

# MOLECULAR SPECTROSCOPY WITH OPTICAL MASERS†

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## INTRODUCTION

In the five years since optical maser emission was first suggested in the classic paper of Schawlow and Townes<sup>1</sup>, and achieved by Maiman<sup>2</sup>, there have been many new developments of potentially great importance to molecular spectroscopy. Stimulated radiation with its characteristically high intensity, monochromaticity and directionality is now available at several hundred different wavelengths from the far infrared to the near ultraviolet. Such radiation is produced continuously or in short pulses from excited atoms, ions and molecules. The various sources themselves are of considerable spectroscopic interest and their use in a wide variety of preliminary investigations has already underlined their advantages and possibilities in molecular spectroscopy. These investigations have embraced many areas in classical spectroscopy and have led to the discovery of new effects made possible by the remarkable properties of stimulated radiation.

It is the purpose of this paper to briefly review these recent developments and achievements.

## OPTICAL MASER SOURCES

Up to the present time, the most useful sources of stimulated radiation for spectroscopic applications have been the He—Ne gas maser<sup>3,4</sup> and the ruby pulsed maser<sup>2,5</sup>. The He—Ne maser is a gas discharge operating continuously, with intense emission at 6328 Å, 1.15 μ and 3.39 μ. The 6328 Å radiation has been used in various experiments on light scattering, and the infrared radiation in absorption studies. Typical values of output power are in the range of a few milliwatt, although up to one watt output of 6328 Å radiation has been achieved. The “giant pulse” ruby maser<sup>5</sup> is an extremely powerful source of radiation at 6940 Å. A typical power output is 10<sup>6</sup> watt in a pulse of 10<sup>-8</sup> sec. duration. The availability of such high powers has led to the rapid development of the new field of “nonlinear optics” which is of considerable interest in molecular spectroscopy.

Many other sources of stimulated radiation in the wavelength range of 373 μ to 2300 Å are presently available. Discharges of the rare gases, notably mixtures of He—Ne have produced radiation<sup>4</sup> at several hundred different wavelengths from 1 μ to 133 μ. These operate continuously with powers of a few milliwatt at 1 μ, and with steadily decreasing power to about 10<sup>-9</sup> watt at 133 μ. The electronic transitions  $2s\ ^1\Sigma_g^+ \rightarrow 2p\ ^1\Sigma_u^+$  in H<sub>2</sub>, HD and D<sub>2</sub> produce<sup>6,7</sup> radiation in the region 0.8 to 16 μ. In N<sub>2</sub> emission<sup>6</sup> from

† Supported in part by a research grant from the National Research Council, Ottawa, Canada.

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2.6 to 8.2  $\mu$  represents the first observation of a  ${}^1\Pi \rightarrow {}^1\Sigma^-$  transition in a homonuclear molecule. In NO, emission<sup>8</sup> is induced in the transition  $B^1\Delta \rightarrow C^2\Pi$  with population inversion being achieved because of a weakly predissociating lower state. Rotation vibrational transitions in HCl<sup>9</sup>, produced in a highly excited vibrational level by flash photolysis of a mixture of H<sub>2</sub> and Cl<sub>2</sub> provide stimulated emission at 3.7  $\mu$ . Such transitions in gas discharges of CO<sup>10</sup>, CO<sub>2</sub><sup>11</sup> and N<sub>2</sub>O<sup>12</sup> have also produced emission in the near infrared. Very powerful emission (up to 16 watts) at 10.6  $\mu$  has recently been produced continuously in a discharge with a mixture of CO<sub>2</sub> and N<sub>2</sub><sup>13,14</sup>; the CO<sub>2</sub> molecules are selectively excited to the 00<sup>0</sup>1 vibrational level by collisions with N<sub>2</sub> molecules in their long-lived ( $v = 1$ ) level of nearly the same energy, and give rise to intense emission in making the transition 00<sup>0</sup>1  $\rightarrow$  10<sup>0</sup>0. A similar process in a mixture of N<sub>2</sub>O and N<sub>2</sub><sup>15</sup> produces stimulated radiation at 10.9  $\mu$ .

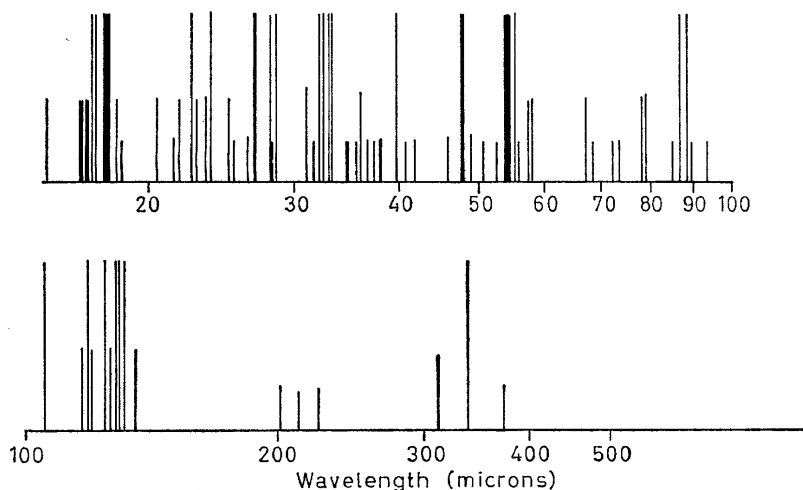


Figure 1. Wavelengths at which maser radiation is presently available in the far infrared (after C. G. B. Garrett<sup>16</sup>)

