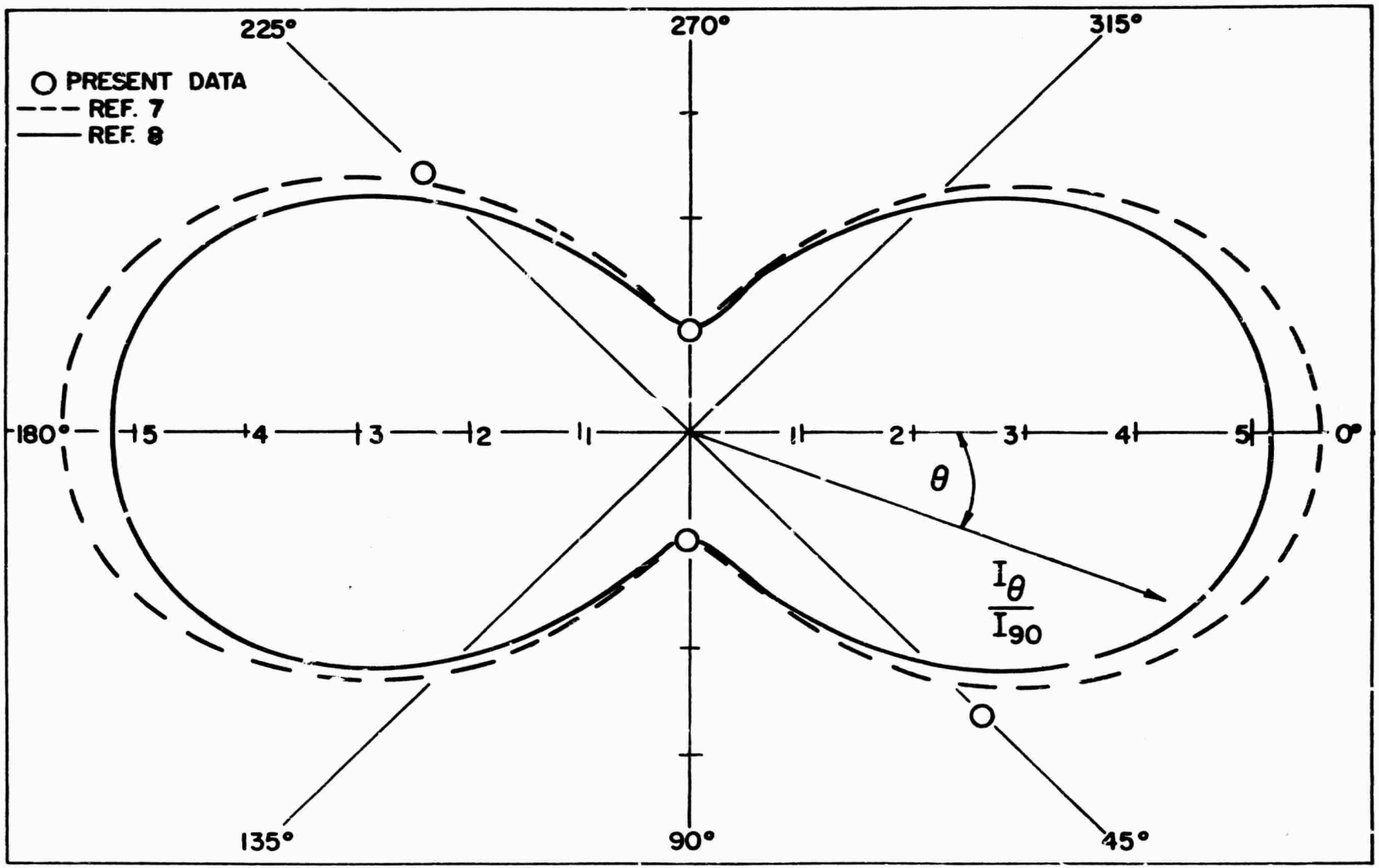


FIG. 6 PLOT OF θ VS. I_θ / I_{90} FOR NITROGEN WITH HORIZONTALLY POLARIZED LASER