Semi-Annual Report 7
December 1968

STIMULATED RAMAN EMISSION AND ABSORPTION SPECTROSCOPY

B.P. Stoicheff
University of Toronto
Department of Physics

<table>
<thead>
<tr>
<th>Order No.</th>
<th>NR 015-813/4-14-65</th>
</tr>
</thead>
<tbody>
<tr>
<td>Code No.</td>
<td>5730K21</td>
</tr>
<tr>
<td>Contractor</td>
<td>The Governors, University of Toronto</td>
</tr>
<tr>
<td>Date of Contract</td>
<td>1 June 1965</td>
</tr>
<tr>
<td>Contract No.</td>
<td>Nonr-5012 (00) M-2</td>
</tr>
<tr>
<td>Expiration Date</td>
<td>31 May 1969</td>
</tr>
<tr>
<td>Project Scientist</td>
<td>Prof. B.P. Stoicheff</td>
</tr>
<tr>
<td>Business Home</td>
<td>(416) 928-2948</td>
</tr>
<tr>
<td>Home</td>
<td>(416) 225-6421</td>
</tr>
</tbody>
</table>

Reproduction in whole or in part is permitted for any purpose of the United States Government.
INTENSITY AND AIN MEASUREMENTS OF THE
STIMULATED RAMAN EMISSION IN LIQUID \( \ce{O_2} \) AND \( \ce{N_2} \).

J.B. Grun, A.K. McQuillan and B.P. Stoicheff
Department of Physics, University of Toronto,
Toronto 5, Canada
ABSTRACT

In liquid $O_2$ and $N_2$ the threshold for stimulated Raman emission is found to be much lower than for other nonlinear processes. Thus it is possible to make reliable measurements of the intensity of Raman emission over a large range of incident laser power by using a simple longitudinal geometry. Several distinct regions of emission were investigated, including normal Raman scattering, exponential gain, onset of oscillation and saturation. There is good agreement with theory.
INTRODUCTION

It is well-known\(^1\) that the comparison of theoretical and experimental values of intensity and gain in stimulated Raman emission is complicated by several competing processes such as self-focusing, and Brillouin and Rayleigh scattering, all of which may have similar appearance thresholds. Thus, anomalous intensity behaviour in many liquids and even in gases\(^4\) - \(6\) and solids\(^7\) appears to be the rule rather than the exception. One important consequence is that the premature onset of oscillation has precluded the observation of the expected exponential gain in most materials with the exception of gaseous hydrogen and liquid acetone and carbon tetrachloride\(^8\). Bloembergen and Lallemand\(^3\), \(^6\) have overcome some of these difficulties by the use of a Raman amplifier and have demonstrated its importance in obtaining reliable values of the Raman gain. Other useful experimental arrangements in such studies include, the transverse resonator of Dennis and Tannenwald\(^9\), the off-axis resonator of Jennings and Takuma\(^10\) and the diffusely pumped amplifier of Bortfeld and Sooy\(^11\). More recently, Shapiro, Giordmaine and Wecht\(^12\), Bret and Weber\(^13\), and Kaiser and Maier\(^14\) have shown that with picosecond and sub-nanosecond laser pulses stimulated Raman scattering is the dominant nonlinear scattering process in several liquids and thus have obtained good agreement with theoretical intensities.
The present investigation of laser stimulated Raman emission from liquid $O_2$ and $N_2$ arose from the results of earlier studies of the spectra of the normal and stimulated scattering. In one, it was shown that the linewidth of the normal Raman scattering was exceptionally narrow indicating a large Raman gain\textsuperscript{15}; in another, concerning the stimulated Raman emission, extremely sharp spectral lines were observed (Fig.1) without any evidence of broadening\textsuperscript{16}, thus indicating that self-focusing and other scattering processes were not prominent. From these results we concluded that possibly the threshold for stimulated Raman scattering is lower than for the competing processes, in which case liquid $O_2$ and $N_2$ would be ideal substances for experimental study. Indeed, the present investigation has shown that liquid $O_2$ and $N_2$ are unique in this respect and no self-focusing or stimulated Brillouin scattering has been detected up to the highest incident laser power.