The many wavelengths in the far infrared region<sup>16</sup> at which stimulated emission has been observed are given in Figure 1. Most of these emissions have been obtained with pulsed discharges in molecular gases yielding peak powers of several watts. For example, radiation from 16  $\mu$  to 121  $\mu$  has been obtained with a discharge in H<sub>2</sub>O<sup>17-19</sup>; radiation from 33  $\mu$  to 108  $\mu$  using D<sub>2</sub>O<sup>18</sup>; from 21  $\mu$  to 32  $\mu$  using NH<sub>3</sub><sup>20</sup>; at 337  $\mu$  using HCN or CH<sub>3</sub>CN<sup>21</sup>; and from 126  $\mu$  to 373  $\mu$  using dimethylamine<sup>22</sup>. One of the outstanding problems with these molecular masers is the identification of the emitting species (atom, ion, molecule or free radical) and the assignment of the observed transitions. With the possible exception of the emission at 337  $\mu$ , suggested to be due to CN<sup>23</sup>, and that at 78  $\mu$  which is very close to a known emission line in OH<sup>19</sup>, all of the above emissions have escaped recognition so far.

The most prolific sources of stimulated emission in the visible and near ultraviolet region are high current-density discharges of the rare gases and Hg, O, N and C, the emitting species being ions of these elements<sup>24,25</sup>. The most intense emission is due to Ar<sup>+</sup> and occurs at 4880 Å. A continuous power output of about 20 watt has already been achieved. The only molecular sources of stimulated radiation in the visible region are pulsed discharges in CO<sup>26</sup> (with emission in the Angstrom and Herzberg bands) and in N<sub>2</sub><sup>27</sup> (with emission in the extensive first- and second-positive systems).

In addition to the ruby maser, many other solid state sources<sup>28</sup> have been developed with emission in the ultraviolet, visible and near infrared regions. They make use of the intense fluorescence of rare earth ions in various host crystals, in glasses and in chelates. Many different types of semiconductor junctions masers are also available and various "chemical masers" have been suggested<sup>29</sup>.

## APPLICATIONS TO SPECTROSCOPY

This review of present accomplishments is divided into two main parts. In the first part, "Classical Spectroscopy" are included experiments in fluorescence, flame emission, infrared absorption and Rayleigh, Raman and Brillouin scattering. In the second part, entitled "New Effects and Non-linear Optics" are included those experiments which only became possible once optical maser sources of high power were available. Here are included multiple photon absorption, stimulated Raman and Brillouin scattering, induced absorption at optical frequencies and nonlinear scattering. In 1961 Townes<sup>30</sup> discussed the possible applications of optical masers to some of these experiments and in 1962 Stoicheff<sup>31</sup> presented preliminary results obtained with the ruby maser and briefly summarized some of the potentialities and difficulties. More recent reviews are given in the books "Optical Masers" by Birnbaum<sup>28</sup> and "Nonlinear Optics" by Bloembergen<sup>32</sup>.

