Optoacoustic and Optogalvanic Spectroscopy [and Discussion]

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Optoacoustic and optogalvanic spectroscopy

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The optoacoustic effect (generation of sound by absorbed radiation) and the opto-galvanic effect (change in impedance of a gas discharge due to absorbed radiation) are becoming increasingly widely used in spectroscopy. Both are very sensitive and have been used in diverse applications. Several examples of the use of techniques based on these effects are described.

Introduction

The interaction of light with matter can be investigated in two main ways. We can either observe the effect that matter has on light or look at the effect that light has on matter. An example of the former method is absorption spectroscopy, where changes in the transmitted intensity of a light beam are observed. The sensitivity of this method is usually rather poor because it relies on detecting small changes in a large signal.

On the other hand, techniques that depend on detecting changes in the sample due to its interaction with light can be extremely sensitive. Examples of this class of technique are fluorescence detection, photoionization, and optoacoustic and optogalvanic spectroscopy. Although fluorescence and photoionization spectroscopy are perhaps more familiar than optoacoustic and optogalvanic spectroscopy the latter methods are becoming increasingly important as spectroscopic methods and they are now valuable tools in the armoury of the spectroscopist.

The optoacoustic and optogalvanic effects were discovered in 1880 and 1928, respectively. One might therefore be excused for wondering why a paper at a meeting on new techniques in spectroscopy should be devoted to these methods. The answer is that despite their long history neither of the methods assumed much importance until lasers were used. Throughout the past decade hundreds of papers on optoacoustic and optogalvanic spectroscopy have appeared in the literature, covering the fields of physics, chemistry, biology and medicine.

In the space available it is impossible to do justice to the fields in question and I shall only be able to pick out a few of the highlights in what are very active fields. I shall explain the salient features of optoacoustic and optogalvanic spectroscopy and discuss a small selection of the applications of the methods.

Optoacoustic effect

The optoacoustic effect was discovered by Alexander Graham Bell in 1880. He noted that when a chopped beam of sunlight was focused onto solid surfaces he could hear a note at the chopping frequency. His further investigations and those of Tyndall (1881) and Röntgen (1881) extended this observation of optically generated sound to liquids and gases as well as solids. In the intervening period until the 1970s very little work was done on the optoacoustic effect. The development of sensitive microphones and improved light sources has led to a revival of interest in photoacoustics. Indeed, two conferences have been devoted to the topic and at least

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three books reviewing the field have been published (Pao 1977; Rosencwaig 1980; Coufal *et al.* 1982).

The basic physics of the optoacoustic effect is that the energy absorbed by a gas, liquid or solid is converted into thermal energy by non-radiative processes. This thermal energy is detected either by directly measuring the strain induced in the sample by using piezoceramics (Farrow 1978; Wetsel 1980; Jackson & Amer 1980; Patel & Tam 1981; Ironside & Denning 1982; Shaw & Howell 1982) or, particularly in solids, by an interaction that transfers the thermal energy from the sample into a surrounding gas (Rosencwaig 1980). The periodic heating and cooling of this gas then gives rise to pressure fluctuations, which can be detected by using a conventional gas microphone.
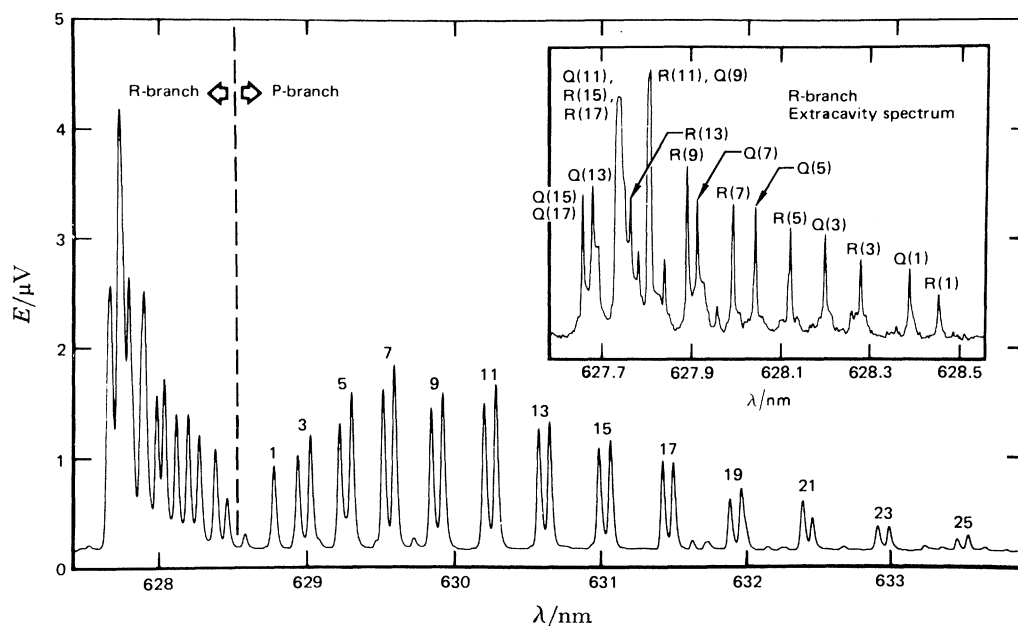

FIGURE 1. Photoacoustic spectrum of O_2 $b^1\Sigma_g^+$—$X^3\Sigma_g^-$ (2, 0) band. The insert shows an expansion of the R-branch.

One of the simplest forms of optoacoustic spectroscopy is the spectroscopy of gas samples by using gas microphones. Optoacoustic spectroscopy was revived when it was shown that infrared He–Ne lasers could be used to detect methane with very high sensitivity. Kreuzer (1971) showed that it was possible to detect methane in nitrogen at a level of about 1 part in 10^8 and speculated that impurity levels of as low as 1 part in 10^{13} might be detected.