We wish to report our observations of the intensity of Raman Stokes radiation corresponding to the vibrational frequencies 1552.0 cm$^{-1}$ and 2326.5 cm$^{-1}$ of liquid $O_2$ and $N_2$ respectively. A simple longitudinal arrangement was used. The range of Raman intensity measurements includes the normal emission which varies linearly with incident laser power, a region of exponential gain over several orders of magnitude, the onset of oscillation with feed-
back by Rayleigh scattering and finally a region of saturation
and depletion. The observed gain is in good agreement with
that calculated from our experimentally determined cross-
section for scattering.

APPARATUS AND EXPERIMENTAL PROCEDURE

The exciting source was a giant-pulse ruby laser with a
rotating prism at one end and at the other a plane parallel
reflector (≈25% reflectivity) of Corning 2-58 glass which
served as a mode selector and also as a filter. The radiation
was emitted in a single pulse of ≈30 ns duration and in a single
(or nearly single) axial mode. Good reproducibility in the laser
pulse was obtained by firing the laser at constant power near
threshold, at regular (3 min.) intervals with the ruby at a
constant temperature (−10°C). This procedure also eliminated any
spatial drift of the laser beam at the distant spectrometer slit.

The temporal behaviour of a typical laser pulse is shown
in Fig. 2a. A study of the spatial intensity distribution of the
laser beam was made at a magnification of 20X and by photo-
graphing the beam after attenuation by neutral density filters.
This showed the presence of several intensity maxima (Fig. 3a)
which increased the effective intensity of the laser beam to
twice the average intensity. Also, the laser radiation was
found to be plane polarized to better than 2000:1.

The longitudinal arrangement shown in Fig. 4 was used for
the measurements of Raman scattering intensity and state of polarization, in the forward direction. The sample container was a simple dewar of 1 litre capacity with a path length of 5.8 cm between the two inner windows. It was positioned approx. 4 m from the laser in order to reduce possible feedback of scattered radiation to the laser. At each filling of the dewar the liquid was passed through a 5 μm millipore filter to remove any dust particles. A short time after a filling, the liquid became quiescent.

In order to increase the laser power density incident on the samples, the beam diameter was reduced by a factor of about 10 (to 0.6 mm) with a system of two lenses. The incident laser power was varied from 30 KW to 600 KW by inserting calibrated neutral density filters of glass in the beam at the entrance diaphragm D₁ and lens L₁. The laser pulse was monitored with an EG & G photodiode (SGD-100) and displayed on a Tektronix 555 (or 519) oscilloscope. An essentially parallel laser beam was incident on the sample. The radiation scattered in the forward direction was collected through the exit diaphragm D₂ and focused on the slit of the spectrometer. The laser light entering the spectrometer was attenuated with calibrated filters. A grating spectrometer (Spex 1700) having a dispersion of 10 Å/mm was used with both entrance and exit slits open to 3 mm. Measurements of Stokes intensities were made with an RCA 7102 Photo-
multiplier having a cooled photocathode (−10°C). The signal was amplified 40 times by a two-stage emitter follower and fed into a type L preamplifier of the oscilloscope. The pulse heights from the oscilloscope traces gave an effective measurement of the intensity of Stokes emission during each laser pulse. Brief studies of the laser and Stokes pulse envelopes were made with a fast photodiode (ITT FW 114A) and a Tektronix 519 oscilloscope. Depolarization measurements were carried out with a Nicol prism placed at the slit of the spectrometer.

Several precautions were taken to reduce any stray light and to minimize its effect on the intensity measurements, especially of the low intensity normal Raman scattering. The main sources of unwanted stray light were found to be the laser flashlamp, and optical filters and lenses of glass along the laser beam which emitted relatively intense fluorescence radiation. Thus, all of the optics and sample dewar were enclosed in a light-tight box having a 6 mm entrance aperture; diaphragms were placed along the laser beam path in front of lenses; and quartz lenses were used instead of glass lenses to minimize the fluorescence. Finally, the effects of the broad band fluorescence were suppressed by the use of a high dispersion spectrometer.

For each liquid, the intensity measurements were carried out in two stages. In the low intensity region of the normal
Raman scattering, the light collecting cone was $1.45 \times 10^{-3}$ ster. for $N_2$ and $5.80 \times 10^{-4}$ ster. for $O_2$. Calibrated filters were inserted in front of the spectrometer slit to cover the intensity range. In the high intensity region of stimulated Raman emission the light collecting cone was smaller, being $1.30 \times 10^{-4}$ ster. for both $N_2$ and $O_2$. Again, calibrated filters were used to make intensity measurements over approximately ten orders of magnitude. The laser pulse energy was measured with a calibrated thermopile (TRG 100). The many optical filters used to attenuate the laser and Raman radiation were calibrated spectrophotometrically (Beckman DU) each to an accuracy of 3%. The transmission characteristics of the spectrometer and the sensitivity of the photomultiplier were measured over the required wavelength region (and for light of parallel and perpendicular polarization) using a NBS standard lamp.