### Classical Spectroscopy

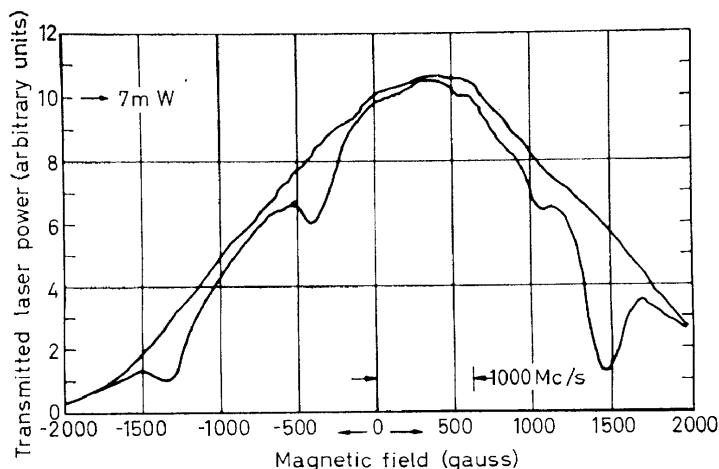
*Fluorescence.* Ruby maser radiation at 6940 Å has been used to excite intense fluorescence in crystals of Sm<sup>2+</sup>:CaF<sub>2</sub>, Tm<sup>3+</sup>:CaF<sub>2</sub>, Tm<sup>3+</sup>:LaCl<sub>3</sub>, Nd<sup>3+</sup>:LaCl<sub>3</sub> and Nd<sup>3+</sup>:LaBr<sub>3</sub> (Singh and Stoicheff<sup>33</sup>). Most of the fluorescence appeared at longer wavelengths, but with the Nd<sup>3+</sup> ions intense fluorescence at shorter wavelengths, down to 3580 Å, was observed. This was explained by step-wise excitation with two photon absorption. Lifetimes of some of the emitting states were measured from the fluorescence decay and found to be approximately  $50 \times 10^{-6}$  sec. Much shorter times,  $\sim 10^{-8}$  sec, can now be measured with the development of the giant pulse masers<sup>5</sup>. A novel method using phase shift techniques has been described by Carbone and Longaker<sup>34</sup> to measure lifetimes as short as  $10^{-11}$  sec using continuously operating masers. As is well known, observations of fluorescence in the infrared region are rare and it is here that maser sources may be of great importance. Recently, Gerritsen<sup>35</sup> has excited fluorescence in CH<sub>4</sub> with 3.39 μ radiation from the He—Ne maser, the observed intensity corresponding to  $10^{-8}$  of the incident photons.

*Flames.* High temperatures ( $\sim 10^4$  °K) are easily reached when high

powered maser beams are focused on the surfaces of materials which absorb this radiation. The surface erupts with the emission of hot particles which ignite in the surrounding gas, forming various atomic, molecular, and free radical species in excited states. Spectra of  $C_2$ , CN and  $BO_2$  have been obtained in this way (Stoicheff<sup>31</sup>). More detailed studies of the spectra of  $C_2$  and CN by Howe<sup>36</sup> have yielded values of the rotational and vibrational temperatures. Lifetimes of the  $v = 1, 2, 3$  levels of the  $A^2\Pi$  electronic state of  $C_2$  have also been measured and Jeunhomme and Schwenker<sup>37</sup> have determined the oscillator strength of the (0, 0) band of the  $A^3\Pi_g \rightarrow X^3\Pi_u$  system.

*Infrared Absorption.* While stimulated emission at many different wavelengths in the infrared region is presently available<sup>16</sup>, the outstanding requirement is the development of a source whose frequency is continuously variable (or tunable) over a range of several wavenumber units. At present, the extent of such variation is approximately  $1\text{ cm}^{-1}$  and is achieved by the Zeeman effect with the maser itself placed in a variable magnetic field. In spite of this limitation several important exploratory experiments have been carried out using the  $1.15\ \mu$  and  $3.39\ \mu$  radiation from a He—Ne maser. Gerritsen and Ahmed<sup>38</sup> have tuned  $3.39\ \mu$  maser radiation through two components of the P(7) line in the  $\nu_3$  band of  $CH_4$  and have studied the line broadening by various gases up to 50 mm pressure. From the broadening they have determined absolute optical collision diameters in methane. Edwards and Burch<sup>39</sup> have extended the pressure broadening of  $CH_4$  by  $N_2$  up to pressures of 5 atm. More recently, Gerritsen<sup>35</sup> has observed absorption in  $C_2H_6$  and  $CH_3F$  at pressures of a few mm and path lengths of 15 cm. A spectrum of  $CH_3F$  is shown in *Figure 2*.

A similar spectrometer of high sensitivity has been developed by Feld *et al.*<sup>40</sup>. By using Stark modulation they have detected absorption in  $CH_4$ ,  $CH_3Cl$  and  $CH_3OH$  at  $3.39\ \mu$  at pressures as low as a few microns. They are attempting to shift the molecular levels by means of the Stark effect and in



*Figure 2.* Tuned-maser spectrogram of absorption in  $CH_3F$  at  $3.39\ \mu$ . Upper trace—empty cell; Lower trace with 4 mm pressure of  $CH_3F$  and path length 15.5 cm (after H. J. Gerritsen<sup>35</sup>)

this way will be able to determine dipole moments of molecules in vibrationally excited levels. One of the difficulties encountered in this work so far is the problem of line identification.

Recently, Javan and coworkers<sup>41</sup> have described an elegant method of extremely high resolution absorption spectroscopy which overcomes the limitations of Doppler broadening and for the first time appears to make full use of the high monochromaticity of a stable maser.