In modern gas-cell microphone experiments it is quite usual to use commercially available electret microphones and to use a tunable dye laser as a light source. An example of results obtained with this combination is shown in figure 1 (Reddy 1981). This shows the spectrum of oxygen in the red region of the spectrum. The spectrum was taken by inserting a cell containing oxygen atatmospheric pressure into the cavity of a continuous-wave dye laser. The resonances correspond to the band $b^1\Sigma_g^+$—$X^3\Sigma_g^-$ (2, 0) in O_2. Also shown in the insert to figure 1 is an expanded trace of the R-branch of the O_2 spectrum, which was taken outside the laser cavity. By using this detection scheme it is estimated that absorption cross sections of as small as 10^{-28} cm^2 could be measured. If an absorption experiment was to be used to measure a cross

section of this magnitude a path length of some 2×10^6 m would be required for 1% absorption. The impressive sensitivity of this method makes it ideally suited for trace-element detection and atmospheric absorption measurements.

A great deal of work has been done with the use of gas microphone detection to study condensed matter. This work has been extensively reviewed (Rosencwaig 1977, 1978, 1980). When a gas microphone is used to detect absorption in materials other than gases, complex mechanisms come into play. The primary absorption takes place in the solid, liquid or powder sample. The sample converts the light energy into heat by non-radiative processes. The heat is then transferred to a gas surrounding the sample. The periodic change in temperature of the gas gives rise to pressure changes. These pressure changes are finally detected by a microphone. Despite the complex nature of these processes there exist theories that have been successfully applied to most experimental situations (Rosencwaig & Gersho 1976; Bennett & Forman 1976).

These theories predict a photoacoustic signal that varies inversely with chopping frequency. This dependence on chopping frequency has been verified experimentally in many cases (Rosencwaig 1980). A rather useful property of coupling between the condensed matter sample and the surrounding gas is that by changing the chopping frequency a depth-profile analysis of the optical properties of the material can be obtained. At high chopping frequencies, information about the sample near the surface is obtained, while at low frequency the data come from deeper within the sample. Furthermore the gas-microphone photoacoustic technique can be used to measure the absorption of opaque samples. A wealth of data on inorganic, organic and biological systems have been measured with this method (Rosencwaig 1980).

The gas-microphone technique suffers from several disadvantages. These include a very limited frequency response, inefficient coupling between the sample and surrounding gas, and a saturation of the effect for large absorptions. Some of these problems can be overcome by acoustically coupling a piezoelectric ceramic directly to the sample (Hordvick & Schlossberg 1977; Farrow et al. 1978). The method has been reviewed by Patel & Tam (1981).

The basic processes that take place in piezoelectric detection are that the absorbed radiation heats the sample by non-radiative processes and this heating causes a local expansion that manifests itself as a pressure wave propagating through the sample. The electrical signal coming from a piezoelectric transducer is proportional to this pressure (Patel & Tam 1981; Liu 1982).

The response time of piezoelectric detection of photoacoustic signals is quite fast. Transducers with resonance frequencies in the region of 100 kHz are quite common. This rapid response has been used to good advantage by Patel & Tam (1981). They have shown that by using pulsed excitation it is possible to overcome spurious signal problems due to absorption in windows. By gating the detection it is possible to identify signals that have come from different parts of the sample chamber by their different times of arrival. Furthermore, by compressing the optical energy into short pulses the signal can be readily brought above constant background contributions. This technique is capable of measuring absorptions in the region of 10^{-7} with a 1 mJ pulse. The comparable minimum detectable absorption with continuous wave excitation is about 10^{-5} with a power of 1 W (Nelson & Patel 1981 a, b; Patel et al. 1980).

Many highly sensitive measurements have been made by using piezoelectric detection (Patel & Tam 1981; Patel et al. 1981 b). A remarkable example of such measurements is the recent study performed on the vibrational overtone spectra of solid hydrogen. An example of the third overtone spectrum of hydrogen at 13 K is shown in figure 2. This was the first observation of

this very weak overtone. In solid H_2 the rotational quantum number, J, remains a good quantum number for the H_2 molecules. Because of the small mass of H_2, molecular solid H_2 exhibits large zero point motion. Dipole moments induced in pairs of neighbouring H_2 molecules by intermolecular forces lead to infrared absorption on vibrational overtones of H_2 molecules reminiscent of that in high-pressure H_2 gas. However, in the solid phase the overtone spectra are very narrow compared with the broad features seen in high pressure gas phase data. Patel *et al.* (1981 *a*) have been able to identify the observed lines and relate them to the isolated molecule transition frequencies.
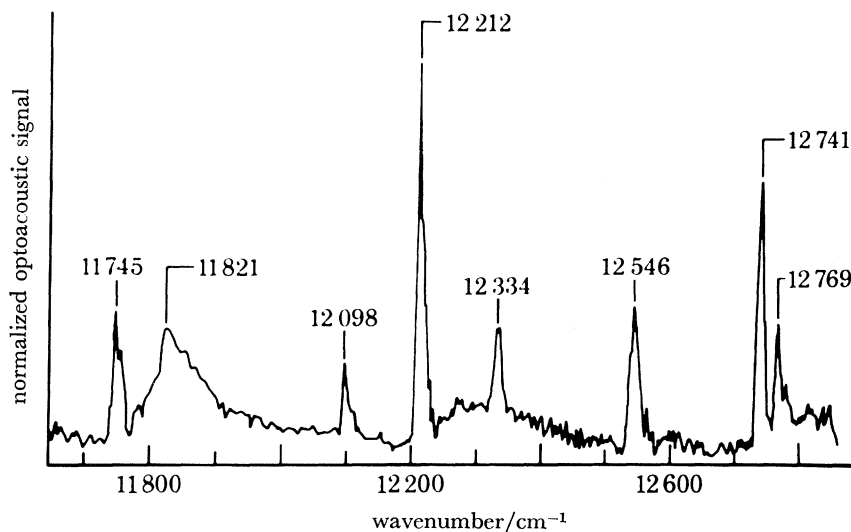

FIGURE 2. Optoacoustic signal from the $0 \to 3$ vibrational overtone absorption in solid hydrogen.