An estimate of the possible errors in making absolute intensity measurements of the Raman scattering indicated an accuracy of ±50%, the main source of error arising from the many filters used in attenuating the laser radiation. However, the accuracy of relative intensity measurements was considered to be better than ±30%.
BRIEF RESUME OF THEORY

The theory of stimulated Raman scattering has been developed by many authors, notably, Hellwarth, Bloembergen and Shen, Townes and co-workers and Maker and Terhune. They have shown that the stimulated Stokes emission grows exponentially from noise according to the relation

\[ I_s(t) = I_s(0)e^{+gIL_0} \]  

(1)

Here, \( I_s(t) \) is the intensity of the stimulated Stokes emission, \( I_s(0) \) is the intensity of the normal (spontaneous) Stokes emission, \( I_0 \) is the incident laser power density, and \( L \) is the length of the amplifying medium. The gain \( g \) is given by

\[ g = \frac{2c^2}{\hbar n^2} \frac{N}{\Delta v(v_o - v_R)^3} \frac{d\sigma}{d\Omega} \]  

(2)

In general, and in the present work, \( g \) represents the gain for radiation polarized in the same plane as the incident plane-polarized laser radiation. In Eq. (2), \( c \) is the velocity of light, \( \hbar \) is Planck's constant, \( n \) the refractive index, \( N \) is the effective number of molecules per cm\(^3\), \( \Delta v \) is the normal Raman linewidth, \( v_o - v_R \) is the frequency of the Raman line, and \( d\sigma/d\Omega \) is the total differential cross-section per molecule per ster. for the one polarization.

The total differential cross-section, \( d\sigma/d\Omega \) may be determined from absolute intensity measurements of the normal
Raman scattering. For plane polarized incident light, it is defined as

\[ \frac{d\sigma}{d\Omega} = \frac{2\pi \hbar^4}{c^3} \left( \frac{\hbar}{8\pi^2 v_R} \right) \frac{d}{\mu} \frac{(v_o - v_R)}{1 - \exp(-\hbar v_R/kT)} \cdot K \alpha' \gamma' \left( \frac{1}{4} - \frac{\gamma'^2}{\alpha'^2} \right) \]  

(3)

according to the polarizability theory of Placzek.\(^{21}\)

Here \(v_R\) is the frequency of the Raman-active molecular vibration, \(d\) is the degree of degeneracy of the vibration (\(=1\) for the totally symmetric vibrations), \(\mu\) is the reduced mass, \(k\) and \(T\) are the Boltzmann constant and absolute temperature, and \(\alpha'\) and \(\gamma'\) are, respectively, the isotropic and anisotropic parts of the derivative of the polarizability with respect to the internuclear coordinate at the equilibrium position. The constant \(K\) is the local field correction given by\(^{22}\)

\[ K = \frac{n_s^2 + 2}{n_o^2 + 2} \left( n_s^2 + 2 \right)^2 / 81 \]  

(4)

where \(n_o\) and \(n_s\) are the indices of refraction at the laser and Stokes frequencies, respectively. In order to evaluate \(\gamma'\) and \(\alpha'\) it is necessary to measure the depolarization ratio \(\rho = I_\perp/I_\parallel\)

\[ = \frac{3\gamma'^2}{(45\alpha'^2 + 4\gamma'^2)}. \]  

Here \(I_\perp\) and \(I_\parallel\) are the intensities of scattered light polarized \(\perp\) and \(\parallel\), respectively, to the plane-polarized incident light.

It may be mentioned that Eq. (3) is valid only when the frequency of the incident exciting light is far from the
main absorption bands of O₂ and N₂ which occur in the vacuum ultraviolet region.

EXPERIMENTAL RESULTS AND DISCUSSION

The observed intensity of first-order Stokes radiation over a range of incident laser intensity is shown in Fig. 5 for liquid O₂ and in Fig. 6 for liquid N₂. For both liquids, it was possible to investigate the Raman intensity over a range of approx. 12 orders of magnitude, from the very low intensity of normal scattering through a region of exponential amplification and oscillation to an intensity approaching the incident intensity, and finally saturation. These results will be discussed below under the headings (a) normal Raman scattering, (b) exponential gain, and (c) oscillation and saturation.

