Modern Microwave Technology Revitalizes a Specific and Sensitive Analytical Technique [and Discussion]

J. F. Alder and D. Littlejohn

Phil. Trans. R. Soc. Lond. A 1990 **333**, 19-27
doi: 10.1098/rsta.1990.0133

Modern microwave technology revitalizes a specific and sensitive analytical technique

By J. F. Alder

Department of Instrumentation and Analytical Science, UMIST, P.O. Box 88, Manchester M60 1QD, U.K.

A review of the present status of analytical microwave spectroscopy is presented and its potential for the analysis of gaseous atmospheres discussed. The technique is attractive in terms of both sensitivity and selectivity. Modern advances in microwave technology permit instrumentation that is making it even more applicable to both process analysis and atmosphere monitoring.

1. Analytical microwave spectroscopy

Microwave rotational spectroscopy is a powerful spectroscopic method for the determination of small molecule structure and for the study of intra- and intermolecular interactions. It is also useful for the quantitative analysis of gaseous mixtures providing selective, and in many cases, sensitive determination capability. As an analytical method it is generally applicable to molecules possessing a dipole moment, and is more sensitive with lower molecular mass gases possessing simple spectra, due to the population of most rotational levels of normal ambient temperatures.

Determination of gas composition is usually undertaken for one of three general reasons: quality control or process control; long-term study of workplace or ambient atmospheres for hygiene or pollution monitoring; personal protection for entry into potentially dangerous environments. In the first of these one would often be looking for quite high gas concentrations, typically percent by volume, and the target species would be commonly known and their concentrations well defined. Microwave spectroscopy is well suited to application in this area of gas analysis, possessing more than adequate sensitivity and requiring none – or minimal – separation of the gases before analysis.

Industrial hygiene and pollution monitoring studies are less appropriate to analysis by microwave techniques. Most atmospheres will contain trace (sub-p.p.m. (parts per million by volume)) concentrations of interesting pollutants, whereas without preconcentration the microwave technique can only offer currently at best 0.1–100 p.p.m. sensitivities. If one is able to preconcentrate the gases, however, this situation will obviously be improved. One particular area of potentially very useful application of microwave spectroscopy is in the quantitative analysis of chlorofluorocarbon mixtures and fragments in high vibrational states, which conditions prevail in the upper atmosphere subjected to solar radiation. Clearly there can be no direct application to real systems because of the low number densities, but in higher concentration model experiments this approach has shown great potential.

For personal protection applications, microwave spectroscopy has certain

Phil. Trans. R. Soc. Lond. A (1990) **333**, 19–27
Printed in Great Britain

appealing characteristics. That one can monitor an atmosphere continuously without chemical species separation is very attractive if acceptable analytical sensitivity can be achieved for the potential target gases. One has also the ability to identify gases from their spectral transition frequencies, three lines alone giving better than 98% probability of correct identification if the spectrum is known (Jones & Beers 1971). While recognizing that not all features of the technique are so attractive for this application, particularly the need for a vacuum pump, expensive frequency synthesiser and a computer, for certain applications, the means to achieve this broad spectrum interrogation capability will be justified by the end utility.

Microwave spectroscopy, although imperfect, stands up well against potential competitors for these applications. Infrared spectrometry is a simpler, atmospheric pressure technique, but the overlapping bands makes identification and quantification rather difficult in all but the simplest cases. Mass spectrometry is undoubtedly the best alternative method, but it must be coupled to gas chromatography for analysis of mixtures, which has significant cost and complexity penalties, and the vacuum requirements are several orders of magnitude more demanding (10^{-6} mbar (10^{-4} Pa)) than for microwave spectroscopy (10^{-3} mbar (10^{-1} Pa)). Microwave spectrometry has one major advantage over mass spectrometry in being able to differentiate between *cis* and *trans* isomers or other types of orientational isomeric species. It is also able to quantitatively identify and determine molecules in high vibrational or torsional states. Whilst recognizing that the latter advantage may not often be of value in routine analytical use, understanding gas phase reaction processes may be helped enormously by such a facility. Ion mobility spectrometry has achieved remarkable sensitivity for relatively high molecular mass molecules using relatively simple equipment at low cost (see, for example, Leasure *et al.* 1986). One awaits with interest the potential application of this technique to a much wider range of gases, to determine its future role in monitoring applications.