The very great sensitivity of optoacoustic detection has led to the use of this method for detecting nonlinear optical effects. Examples of this are two-photon spectroscopy (Patel & Tam 1981), Raman spectroscopy (Patel & Tam 1979; Barrett & Heller 1981; West & Barrett 1979; Barrett & Berry 1979) and Doppler-free saturation spectroscopy (Di Lieto *et al.* 1979; Marinero & Stuke 1979 *a*).

Nonlinear spectroscopy with optoacoustic detection will become increasingly important as more powerful tunable lasers become available and more sensitive detection techniques are developed. I only have space to show one example in this important category of method.

The optoacoustic detection of Raman processes has been very successful in recent years. In this method two laser beams are directed at the sample. Normally one beam is tunable while the other is of fixed frequency. If the difference frequency between these two lasers is equal to a Raman active mode of the sample, a Raman process takes place and the difference in energy between the pump and Stokes beams is carried off by the sample and manifests itself as a local heating. The method has been demonstrated in gases, liquids and solids. Raman gains of less than 10^{-5} cm^{-1} have been observed. An example of a optoacoustic Raman spectrum is shown in figure 3. This shows the Raman spectrum of carbon dioxide. The spectrum shows pure rotational spectra with the selection rule $\Delta J = +2$. Interestingly, only odd-J levels appear in the carbon dioxide spectrum due to the nuclear statistics. The pump beam wavelength was 532 nm and the Stokes beam wavelength was tuned from 532 to 535 nm. In this particular example 10 ns pulses from a Nd:YAG laser and Nd:YAG-pumped dye laser were used (West

& Barrett 1979), although continuous-wave (c.w.) lasers have been used in other experiments (Barrett & Berry 1979).

The absence of any elastic Rayleigh scattering should be noted from figure 3. This is a consequence of the acoustic detection scheme, which is sensitive only to energy deposited in the sample. This means that the technique is particularly well suited to studies of very small Raman shifts.
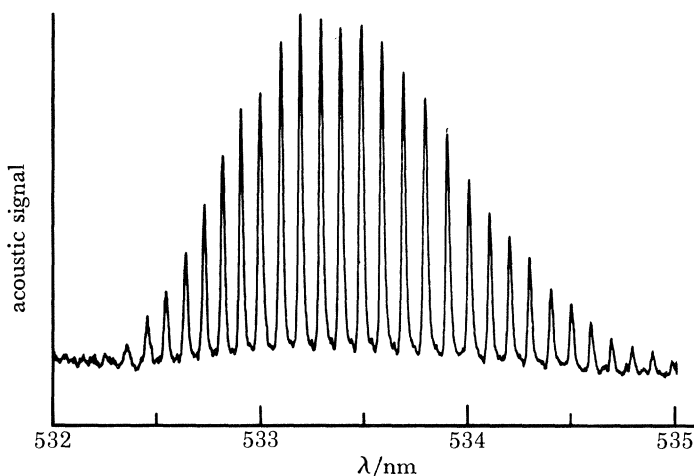

FIGURE 3. Rotational Raman spectrum of carbon dioxide with the use of optoacoustic detection.

This summary of recent work in optoacoustic spectroscopy has been rather brief and many important applications of the method have had to be omitted. Some indication of the considerable range of topics being studied by using optoacoustic detection can be obtained by consulting the digests of technical papers for the First and Second Topical Meetings on Photoacoustic Spectroscopy held in Ames, Iowa, and Berkeley, California, respectively.
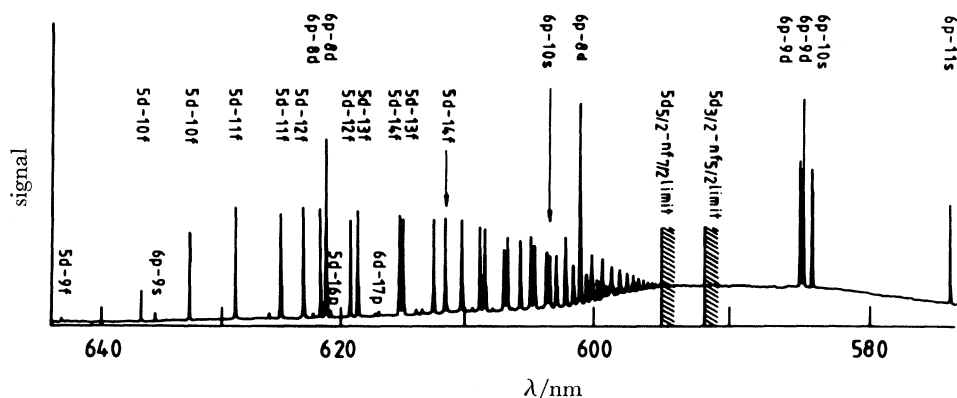
OPTOGALVANIC SPECTROSCOPY

The optogalvanic effect has been known for many years. It was first described by Penning (1928) when he noted that the properties of a discharge could be perturbed by the light emitted by an adjacent discharge. Although the optogalvanic effect has been observed and used for a number of applications over the years, it was not until the advent of tunable dye lasers that the usefulness of the effect as a spectroscopic tool was realized. In 1976 Green and his collaborators showed that the use of a c.w. dye laser could enable high sensitivity to be obtained by using the optogalvanic effect in a neon hollow cathode discharge (Green et al. 1976).

The basic physics of the optogalvanic effect depends on the exact details of the system considered. In atomic discharges, where optical excitation is usually used, the most probable mechanism is increased ionization. This mechanism assumes that the rates of ionization in the gas discharge are different for the various atomic states connected by the incident radiation. The radiation perturbs the populations of the levels and so changes the net ionization. This causes a change in the discharge current or discharge impedance (Lawler 1980; Pepper 1978; Erez 1979). Whether the impedance increases or decreases depends on the properties of the

levels involved. In molecular discharges and with the use of infrared radiation, thermal effects appear to play an important role (Smith & Brooks 1978).

A typical experimental arrangement for observing the optogalvanic effect is very simple. It consists of a tunable laser as the exciting source and a chopper to modulate the intensity of the source. The change in current in the discharge due to the presence of absorbed radiation is monitored by measuring the voltage change across a ballast resistor. The modulated component of this voltage is detected by using a lock-in amplifier.