(a) Normal Raman Scattering.

The region of normal Raman scattering is one of very low intensity. Our measurements for O₂ and N₂ are given in Fig. 7. Although the data show considerable scatter, it is seen that there is a linear dependence of Raman intensity on incident laser intensity, as expected from theory. The slopes of the graphs of Fig. 7 were used to determine values of the differential scattering cross-section.

As already mentioned the errors in making these
absolute intensity measurements are approx. ±50% whereas the accuracy of the relative measurements is perhaps ±30%. Thus the present method of determining the absolute Raman intensities was checked by measuring the scattering for the 992cm⁻¹ line of liquid benzene and comparing the resultant value of the total differential scattering cross-section dσ/dΩ with values measured by other experimenters. This cross-section is related to experimentally measurable quantities by the equation

\[
\frac{d\sigma}{d\Omega} = \frac{P_R}{P_o} \frac{1}{N\lambda\Omega}
\]

Here, \(P_R\) is the Raman power for the whole line scattered into the solid angle \(\Omega\) and \(P_o\) is the corresponding laser power, \(N\) is the density of molecules per cm³ in the scattering medium and \(\lambda\) is the path length (\(\lambda = 10\) cm in our \(C_6H_6\) experiment). Some of the recent values of \(d\sigma/d\Omega\), for benzene are shown in Table I along with our value of \(6.6 \pm 3 \times 10^{-30}\) cm² per molecule per ster. It is seen that the most accurate values are those obtained by Damen, Leite and Porto with a He-Ne laser and by Skinner and Nilsen with an Ar⁺ laser, which after correction for the \(ν^4\) frequency dependence, are in very good agreement. We have therefore taken the value \(d\sigma/d\Omega = 4.50 \times 10^{-30}\) cm² for benzene (at \(λ = 694.3\) nm) as a basis for our evaluations and have measured the ratio of the Raman intensities of the
2326 cm\(^{-1}\) line for \(N_2\) and 1552 cm\(^{-1}\) line for \(O_2\) relative to the 992 cm\(^{-1}\) for \(C_6H_6\).

The results of these intensity measurements are given in Table II along with measurements of the depolarization ratio \(\rho\) for liquid \(O_2\) and \(N_2\). (We have also included values obtained for liquid \(CS_2\).) The measured values of \(\partial \sigma / \partial \Omega\) and of \(\rho\) were used to calculate values of \(\alpha' = \partial \sigma / \partial \rho\), the rate of change of polarizability with nuclear displacement, from Eq. (3) after applying the local field correction \(K\) (Eq. (4)) and these are included in Table II. The values \(\alpha' = 1.6 \times 10^{-16}\) cm\(^2\) and \(1.35 \times 10^{-16}\) cm\(^2\) for liquid \(N_2\) and \(O_2\), respectively, are the same as the values obtained for gaseous \(N_2\) and \(O_2\) by Stansbury, Crawford and Welsh. Our measured value of \(\rho\) for liquid \(N_2\) agrees with that measured in the gas by Cabannes and Rousset, but our value of \(\rho\) for \(O_2\) is considerably lower than theirs.

(b) Exponential gain.

Under the present experimental conditions, the region of normal Raman scattering appears to hold up to incident laser powers of \(\sim 70\) KW. At higher laser powers, both liquids exhibit regions of exponential gain, as shown by the linear portions of the graphs (plotted on semilog scales) in Figs. 5 and 6. For \(N_2\) this region extends over a range of three orders of magnitude and for \(O_2\), four orders of magnitude of Stokes amplification. These results represent stable regions of gain up to factors of at least \(e^6\) and \(e^8\) for liquid \(N_2\) and \(O_2\) respectively.

Values of the gain, \(g\) (exp), were obtained from the slopes
of the linear portions of the intensity curves (Figs. 5 and 6). These are given in Table III. Also listed for comparison are calculated values of the gain, \( g(\text{calc.}) \). The calculated values are based on the scattering cross-section \( \frac{d\sigma}{d\Omega} \) evaluated here and on the linewidths 0.067 cm\(^{-1}\) for \( N_2 \) and 0.117 cm\(^{-1}\) for \( O_2 \) measured by Clements and Stoicheff\(^{15} \), making use of Eq. (2). It is seen that the values \( g(\text{exp.}) \) and \( g(\text{calc}) \) are in good agreement.