*Rayleigh Scattering.* The emission of intense and monochromatic radiation (usually linearly polarized) in a well-collimated beam make the optical maser an ideal source for light scattering experiments. Several exploratory investigations of Rayleigh scattering have been carried out using the 6328 Å line of the He—Ne maser. Amongst these may be mentioned a study of the state of polarization of Rayleigh scattering in gases by Bridge and Buckingham<sup>42</sup>, and in liquids by Leite *et al.*<sup>43</sup>. The angular dependence of the scattered intensity in liquid benzene, toluene and carbon tetrachloride has been shown to follow the expected  $1 + \cos^2 \phi$  relation by Leite *et al.*<sup>44</sup>. The Doppler-broadened profile of the Rayleigh line of hydrogen and argon at one atmosphere pressure has been measured by May *et al.*<sup>45</sup>, and diffusion broadening ( $\sim 100$  c/s) in a dilute solution of polystyrene molecules has been reported by Cummins *et al.*<sup>46</sup>, who used optical heterodyne detection with an effective resolving power of approximately  $7 \times 10^{13}$ .

*Raman Scattering.* Preliminary studies of normal Raman scattering excited with the ruby pulsed maser by Porto and Wood<sup>47</sup> and Stoicheff<sup>31</sup>, revealed many difficulties with this new source. However, the subsequent successful use of the He—Ne maser in a variety of experiments with gases, liquids and solids has shown that the maser is indeed an important new exciting source for Raman spectroscopy. Leite and Porto<sup>48</sup>, and Koningstein and Smith<sup>49</sup>, have reported on the continuous photoelectric recording of the Raman spectra of liquid CS<sub>2</sub>, CCl<sub>4</sub> and C<sub>6</sub>H<sub>6</sub> with the sample cell placed in the maser cavity, and external to the maser. Although their observed spectra are somewhat inferior to those obtained by conventional methods it is well to recognize that such measurements allow for precise determination of absolute scattering intensities and cross-sections. The investigation of the angular dependence of the Raman scattering from liquid C<sub>6</sub>H<sub>6</sub> by Damen *et al.*<sup>50</sup> is of especial interest. Their measurements have confirmed Placzek's theoretical predictions for vibrations of A<sub>1g</sub> and E<sub>2g</sub> symmetry: For A<sub>1g</sub> symmetry, the intensity distribution is constant with angle of observation when the incident electric field vector is perpendicular to the plane of observation, and varies as  $\cos^2 \phi$  when the electric vector is parallel to the plane of observation: For E<sub>2g</sub> symmetry, the respective distributions are constant or vary as  $1 + \cos^2 \phi/6$ . This characteristic dependence of intensity on scattering angle should be a useful addition to depolarization and band contour studies for the identification of vibrational symmetries.

Two reports on the Raman spectra of crystals are also of considerable interest. Hobden and Russell<sup>51</sup> have photographed the first- and second-order spectra of gallium phosphide (a III-V semiconductor), for the first time. Also, Russell<sup>52</sup> has observed the first-order scattering from silicon by focusing the maser radiation on the surface of this absorbing crystal and analyzing the back-scattered radiation.

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It is evident that high resolution Raman spectroscopy will also benefit from the use of maser sources. With conventional techniques, the effective resolution is limited to approximately  $0.3 \text{ cm}^{-1}$  by the width of the mercury exciting lines. The width of the  $6328 \text{ \AA}$  line of the He—Ne maser is considerably narrower, the maximum width being  $\sim 0.05 \text{ cm}^{-1}$ . This value may represent a practical limit of resolution since Doppler widths and the effective resolution available with the best spectrographs approach this value. It may be mentioned here that, in principle, even higher resolution is possible since first-order Doppler broadening is not effective in scattering in the forward direction<sup>30</sup>. Weber and Porto<sup>58</sup> have successfully photographed the pure rotational spectrum of methyl acetylene at high resolution, with a reciprocal linear dispersion of  $2 \text{ cm}^{-1}/\text{mm}$ . A small volume of gas ( $\sim 1 \text{ cm}^3$ ) at  $1/2 \text{ atm}$ . pressure contained in a cell with Brewster angle windows was placed within the cavity of a He—Ne maser, where the power was approximately 2 watt. The exposure time was 58 hr: a direct comparison showed this to be about ten times the length of exposure necessary to photograph the same spectrum with the Hg 4358 line and conventional techniques. Further developments in cell geometry as well as in optical masers should soon overcome this unfavourable intensity ratio.

*Brillouin Scattering.* The Brillouin spectrum arises from the scattering of monochromatic light by the periodic fluctuations of refractive index produced by thermally excited sound waves existing in the scattering medium (usually a liquid or solid). The resulting line spectrum is a closely spaced triplet (in liquids) consisting of a central component with the same frequency as the incident light and two Brillouin components (or Doppler components) of changed frequency, one on either side of the central line. Their frequency separation from the central line is given by  $\Delta\nu = \pm 2\nu_0 n (V/c) \sin \phi/2$ . Here  $\nu_0$  is the frequency of the incident light,  $n$  the refractive index at  $\nu_0$ ,  $V$  is the velocity of the thermal (or acoustic) waves of frequency  $\Delta\nu$  in the medium,  $c$  the velocity of light and  $\phi$  is the scattering angle. According to this equation, if  $\nu_0$  is monochromatic and  $\phi$  well-defined, accurate values of  $\Delta\nu$  can be obtained and hence precise values of the acoustic velocity  $V$ . Also, if  $\nu_0$  is