FIGURE 4. Optogalvanic spectrum of caesium vapour.

A beautiful example of an optogalvanic spectrum is shown in figure 4 (Bridges 1978). In this experiment a c.w. dye laser of 0.05 nm line width was tuned from 570 to 640 nm. The laser was directed at a gas discharge in caesium vapour. Several series can be observed in this spectrum, including the 6p to ns series, 6p to nd series and 5d to nf series. In particular, the clear progression of the two 5d to nf series to their ionization limit can be seen.

One of the immediate benefits of the use of optogalvanic spectroscopy is that almost every element becomes accessible to optical spectroscopy. Hollow-cathode discharge tubes are commercially available for nearly all the stable elements. These devices normally consist of a gas discharge such as argon or neon and a cathode made of the element of interest. The element is introduced into the discharge by sputtering from the cathode walls. Remarkably, it has been found that nearly all hollow-cathode lamps, from certain manufacturers, show extremely quiet discharge behaviour and can be run close to the shot noise limit. This has opened up a whole new area of Doppler-limited spectroscopy. It is now quite simple to conduct experiments in such exotic, refractory materials such as V, Zr, Y, Mo and W by simply purchasing the appropriate hollow-cathode lamp.

The availability of many transitions within the tuning range of single-frequency dye lasers has suggested the use of optogalvanic detection in Doppler-free spectroscopy of atoms in excited states. The first demonstration of Doppler-free optogalvanic spectroscopy was by Lawler *et al.* (1979) using a technique that they called intermodulated optogalvanic spectroscopy or IMOGS. The experimental arrangement for IMOGS is shown in figure 5. A single-mode dye laser beam is split into two components and directed through a positive column discharge in opposite directions. One beam is chopped at a frequency f_1 and the other at f_2. In general, the two beams will interact with different velocity classes of atoms because of the Doppler effect. However, if the laser is tuned to within a homogeneous line width of line centre, the two beams will interact with the same atoms. The saturation of the transition leads to the generation of sum and
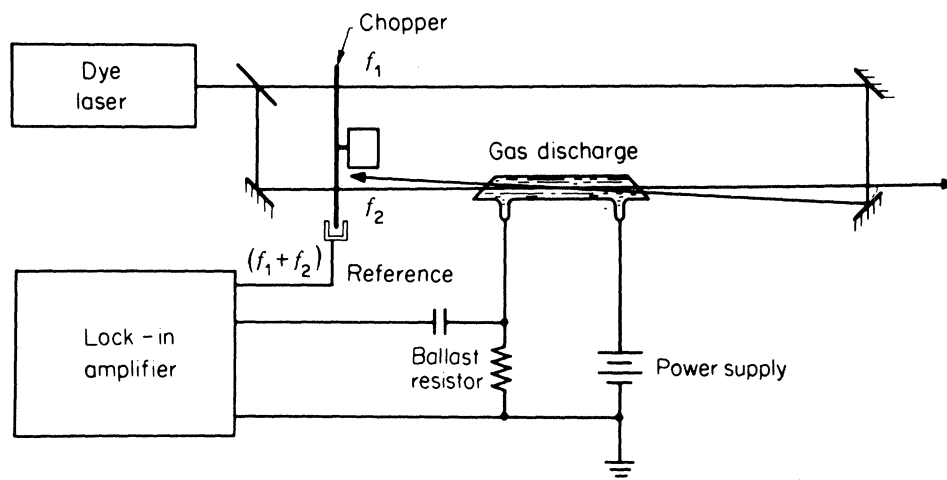
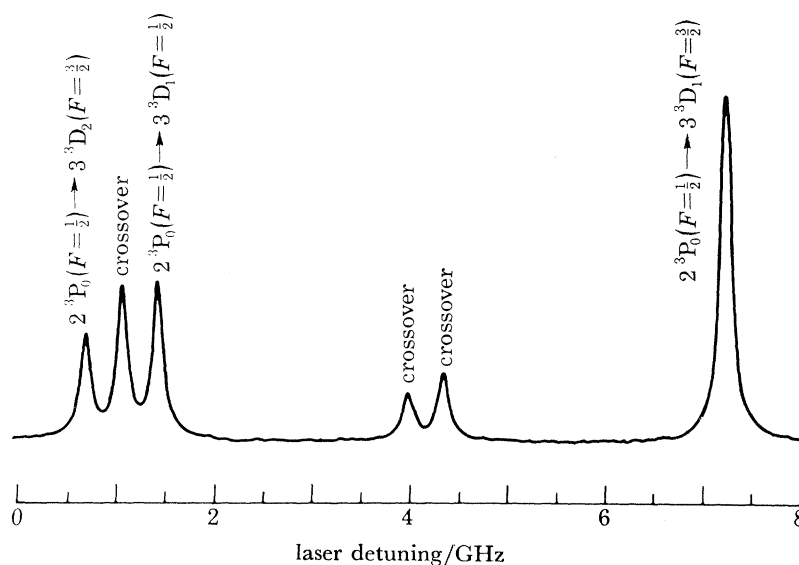FIGURE 5. Experimental apparatus for Doppler-free intermodulated optogalvanic spectroscopy.

FIGURE 6. Intermodulated optogalvanic spectrum of part of the ^{3}He 2^3P–3^3D transition at 587.5 nm.

difference frequencies (intermodulation products) in the optogalvanic signal. By observing one of these frequencies, say the sum frequency $f_1 + f_2$, it is possible to plot a Doppler-free spectrum. Lawler et al. (1979) have demonstrated this effect in the 2^3P—3^3D multiplet of ^{3}He at 587.5 nm. The part of the spectrum connected to the 2^3P$_0$ level is shown in figure 6. The observed line widths of 130 MHz are considerably less than the Doppler width and are consistent with pressure broadening. From these data Lawler et al. (1979) have been able to make the first Doppler-free measurements of the hyperfine structure of the 3^2D level. They have also shown that the IMOGS method can be much more sensitive than conventional saturation spectroscopy.