(c) Oscillation and Saturation.

For both liquids, the regions of exponential gain are abruptly terminated as shown by the discontinuity in slope of the Stokes intensity curves, Figs. 5 and 6. These sharp changes in slope represent the onset of Raman oscillation with a rapid rise in output power. The oscillation threshold for \( N_2 \) occurs at somewhat lower laser power than for \( O_2 \), 0.13 MW compared with 0.16 MW for \( O_2 \). These values were not significantly affected by tilting the dewar with respect to the incident laser beam or by the presence of ice particles in the liquids (although in the latter case the experimental error was greatly increased). The onset of oscillation is therefore not considered to arise from reflection at the windows or from scattering by bubbles or dust or ice particles. Also, we have experimentally ruled out the possibility that the rapid rise in output power is caused by self-focusing. Near-field photographs of the laser and Stokes
radiation at the exit window show no evidence of filament forma-
tion and uniform Stokes emission over the beam cross-section 
(Fig: 3b). No filaments were observed up to the highest laser 
power used, 1 MW, where the self-focusing length is calculated 
to be 5 cm for O₂ and 9 cm for N₂. The critical power for self-
focusing calculated from the known Kerr constants is 200 kW 
for O₂ and 600 kW for N₂. The observed onset of oscillation occurs 
at lower laser powers as mentioned above. Moreover, the ratio of 
laser power at threshold of oscillation in O₂ to that in N₂ was 
measured to be 1.20 ± 0.006 as compared with the ratio of 0.3 for 
the respective critical powers for self-focusing.

We believe that the most likely cause of oscillation is 
feedback of Stokes radiation scattered in the backward direction 
by Rayleigh scattering. This is suggested by the high Raman gain 
for these liquids and by the ratio of 1.2 for the gain constants 
of O₂ and N₂, which is the same value as the ratio of laser power 
for oscillation. The Rayleigh scattering intensity determined by 
Stansbury, Crawford and Welsh for gaseous O₂ and N₂ together with 
the local field factor for the liquids leads to a feedback factor 
of \( \frac{\partial \sigma}{\partial \Omega} \) (Rayleigh) = 6.1 x 10⁻⁶ per cm per unit solid angle for 
liquid N₂ and 6.6 x 10⁻⁶ units for O₂. For the effective solid 
angle of our experiments (~10⁻⁴ ster.) the feedback factor is 
approx. 10⁻⁹ per cm, which is sufficient to explain the onset of 
oscillation.
In the region of oscillation the rise in Stokes intensity is very steep and represents an increase of five orders of magnitude for liquid $O_2$ and seven orders of magnitude for liquid $N_2$. The uppermost portions of the intensity curves (Figs. 5 and 6) are similar and indicate strong depletion of laser radiation and conversion to Stokes radiation. The oscilloscope trace in Fig. 2b shows a typical pulse of Stokes radiation in this region with the corresponding laser pulse severely distorted. This process results in the flat tops of the intensity curves and is the region of saturation. At still higher incident laser powers, the first-order Stokes radiation is converted to second-order Stokes (and anti-Stokes radiation) which results in depletion of the first-order Stokes intensity. This depletion is shown in the oscilloscope trace of Fig. 2c.

A brief study of the conversion of laser radiation to first-order Stokes radiation for liquid $N_2$ was carried out and the results are presented in Fig. 8. Here is plotted the ratio $P_{out}/P_{in}$, normalized for the laser radiation. The general behaviour of this ratio is in good agreement with the theory of Shen and Bloembergen. Fig. 8 shows high conversion of approx. 75% laser radiation to first-order Stokes radiation in the saturation region.
CONCLUSION

This experiment has shown that liquid $N_2$ and $O_2$ are important materials for the study of stimulated Raman scattering. Because of their high Raman gain the stimulated Raman effect emerges as the dominant nonlinear process in these liquids. Thus it was possible to investigate the intensity characteristics and build-up of Stokes radiation over a range of 12 orders of magnitude, from the low intensity normal scattering through exponential amplification, oscillation and saturation and eventual depletion. A detailed study of the region of normal scattering and exponential gain shows very good agreement with theory. The regions of higher intensity also reveal the expected theoretical behaviour and warrant closer study. Finally, the high conversion efficiency of laser to Raman Stokes radiation indicates that these liquids are very useful as new frequency sources.