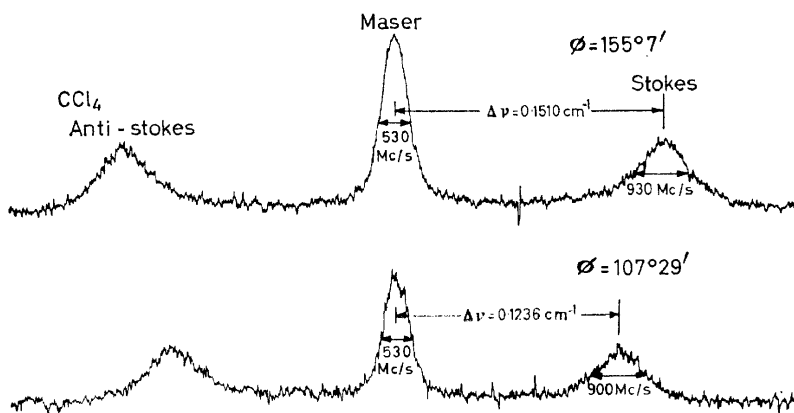


Figure 3. Brillouin spectra of liquid  $\text{CCl}_4$  at two different scattering angles (after Gornall *et al.*<sup>59</sup>)

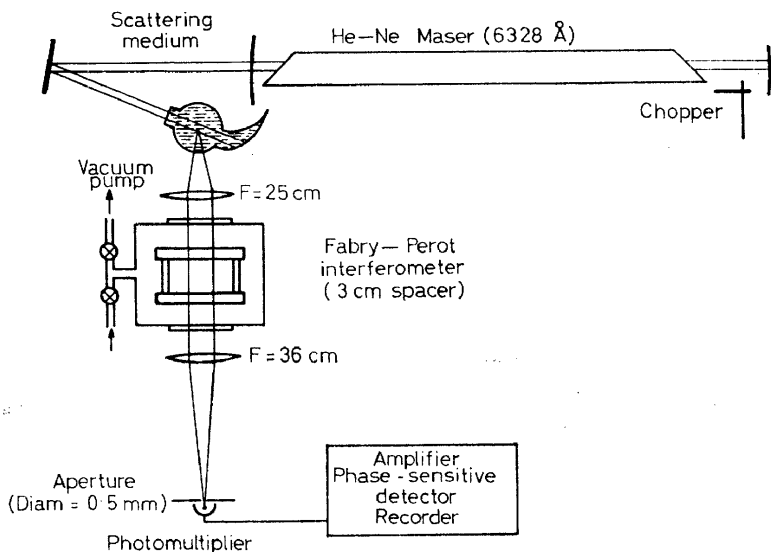


Figure 4. Experimental arrangement for high resolution Brillouin spectroscopy

sufficiently sharp the Brillouin line width can be measured and hence the decay time involved in the absorption processes. By varying the scattering angle  $\phi$ , the velocity dispersion and absorption can be studied over a reasonably wide range of frequencies  $\sim 10^9$  to  $10^{10}$  c/s, thus extending the range of acoustical spectroscopy.

The optical maser is of course, ideally suited to such investigations in liquids and in solids. Mash *et al.*<sup>54</sup>, have photographed the Brillouin spectra of  $\text{CCl}_4$  and  $\text{C}_6\text{H}_6$  using a Fabry-Perot etalon. Benedek *et al.*<sup>55</sup> have observed the spectra of various liquids and solids using a grating and photoelectric recording. Chiao and Stoicheff<sup>56</sup> have used a pressure scanning Fabry-Perot spectrometer to record the spectra of several liquids and have demonstrated line broadening in the Brillouin spectrum. Shortly after these initial reports, investigations of the depolarization ratio in liquid  $\text{C}_6\text{H}_6$  and of the intensity ratios of the Brillouin components to the central line were published by Cummins and Gammon<sup>57</sup>, and Rank *et al.*<sup>58</sup>, respectively. Typical Brillouin spectra of  $\text{CCl}_4$  are shown in Figure 3 and an experimental arrangement in Figure 4<sup>59</sup>.