A further application of the use of the optogalvanic effect in Doppler-free spectroscopy was demonstrated by Goldsmith et al. (1979) when they showed that Doppler-free two-photon absorption could be detected optogalvanically (TOGS). In TOGS a single-mode laser is directed through a discharge and then back on itself to form a standing-wave region in the discharge.

If the laser is tuned to a two-photon resonance then a sharp Doppler-free peak can be detected owing to the cancellation of the first-order Doppler effect. Two-photon absorption is relatively weak and is normally only detected by fluorescence. However, by putting the discharge tube into the cavity of a dye laser, Goldsmith *et al.* (1979) have been able to detect Doppler-free resonances with very good signal:noise ratios. These experiments enabled the first observation of two-photon resonances from levels other than ground or metastable states. Some 13 two-photon resonances in neon were observed within the tuning range of Rhodamine 6G.
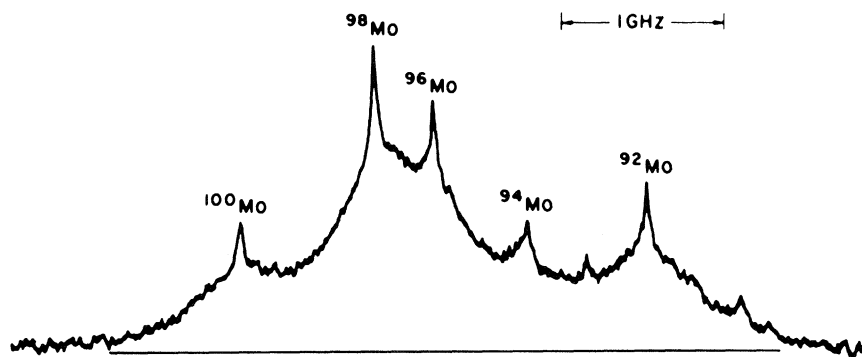
FIGURE 7. Doppler-free intermodulated optogalvanic spectrum of a Mo I line at 603.1 nm.

The Doppler-free method of IMOGS has been extended to look at refractory materials by Siegel *et al.* (1981), who used a hollow-cathode lamp developed specifically for high-resolution spectroscopy (Lawler *et al.* 1981). A typical spectrum with the use of IMOGS in Mo I is shown in figure 7. Using this and similar data Siegel *et al.* (1981) have reported on the isotope shifts of nine lines from ^{92}Mo I to ^{100}Mo I. One point to note about the spectrum shown in figure 7 is the shape of the lines. They have sharp peaks on top of broad pedestals. This kind of feature is well known in saturation spectroscopy and has been attributed to velocity-changing collisions that reduce the velocity selection of the saturating beams and thereby broaden the spectrum.

This problem has been beautifully overcome by the method of polarization-intermodulated excitation (POLINEX) (Hänsch *et al.* 1981). The set-up is very similar to that used for IMOGS with the exception that the two beams are no longer amplitude-modulated. In POLINEX the polarization of one or both of the beams is modulated. As before there is no interaction between the beams until the laser is tuned to within a homogeneous line width of line centre. Because of saturation, the absorption of the sample will be less when both beams have the same polarization than when the beams are orthogonally polarized. A Doppler-free signal at the intermodulated frequencies would therefore be expected.

The method has several advantages over IMOGS. Firstly, there is no strong signal at either f_1 or f_2 because the lasers are not amplitude-modulated. Secondly, intermodulated signals can be observed with good sensitivity even if only one beam is modulated. The third advantage is that collisions which take place in the discharge tend to disorient the atoms and so atoms that experience a velocity-changing collision will probably also be disoriented and not give rise to a signal. The improvement obtained by using POLINEX is shown in figure 8. This shows a Doppler-free spectrum of the Ne $1s_5$ to $2p_2$ transition. The upper trace shows the spectrum with the POLINEX method, whereas the lower trace shows the spectrum obtained by using intermodulated fluorescence detection. This latter trace is similar to that which would be obtained with IMOGS. The Doppler pedestal is clearly eliminated by using the POLINEX method. Similar

improvements have been demonstrated by Dabkiewicz & Hänsch (1981) in a study of the Cuɪ transition at 578.2 nm. The POLINEX method clearly provides a rather general method for obtaining clean Dopper-free spectra even under the non-ideal conditions that exist in a hollow-cathode discharge tube.

A further extension in Doppler-free optogalvanic spectroscopy has been demonstrated by Lyons *et al.* (1981). They have replaced a d.c. discharge with an r.f. discharge and detected the change in discharge impedance by its reaction on the r.f. oscillator. Lyons *et al.* (1981) have shown that regenerative oscillators can make very sensitive optogalvanic detectors. The
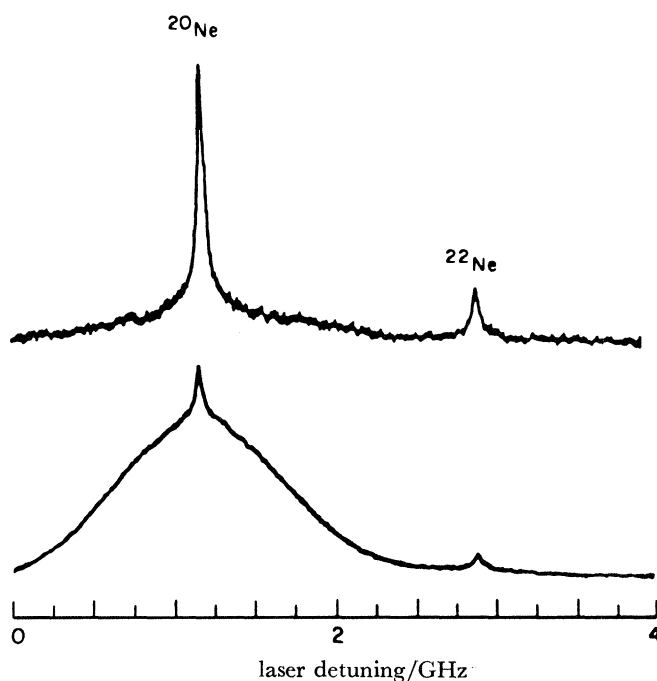
FIGURE 8. The upper trace shows a Doppler-free signal in the Ne $1s_5$—$2p_2$ transition taken with the POLINEX method. The lower trace shows the same transition taken with IMOGS.

advantage of the r.f. discharge method is that r.f. discharges can be maintained at low pressures and hence minimize pressure broadening. Furthermore, because they are electrodeless they are particularly suitable for spectroscopy of scarce or corrosive gases. Stanciulescu *et al.* 1980 and Suzuki 1981 have also demonstrated the use of r.f. discharges in optogalvanic spectroscopy. Unlike Lyons *et al.* (1981), Suzuki (1981) detects the r.f. optogalvanic signal by using an r.f. pick-up coil.