We are very grateful to Dr. Fujio Shimizu for many helpful discussions.
Footnotes and References

*This research is part of Project DEFENDER under the joint sponsorship of the Advanced Research Projects Agency, the U.S. Office of Naval Research, and the Department of Defense. Also supported by the National Research Council, Canada, and the University of Toronto.

†On leave from Laboratoire de Spectroscopie, Université de Strasbourg, France.

‡Holder of Province of Ontario Government Scholarships 1965-68.


Table I

Values of the total differential scattering cross-section for the 992 cm$^{-1}$ Raman radiation of liquid benzene.

<table>
<thead>
<tr>
<th>Authors</th>
<th>$(\frac{d\sigma}{d\Omega}) \times 10^{-30}$</th>
<th>$(\frac{d\sigma}{d\Omega}) \times 10^{-30}$ corrected for 6943 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Damen, Leite, Porto$^{23}$</td>
<td>6.7±1.2</td>
<td>4.5$^a$</td>
</tr>
<tr>
<td>Skinner and Nilsen$^{24}$</td>
<td>37.5±4</td>
<td>4.95$^b$</td>
</tr>
<tr>
<td>McClung and Weiner$^{22}$</td>
<td>5.9±3</td>
<td>5.9</td>
</tr>
<tr>
<td>Bret et al$^2$</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>Present authors</td>
<td>6.6±3</td>
<td>6.6</td>
</tr>
</tbody>
</table>

$^a$ Calculated from $I_a(v-v')^b$, since the frequency of the exciting radiation, $v$, is far from principal absorption frequencies. The Raman vibrational frequency is $v'_v$.

$^b$ Calculated from $I_a(v-v'_v)/((v_a-v)^2$, since the frequency of the exciting radiation is near an absorption frequency, $v_a$. 


### Table II

Values of the total differential cross-section, derivative of the polarizability and depolarization ratio.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>$v_v$ (cm$^{-1}$)</th>
<th>$(\frac{d\sigma}{d\Omega})_{\text{Liquid}}$ C$_6$H$_6$</th>
<th>$(\frac{d\sigma}{d\Omega})_{\text{Liquid}} C_6H_6 \times 10^{30}$ cm$^2$ sr$^{-1}$</th>
<th>$a' \times 10^{16}$ cm$^2$</th>
<th>$\rho$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$</td>
<td>1552.0</td>
<td>0.056 ± 0.017</td>
<td>0.250 ± 0.075</td>
<td>1.35</td>
<td>0.11 ± 0.01</td>
</tr>
<tr>
<td>H$_2$</td>
<td>2326.5</td>
<td>0.041 ± 0.012</td>
<td>0.185 ± 0.055</td>
<td>1.60</td>
<td>0.10 ± 0.01</td>
</tr>
<tr>
<td>C$_6$H$_6$</td>
<td>992.2</td>
<td>1.00</td>
<td>4.5$^a$</td>
<td>2.84</td>
<td>-</td>
</tr>
<tr>
<td>CS$_2$</td>
<td>655.6</td>
<td>2.03 ± 0.60</td>
<td>9.1 ± 2.7</td>
<td>2.91</td>
<td>0.17 ± 0.02</td>
</tr>
</tbody>
</table>

$^a$ Value of Damen, Leite, Porto$^{23}$ corrected for 6943$^D$ radiation

$^b$ Values given by Stansbury, Crawford, Welsh$^{25}$ for gaseous O$_2$, H$_2$
Table III.

Values of the Raman gain

<table>
<thead>
<tr>
<th>Liquid</th>
<th>(ρdν/dω)10^8 cm(^{-1})sr(^{-1})</th>
<th>Δν(^a) cm(^{-1})</th>
<th>g(calc)10^2 cmMW(^{-1})</th>
<th>g(exp)10^2 cmMW(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(_2)</td>
<td>0.45±0.14</td>
<td>0.117</td>
<td>1.45±0.4</td>
<td>1.60±0.50</td>
</tr>
<tr>
<td>N(_2)</td>
<td>0.29±0.09</td>
<td>0.067</td>
<td>1.70±0.5</td>
<td>1.60±0.55</td>
</tr>
<tr>
<td>C(_6)H(_6)</td>
<td>3.06</td>
<td>2.15</td>
<td>0.28</td>
<td>-</td>
</tr>
<tr>
<td>CS(_2)</td>
<td>7.55</td>
<td>0.50</td>
<td>2.4</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\) Values of linewidths measured by Clements and Stoicheff.\(^1\)
Figure Captions

Fig. 1. Stimulated Raman spectra of liquid $O_2$ and $N_2$ showing the first-order Stokes vibrational lines at 1552.0 and 2326.5 cm$^{-1}$ respectively. The resolving power of the grating spectrograph is $10^5$.