### New Effects and Nonlinear Optics

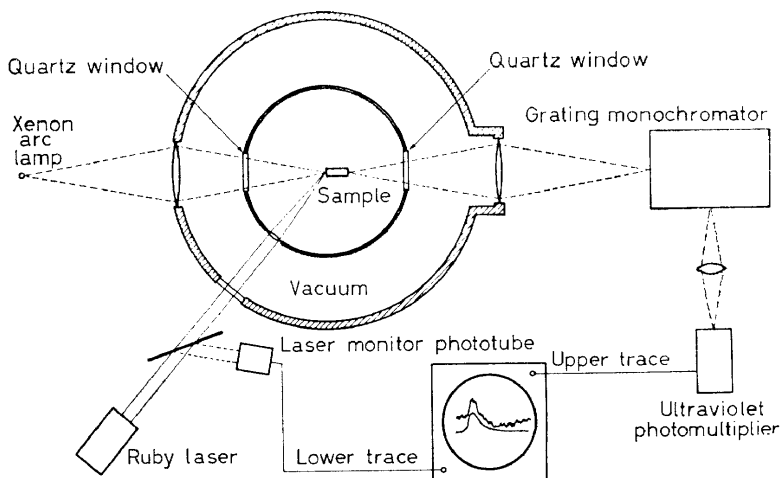
*Multiple Photon Absorption.* Two-photon absorption was observed by Kaiser and Garrett<sup>60</sup> with a crystal of  $\text{Eu}^{2+}:\text{CaF}_2$ . In this crystal, the lowest excited state is known to be  $22,000\text{ cm}^{-1}$  above the ground state and cannot be reached with ruby radiation of  $14,400\text{ cm}^{-1}$ . However, with ruby radiation incident on this crystal fluorescence at  $4200\text{ \AA}$  was observed and its intensity was found to depend on the square of the incident red light. All of these observations point to the excitation of a real state of the  $\text{Eu}^{2+}$  ion at  $\nu = 2 \times 14,400\text{ cm}^{-1}$  by a two-photon process. This is followed by a radiationless transition to the state at  $\nu = 22,000\text{ cm}^{-1}$  and finally by a

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transition to the ground state with emission of 4200 Å radiation which conveniently served to detect the two-photon process. A similar double-photon absorption process followed by fluorescence was reported by Abella<sup>61</sup> in cesium vapour. Here it was possible to identify the excited level and thus to establish that the initial and final states had the same parity, as expected for a two-photon process.

Double-photon excitation of fluorescence in various organic powders was reported by Peticolas *et al.*<sup>62</sup> and in anthracene crystals by Singh and Stoicheff<sup>63</sup>. The latter suggested that an electronic level of the same parity as the ground state,  $^1A_g$  or  $^1B_g$ , must occur in the neighbourhood of 28,800  $\text{cm}^{-1}$  in anthracene. Further discussions on this point are included in the papers of Singh *et al.*<sup>64</sup> and Warlock<sup>65</sup>. Kepler *et al.*<sup>66</sup>, detected delayed fluorescence in anthracene several milliseconds after the maser pulse ended. They explained their results by assuming that the singlet state giving rise to the fluorescence is produced by bimolecular annihilation of triplet excitons generated directly by the ruby maser radiation. Detailed experimental studies by Singh *et al.*<sup>64</sup>, have helped to clarify the characteristics and processes of both the short-lived and delayed fluorescence in anthracene. Quantitative measurements of double-photon absorption in various liquids and solids of polycyclic benzene ring compounds have been made by McMahon *et al.*<sup>67</sup>.

In the above experiments, the absorbed quanta have both been obtained from narrow-band sources, either from the ruby maser itself or from harmonics<sup>64</sup> or from stimulated Raman scattering<sup>64</sup> generated by the ruby maser. A more versatile technique described by Hopfield *et al.*<sup>68</sup> makes use of a continuous source in addition to the maser and thus permits the investigation of a broad spectral region. Their method is shown in *Figure 5*. When two-quantum absorption occurs, that is one photon from the maser and the other from the ultraviolet continuum, a decrease in the ultraviolet trans-



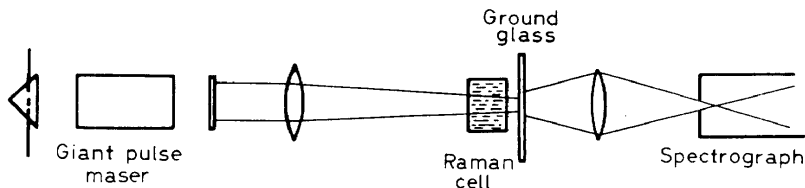
*Figure 5.* Experimental arrangement for two-photon absorption spectroscopy using a monochromatic source (ruby maser) together with a continuum from a xenon arc lamp (after Hopfield *et al.*<sup>68</sup>)



mission proportional to the maser intensity is observed. Absorption in a broad region ( $46,000$  to  $54,000\text{ cm}^{-1}$ ) was measured in a crystal of KI with this technique. In principle, two-photon spectroscopy will be a useful complement to ordinary one-photon spectroscopy since it will give information on energy levels which are not accessible to electric dipole radiation.

Three-photon absorption in crystalline naphthalene has been reported by Singh and Bradley<sup>69</sup>. With intense ruby maser radiation ( $14,400\text{ cm}^{-1}$ ) incident on the sample, ultraviolet fluorescence in the region  $3000\text{ \AA}$  was detected and its intensity was found to vary as the third power of the incident intensity, as expected, for a three-photon process. The selection rule is the same as for electric dipole radiation.