In a number of experiments conducted by Hannaford & Series (1981a, 1982a, b) it has been shown that quantum interference phenomena such as the nonlinear Hanle effect and level-crossing effects can be sensitively detected. In these experiments the optogalvanic signal is monitored while a magnetic field is applied to the discharge. Many level crossings have been observed in Y and Zr, and they have enabled Hannaford & Series to determine Landé *g*-values and magnetic hyperfine interaction constants in these materials with unprecedented accuracy.

In the early days of optogalvanic spectroscopy, simple Doppler-limited absorption spectra were all that were observed. In recent years the powerful and sophisticated techniques of laser spectroscopy are just beginning to be applied and adapted to optogalvanic detection. The vast

number of atomic resonances that hollow-cathode discharges render accessible, combined with this new range of techniques, make optogalvanic spectroscopy one of the most important tools in our attempts to investigate the interaction of radiation with matter.

CONCLUSION

In this short discussion of optoacoustic and optogalvanic spectroscopy many important applications of the techniques have had to be omitted. Some of the important applications that I have not been able to discuss are the use of optoacoustic detection in the following: phase transitions in solids (Pichon *et al.* 1977; Florian *et al.* 1978; Korpium *et al.* 1980), absolute quantum efficiencies of optical processes (Murphy *et al.* 1977; Quimby & Yen 1978, 1980; Powell *et al.* 1980), time-resolved studies (Mandelis 1980; Migliori *et al.* 1980), photothermal spectroscopy (Jackson *et al.* 1981; Boccara *et al.* 1980; Brueck *et al.* 1980), electron spin resonance (Coufal 1981; Netzelmann *et al.* 1982; Melcher 1980), ferromagnetic resonance (Numes 1979; Evora *et al.* 1980; Melcher 1980), photoacoustic microscopy (Pouch 1980), laser energy measurements (Shaw 1981), trace-element detection (Koch & Lahaman 1978; Rosengren *et al.* 1974; Perlmutter *et al.* 1979; Shtrikman *et al.* 1977; Velusamy & Rao 1981) studies of corrosive materials (Marinero & Stuke 1979*b*), studies of surface plasmons in metals (Inagaki 1982) and absolute absorption-coefficient measurements (Wetsel & McDonald 1977; Teng & Royce 1980).

A selected list of important applications of the optogalvanic effect that I have not been able to discuss is: wavelength calibration (Green *et al.* 1977; King *et al.* 1977; Keller *et al.* 1980), spectroscopy in refractory materials (Keller *et al.* 1979), trace-element detection (Turk *et al.* 1979), laser amplitude and frequency stabilization (Smith & Moffatt 1979; Moffatt & Smith 1980, 1981), isotope separation (Bridges 1978; Pepper 1978), optical double-resonance spectroscopy (Vidal 1980; Engleman *et al.* 1980), as a method of detecting dipole–dipole pair absorption (White 1980) and for detecting molecular absorptions (Feldman 1979; Schenck *et al.* 1978; Suzuki 1981).

As more researchers become aware of the sensitivity and ease of use of the optogalvanic and optoacoustic spectroscopy, many new applications are certain to be found.

REFERENCES

Barrett, J. J. & Berry, M. J. 1979 *Appl. Phys. Lett.* **34**, 144–146.
Barrett, J. J. & Heller, D. F. 1981 *J. opt. Soc. Am.* **71**, 1299–1308.
Bell, A. G. 1880 *Proc. Am. Ass. Advmt Sci.* **29**, 115–136.
Bell, A. G. 1881 *Lond. Edinb. Dubl. phil. Mag.* **11**, 510–528.
Bennett, H. S. & Forman, R. A. 1976 *Appl. Opt.* **15**, 2405–2413.
Boccara, A. C., Fournier, D., Jackson, W. & Amer, N. M. 1980 *Optics Lett.* **5**, 377–379.
Bridges, W. B. 1978 *J. opt. Soc. Am.* **68**, 352–360.
Brueck, S. R. J., Kildal, H. & Belanger, L. J. 1980 *Optics Commun.* **34**, 199–204.
Coufal, H. 1981 *Appl. Phys. Lett.* **39**, 215–216.
Coufal, H., Lüscher, E., Koriun, P., Schneider, S. & Tilger, R. (eds) 1982 *Photoacoustics: principles and applications.* Wiesbaden: Vieweg. (In the press.)
Dabkievicz, P. & Hänsch, T. W. 1981 *Optics Commun.* **38**, 351–356.
Di Lieto, A., Minguzzi, P. & Tonelli, M. 1979 *Optics Commun.* **31**, 25–27.
Engleman, R., Jr & Keller, R. A. 1980 *Optics Lett.* **5**, 465–466.

Erez, G., Lavi, S. & Miron, E. 1979 *IEEE J. Quantum Electron.* **QE-15**, 1328.

Evora, C., Landers, R. & Vargas, H. 1980 *Appl. Phys. Lett.* **36**, 864–5.

Farrow, M. M., Burnham, R. K., Auzanneau, M., Olsen, S. L., Purdie, N. & Eyring, E. M. 1978 *Appl. Opt.* **17**, 1093–1098.

Feldman, D. 1979 *Optics Commun.* **29**, 67–72.