Fig. 2. (a) Typical laser pulse monitored with an ITT FWlll4A photodiode and displayed on a Tektronix 519 oscilloscope. (b) Typical first-order Stokes pulse obtained in the saturation region, and the corresponding depleted laser pulse at the right. (c) Same as (b) but with the Stokes pulse also showing some depletion at higher laser power.

Fig. 3. Near-field patterns showing the spatial intensity distribution of the incident laser beam (a) and the first Stokes emission (b), magnified 20X. Mottled appearance of Stokes picture caused by laser attenuating filters.

Fig. 4. Diagram of apparatus used for Raman intensity measurements. Explanation of symbols D-diaphragm, A.F. - attenuating filter, G.G.-ground glass, P.D. - E.G. & G photodiode (SGD-100), L-lens, F-filter.

Fig. 5. Experimental curve for liquid oxygen showing Raman Stokes power as a function of incident ruby laser power.
Fig. 6. Experimental curve for liquid nitrogen showing Raman Stokes output power as a function of incident ruby laser power.

Fig. 7. Experimental measurements of normal Raman scattering for liquids, benzene, oxygen and nitrogen.
(Experimental scatter results from very low light levels used, necessitating a high amplification of the photomultiplier signal.)

Fig. 8. Experimental curves showing how the ratios of the laser power \( P_L \) and the first Stokes power \( P_S \) at the exit of the dewar, to the incident laser power \( P_{LO} \), vary with the incident laser power. The dashed curve in the depleted laser region is only approximate as the laser pulse was severely distorted.
FIG. 1.

FIG. 2.

1552.0 cm\(^{-1}\)

2326.5 cm\(^{-1}\)

FIG. 3.
$C_6H_6$

$O_2$

$N_2$

STOKES RAMAN INTENSITY (arbitrary units)

LASER POWER (arbitrary units)
In liquid O₂ and N₂ the threshold for stimulated Raman emission is found to be much lower than for other nonlinear processes. Thus it is possible to make reliable measurements of the intensity of Raman emission over a large range of incident laser power by using a simple longitudinal geometry. Several distinct regions of emission were investigated, including normal Raman scattering, exponential gain, onset of oscillation and saturation. There is good agreement with theory.
Raman Intensity and Gain
Stimulated Raman Emission in O<sub>2</sub> and N<sub>2</sub>
Raman conversion efficiency in liquid N<sub>2</sub>

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (corporate author) issuing the report.

2a. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Hacking is to be in accordance with appropriate security regulations.

2b. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is on absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year, e.g., March 14, 1973. If more than one date appears on the report, use date of publication.

7a. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8a. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b. E. & S. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system number, task number, etc.

9a. ORIGINATOR'S REPORT NUMBER(s): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. OTHER REPORT NUMBERS: If the report has been assigned any other report numbers (other than the originator's number), also enter this next number.

10. AVAILABLE DATATYPES NOTICES: Enter any limitation notices on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

   (1) "Qualified requesters may obtain copies of this report from DDC."

   (2) "Foreign government and dissemination of this report by DDC is unauthorized."

   (3) "All reports issued from this report directly from DDC. Other qualified DDC users shall request through"

   (4) "Qualified DDC users shall request through"

   (5) "All distribution of this report is controlled. Qualified DDC users shall request through"

   (6) "U.S. Government agencies may obtain copies of this report directly from DDC. Other qualified users shall request through"

   (7) "U.S. Government agencies may obtain copies of this report through DDC. Other qualified users shall request through"

   (8) "U.S. Government agencies may obtain copies of this report through DDC. Other qualified users shall request through"

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SUPPORTING MILITARY ACTIVITY: Enter the name of the supporting military project office or laboratory sponsoring (paying for) the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 140 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, are not acceptable, nor project code names, program location, may be used as key words but will be followed by an indication of technical context. The assignment of labels, rules, and weights is optional.