*Stimulated Raman Scattering.* Stimulated Raman emission excited by extremely intense ruby maser radiation was first reported by Eckhardt *et al.*<sup>70</sup>. Their investigations with a variety of organic liquids showed that this emission possessed many of the properties characteristic of stimulated radiation, namely, a marked appearance threshold, extremely high intensity (up to 10% of the incident radiation), spectral line narrowing and beam collimation. The spectrum revealed that this radiation was displaced from the ruby line at frequencies corresponding to those of the strongest lines in the normal Raman effect; in addition lines at multiples of these frequencies were observed. Further interesting results obtained with inorganic as well as organic liquids were reported by Stoicheff<sup>71</sup> and Maker and Terhune<sup>72</sup>. The effect was subsequently observed in gases under high pressure (Minck *et al.*<sup>76</sup>) and in several solids (Eckhardt *et al.*<sup>77</sup>). A typical experimental arrangement is shown in *Figure 6*, and a typical spectrum in *Figure 7*.



*Figure 6.* Experimental arrangement for stimulated Raman scattering

Many of the observations can be understood from the recent theories of stimulated Raman scattering given by Garmire *et al.*<sup>73</sup>, Zeiger and Tannenwald<sup>74</sup>, Buckingham<sup>75</sup>, Bloembergen<sup>32</sup> and Maker and Terhune<sup>72</sup>. However, many details have yet to be explained. For example, the observed gain is several orders of magnitude larger than predicted, line widths up to  $100\text{ cm}^{-1}$  have been observed<sup>71,80</sup> and the directionality of the anti-Stokes emission in liquids is not completely understood. In spite of these difficulties we can already look forward to several immediate applications of stimulated Raman scattering. Many new wavelengths of coherent radiation to the red and to the blue of the ruby maser can be produced readily, in fact at almost any desired wavelength by suitable choice of molecular medium. This is useful for experiments in fluorescence and two-photon absorption<sup>64</sup>. Investigations of molecular interactions either by observing pressure shifts or solvent shifts<sup>79</sup> and line broadening in mixtures<sup>79</sup>, and the appearance of new combination lines in mixtures as found by Stoicheff<sup>71</sup> and Kaiser *et al.*<sup>78</sup>, may be aided by stimulated Raman spectroscopy.

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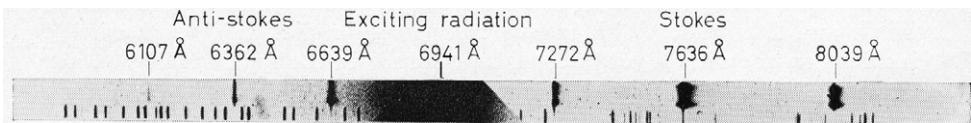


Figure 7. Stimulated Raman emission spectrum of liquid  $\text{CS}_2$  excited with a single flash of giant ruby maser of duration  $3 \times 10^{-8}$  sec