Florian, R., Pelzl, J., Rosenberg, M., Vargas, H. & Wernhardt, R. 1978 *Physica Status Solidi* A **48**, K35–K38.

Goldsmith, J. E. M., Ferguson, A. I., Lawler, J. E. & Schawlow, A. L. 1979 *Optics Lett.* **4**, 230–232.

Goldsmith, J. E. M. & Lawler, J. E. 1981 *Contemp. Phys.* **22**, 235–248.

Green, R. B., Keller, R. A., Luther, G. G., Schenck, P. K. & Travis, J. C. 1976 *Appl. Phys. Lett.* **29**, 727–729.

Green, R. B., Keller, R. A., Luther, G. G., Schenck, P. K. & Travis, J. C. 1977 *IEEE J. Quantum Electron.* **QE-13**, 63–64.

Hannaford, P. & Series, G. W. 1981 *J. Phys.* B **14**, L661–L666.

Hannaford, P. & Series, G. W. 1982 *a Optics Commun.* **41**, 427–430.

Hannaford, P. & Series, G. W. 1982 *b Phys. Rev. Lett.* **48**, 1326.

Hänsch, T. W., Lyons, D. R., Schawlow, A. L., Siegel, A., Wang, Z.-Y. & Yan, G.-Y. 1981 *Optics Commun.* **38**, 47–51.

Hordvik, A. & Schlossberg, H. 1977 *Appl. Opt.* **16**, 101–107.

Inagaki, T., Kagani, K. & Arakawa, E. T. 1982 *Appl. Opt.* **21**, 949–954.

Ironside, C. N. & Denning, R. G. 1982 *J. Phys.* E **15**, 142–144.

Jackson, D. J., Gerhardt, H. & Hänsch, T. W. 1981 *Optics Commun.* **37**, 23–26.

Jackson, W. & Amer, N. M. 1980 *J. appl. Phys.* **51**, 3343–3353.

Jackson, W. B., Amer, N. M., Boccara, A. C. & Fournier, D. 1981 *Appl. Opt.* **20**, 1333–1344.

Keller, R. A., Engleman, R. & Palmer, B. A. 1980 *Appl. Opt.* **19**, 836–837.

Keller, R. A., Engleman, R., Jr & Zalewski, E. F. 1979 *J. opt. Soc. Am.* **69**, 738–742.

King, D. S., Schenck, P. K., Smyth, K. C. & Travis, J. C. 1977 *Appl. Opt.* **16**, 2617–2619.

Koch, K. P. & Lahmann, W. 1978 *Appl. Phys. Lett.* **32**, 289–291.

Korpium, P., Baumann, J., Lüscher, E., Papamokos, E. & Tilger, R. 1980 *Physica Status Solidi* A **58**, K13–K16.

Kreuzer, L. B. 1971 *J. appl. Phys.* **42**, 2934–2943.

Lawler, J. E. 1980 *Phys. Rev.* A **22**, 1025–1033.

Lawler, J. E., Ferguson, A. I., Goldsmith, J. E. M., Jackson, D. J. & Schawlow, A. L. 1979 *Phys. Rev. Lett.* **42**, 1046–1049.

Lawler, J. E., Siegel, A., Couilland, B. & Hänsch, T. W. 1981 *J. appl. Phys.* **52**, 4375–4378.

Liu, G. 1982 *Appl. Opt.* **21**, 955–960.

Lyons, D. R., Schawlow, A. L. & Yan, G.-Y. 1981 *Optics Commun.* **38**, 35–38.

Mandelis, A. & Royce, B. S. H. 1980 *J. opt. Soc. Am.* **70**, 474–480.

Marinero, E. E. & Stuke, M. 1979 *a Optics Commun.* **30**, 349–350.

Marinero, E. E. & Stuke, M. 1979 *b Rev. scient. Instrum.* **50**, 241–244.

Melcher, R. L. 1980 *Appl. Phys. Lett.* **37**, 895–897.

Migliori, A. & Hofler, T. J. 1981 *Rev. scient. Instrum.* **52**, 1865–1867.

Moffatt, S. & Smith, A. L. S. 1980 In *Laser advances and applications* (ed. B. S. Wherrett), pp. 31–34. New York: Wiley.

Moffatt, S. & Smith, A. L. S. 1981 *Optics Commun.* **37**, 119–122.

Murphy, J. C. & Aamodt, L. C. 1977 *J. appl. Phys.* **48**, 3502–3509.

Nelson, E. T. & Patel, C. K. N. 1981 *a Appl. Phys. Lett.* **39**, 537–539.

Nelson, E. T. & Patel, C. K. N. 1981 *b Optics Lett.* **6**, 354–356.

Netzelman, Q., Goldammer, E. V., Pelzl, J. & Vargas, H. 1982 *Appl. Opt.* **21**, 32–34.

Numes, O. A. C., Monteiro, A. M. M. & Neto, K. S. 1979 *Appl. Phys. Lett.* **35**, 656–658.

Pao, Y.-H. (ed.) 1977 *Optoacoustic spectroscopy and detection.* New York: Academic Press.

Patel, C. K. N., Nelson, E. T. & Kerl, R. J. 1980 *Nature, Lond.* **286**, 368–370.

Patel, C. K. N., Nelson, E. T. & Kerl, R. J. 1981 *a Phys. Rev. Lett.* **47**, 1631–1635.

Patel, C. K. N., Nelson, E. T. & Tam, A. C. 1981 *b* In *Laser spectroscopy*, vol. 5 (ed. A. R. W. McKellar, T. Oka & B. P. Stoicheff), pp. 399–407. Berlin: Springer-Verlag.

Patel, C. K. N. & Tam, A. C. 1979 *Appl. Phys. Lett.* **34**, 760–763.

Patel, C. K. N. & Tam, A. C. 1981 *Rev. mod. Phys.* **53**, 517–550.

Penning, F. M. 1928 *Physica, Eindhoven* **8**, 137.

Pepper, D. M. 1978 *IEEE J. Quantum Electron.* **QE-14**, 971–977.