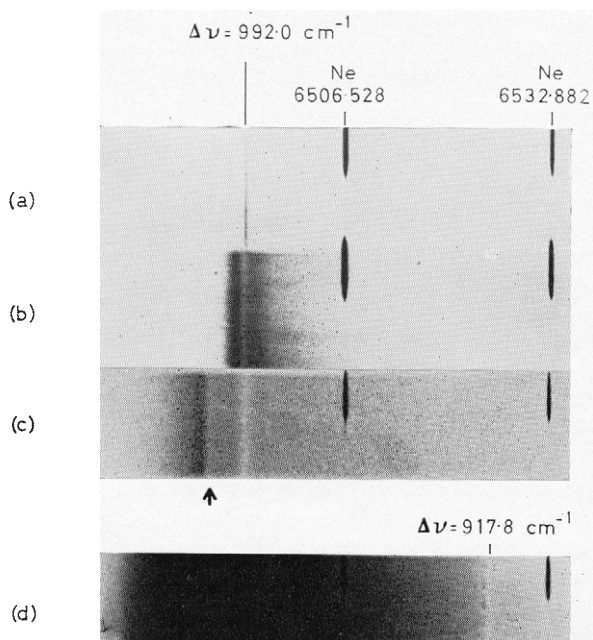


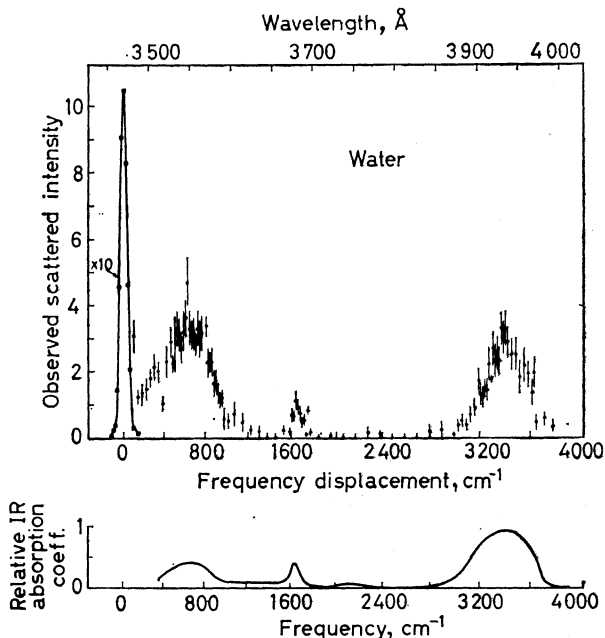
Figure 8. The stimulated Raman emission and absorption spectra of the anti-Stokes line of liquid benzene at  $\nu_0 + 992.0 \text{ cm}^{-1}$ . (a) Sharp, and (b) Broad emission lines obtained under different conditions of maser excitation; (b) also shows the sharp self-absorption from benzene. (c) Inverse Raman spectrum obtained with a single maser pulse using as a background continuum the broad toluene stimulated Raman emission whose intensity maximum is indicated by the arrow. (d) Inverse Raman line of nitromethane at  $\nu_0 + 917.8 \text{ cm}^{-1}$  (after Jones and Stoicheff<sup>80</sup>)

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A related effect, namely, stimulated Brillouin scattering was observed in quartz and sapphire by Chiao *et al.*<sup>81</sup>. It was subsequently found in a variety of liquids by Garmire and Townes<sup>82</sup> and Brewer<sup>83</sup>. Stimulated Brillouin scattering provides a method of generating very intense hypersonic waves at frequencies higher than previously available.

*Induced Absorption at Optical Frequencies: Inverse Raman Spectra.* Jones and Stoicheff<sup>80</sup> have observed Raman absorption spectra when maser radiation (frequency  $\nu_0$ ) and intense continuous radiation are simultaneously incident on a molecular medium. The absorption lines at  $\nu_0 + \nu_m$  arise from the modulation of the electric-field induced dipole moment by the molecular frequencies  $\nu_m$  and are the analogues of stimulated Raman emission lines at  $\nu_0 - \nu_m$ . Typical spectra are shown in *Figure 8*. With further improvements in the technique it should be possible to observe the complete "inverse Raman" spectra of gases, liquids and solids including rotational and electronic transitions in addition to the vibrational transitions already reported. High-speed Raman spectroscopy of interest in the study of free radicals and other short-lived species may be possible.

*Nonlinear Light Scattering.* Terhune *et al.*<sup>84</sup> have found that when a beam of radiation from a giant-pulsed ruby maser is focussed in liquids or in fused quartz, scattered radiation near twice the maser frequency is observed. Only about  $10^{-13}$  of the incident intensity is scattered and the scattering intensity varies as the square of the maser intensity. Both elastic and inelastic scattering with frequency displacements characteristic of the medium was



*Figure 9.* Nonlinear elastic and inelastic scattering spectrum of water occurring near twice the incident ruby maser frequency. The scattering intensity is given in photoelectrons per maser flash of 0.5 M watt peak power. For comparison the infrared spectrum is given below (after Terhune *et al.*<sup>84</sup>)

observed. The observed spectrum of water is shown in *Figure 9*. Recently, Maker<sup>85</sup> has reported on similar observations with methane at a pressure of 100 atm.

The importance of nonlinear light scattering is in the evaluation of second and third order polarizability and in the study of molecular structures and their interactions in liquids. The theory of nonlinear scattering has been given by Kielich<sup>86</sup> and Li Yin-Yuan<sup>87</sup>. A brief outline is attempted here. The dipole moment of any molecule in an electric field may be written as  $P = \mu + \alpha E + \beta E^2/2 + \gamma E^3/6 + \dots$ . If the electric field is that of a light wave  $E = E \sin \omega t$  then the dipole moment will have components oscillating at  $\omega$ ,  $2\omega$  and  $3\omega$  as follows:  $P(\omega) = \alpha E + \gamma E^3/6$ ;  $P(2\omega) = \beta E^2/4$ ; and  $P(3\omega) = \gamma E^3/24$ . Since the intensity of scattering will depend on  $P^2$  then a measurement of the intensity at  $2\omega$  and  $3\omega$  gives directly values of  $\beta^2$  and  $\gamma^2$  respectively. Similarly, for inelastic scattering one obtains values of the derivatives of second and third order polarizability with respect to the normal coordinates.

Detailed discussions of the fundamental theory and basic experimental results of these and other nonlinear effects have been given by Bloembergen<sup>32</sup> and Franken and Ward<sup>88</sup>.

## CONCLUSION

The development of optical maser sources in the past five years has been very rapid indeed and it is safe to predict that many new surprises await us. Their successful application to a wide variety of spectroscopic investigations, briefly summarized here, has clearly demonstrated the importance of these remarkable light sources to molecular spectroscopy.

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