Perlmutter, P., Shtrikman, S. & Slatkine, M. 1979 *Appl. Opt.* **18**, 2267–2274.

Pichon, C., Le Liboux, M., Fournier, D. & Boccara, A. C. 1979 *Appl. Phys. Lett.* **35**, 435–437.

Pouch, J. J., Thomas, R. L., Wong, Y. H., Schuldies, J. & Srinivasan, J. 1980 *J. opt. Soc. Am.* **70**, 562–564.

Powell, R. C., Neikirk, D. P. & Sardar, D. 1980 *J. opt. Soc. Am.* **70**, 486–490.

Quimby, R. S. & Yen, W. M. 1978 *Optics Lett.* **3**, 181–183.

Quimby, R. S. & Yen, W. M. 1980 *J. appl. Phys.* **51**, 1780–1782.

Reddy, K. V. 1981 In *Digest of Technical Papers, Second Topical Meeting on Photoacoustic Spectroscopy*, Berkeley, California, pp. MB9-1–MB9-4.
Röntgen, W. C. 1881 *Phil. Mag.* **11**, 308–311.
Rosencwaig, A. 1977 In *Optoacoustic spectroscopy and detection* (ed. Y.-H. Pao), pp. 193–239. New York: Academic Press.
Rosencwaig, A. 1978 In *Electronics and electron physics*, vol. 46, pp. 207–311. New York: Academic Press.
Rosencwaig, A. 1980 *Photoacoustics and photoacoustic spectroscopy*. New York: Wiley.
Rosencwaig, A. & Gersho, A. 1976 *J. appl. Phys.* **47**, 64–69.
Rosengren, L.-G., Max, E. & Eng, S. T. 1974 *J. Phys. E* **7**, 125–133.
Schenck, P. K., Mallard, W. G., Travis, J. C. & Smyth, K. C. 1978 *J. chem. Phys.* **69**, 5147–5150.
Shaw, R. W. 1979 *Appl. Phys. Lett.* **35**, 253–255.
Shaw, R. W. 1981 *Laser Focus* **17**, 69–72.
Shaw, R. W. & Howell, H. E. 1982 *Appl. Opt.* **21**, 100–103.
Shtrikman, S. & Slatkine, M. 1977 *Appl. Phys. Lett.* **31**, 830–831.
Siegel, A., Lawler, J. E., Couillaud, B. & Hänsch, T. W. 1981 *Phys. Rev.* A **23**, 2457–2461.
Smith, A. L. S. & Moffatt, S. 1979 *Optics Commun.* **30**, 213–218.
Stanciulescu, C., Bobulescu, R. C., Surmeian, A., Popescu, D., Popescu, I. & Collins, C. B. 1980 *Appl. Phys. Lett.* **37**, 888–890.
Suzuki, T. 1981 *Optics Commun.* **38**, 364–368.
Teng, Y. C. & Royce, B. S. H. 1980 *J. opt. Soc. Am.* **70**, 557–560.
Turk, G. C., Mallard, W. G., Schenck, P. K. & Smyth, K. C. 1979 *Analyt. Chem.* **51**, 2408–2410.
Tyndall, J. 1881 *Proc. R. Soc. Lond.* **31**, 307–317.
Velusamy & Rao, M. M. 1981 *Appl. Opt.* **20**, 3828–3829.
Vidal, C. R. 1980 *Optics Lett.* **5**, 158–159.
West, G. A. & Barrett, J. J. 1979 *Optics Lett.* **4**, 395–397.
Wetsel, G. C., Jr 1980 *J. opt. Soc. Am.* **70**, 471–474.
Wetsel, G. C., Jr & McDonald, F. A. 1977 *Appl. Phys. Lett.* **30**, 252–254.
White, J. C., Freeman, R. R. & Liao, P. F. 1980 *Optics Lett.* **5**, 120–122.

Discussion

G. W. SERIES, F.R.S. (*University of Reading, U.K.*). I believe other forms of detector might also be classed as 'optogalvanic'. For example, the space-charge limited diode detectors that are used to provide massive amplification of ions formed directly or indirectly through the absorption of light are surely 'optogalvanic'. One can envisage a whole range of possibilities intermediate between conventional gas discharges and controlled, hot-cathode diodes that could be useful optogalvanic devices.

A. I. FERGUSON. In my presentation I deliberately restricted the range of 'optogalvanic' phenomena under discussion to glow discharges. Professor Series has mentioned the very important technique of space-charge limited thermionic detection, and I agree that this is certainly an optogalvanic phenomenon. A considerable amount of very important work has been done in the recent past with these detectors, particularly in studies of Rydberg levels. We could also extend the range of 'optogalvanic' phenomena to cover the solid state. I believe that photoconductivity could also be considered to be an optogalvanic effect.

B. CAGNAC (*Laboratoire de Spectroscopie Hertzienne de l'ENS, Paris, France*). The discussion about the efficiency of optogalvanic detection (which seems to be generally less than unity) and the remark of Professor Series about thermoionic detection (or space-charge diode) raise the interest of a comparison between these two methods. Both are used in our laboratory. Optogalvanic detection is very easy to bring into play and seems to be more sensitive than fluorescence detection. Thermoionic detection is much more delicate, but it gives an amplification coefficient (10^4 electrons for an excited atom, for example), and is more sensitive than the optogalvanic detection. With this space-charge diode, we are able to detect Rydberg levels

with a quantum number higher than $n = 150$, even when they are perturbed by strong external fields.

A. I. FERGUSON. The question of the efficiency of optogalvanic detection is complicated by the fact that the size of the signal depends on the population of, and ionization from, the levels under study. In a glow discharge this can lead to signals that are either positive, zero or negative. Furthermore the relative magnitude of the lines observed varies at different parts of the discharge and is a reflection of the relative population differences and discharge processes taking place in that region.

There is little doubt that thermionic detection is generally more sensitive than optogalvanic detection. The beauty of optogalvanic detection is its simplicity, the fact that it makes accessible a wide range of refractory materials, and that excited states can be readily studied.