2. Recent developments in microwave technology

The staggering advances in electronics technology of the past two decades have been probably greater at radio and microwave frequencies, than in the more commonly met digital processing applications. One now has available microwave semiconductor sources commercially available to at least 110 GHz with more than adequate power for spectroscopic applications. The new Gunn sources have much lower close-in sideband noise than the older klystrons. Figure 1 shows the spectrum of both types of device working at around 70 GHz (Baker 1990). The spectra are in fact convolutions of the (actual) source spectrum and the spectrum of the local oscillator used to beat the frequency down to 20 MHz before insertion to the spectrum analyser, but as the local oscillator is common to both, the spectra are comparable. One should note the exceedingly narrow centre profile, probably a few hundred hertz of both sources and the high signal:background ratio (60 dB) of the Gunn source, which make these so attractive for spectroscopic analysis. More important, Schottky barrier diodes of high sensitivity, low noise and broadband characteristics are also available at these frequencies. Manufacture of simple, inexpensive instruments is thus within the range of everybody, as these devices are marketed in 'building block' packages, requiring minimal outside circuitry to achieve first-class results. Manufacturers have exploited these developments to provide instrumentation for electronic warfare, radar and telecommunication

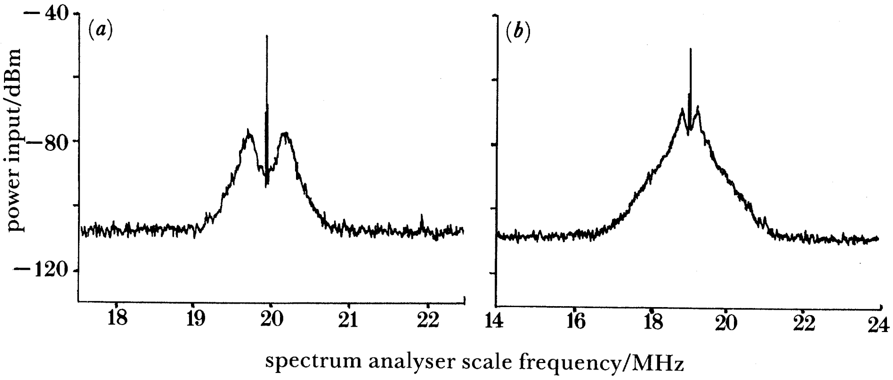

Figure 1. Spectrum of (*a*) Gunn and (*b*) Klystron sources (both 73 GHz) obtained by beating with the same, phase locked local oscillator source, the difference frequency being fed into a radiofrequency spectrum analyser. Ordinate axis shows measured power input to spectrum analyser at the low (beat) frequency, and has no absolute significance, but the intensity magnitudes are directly comparable.

applications. Of particular importance to spectrometry are the high stability, high accuracy synthesizers, which are available off the shelf. Wiltron (Crowthorne, U.K.), for example, manufactures the 6700 B series working up to 60 GHz. This means that one can effectively call up any source frequency with a resolution of down to 1 kHz to 26.5 GHz, 2 kHz to 40 GHz and 3 kHz to 60 GHz, and step over a frequency range up to 1800 steps under computer control. Residual FM, on the CW sweep, is only of the order 15 kHz at 26 GHz, and 30 kHz at 60 GHz. On the step sweep and phase locked CW mode the residual FM is between 280 Hz at 20 GHz and 720 Hz at 60 GHz. Coupled with frequency counters of 100 Hz resolution at 110 GHz and the ability to measure pulsed 100 GHz carrier frequencies to 3 kHz resolution (HP5356D, Hewlett Packard, Stockport), one has tremendous potential for both swept-, stepped- and single-frequency measurements, undreamed of even ten years ago. Ancillary equipment, particularly vector analysers working to 40 GHz (for example, Wiltron 360 series), and scalar analysers working to 110 GHz (for example, Hewlett Packard HP8757) and a new generation of spectrum analysers with 164 dB dynamic range and −134 dBm sensitivity (Hewlett Packard HP8566B) has transformed the design, testing and optimization of the components needed to build the spectrometers, permitting attainment of maximum sensitivity and more important, maximum bandwidth of operation.

Much of the recent advance in microwave technology has hinged on the development of new materials and composites. Semiconductors and their fabrication has of course had a paramount effect, but also engineering materials, particularly the glass filled poly(tetrafluoroethylene) composites have also had their influence. One such material, RT Duroid 5880 (Mektron, Leatherhead), which has ϵ_r of 2.20 and tan δ of typically 9×10^{-4} at 10 GHz is a particularly useful material. Available as a sheet copper clad on both sides, it permits the etching of iris apertures of complex shape and small dimensions onto windows of low loss and reflectivity using normal printed circuit board etching facilities. This, at very modest cost, has also made the construction of vacuum windows a simple operation, as the sheet can be cut, drilled or milled using standard workshop tools, and soldered into position.

3. Recent advances in spectrometer design

The previous generation of spectrometers, originating in the 1960s and 70s, were based on Stark modulation with phase-sensitive detection of the absorption signals, using long path cells. More recently, the development of Fourier transform microwave spectrometry in the middle-to-late 1970s and now by a number of workers, particularly Driezler in Kiel (1986) has provided a rather more sensitive approach to spectroscopic analysis. Using this equipment sensitivity has been obtained of the order $4 \times 10^{-10}\ \mathrm{cm}^{-1}$ for ^{18}OCS in the $\nu = 2$ vibrational state at 22891.654 MHz, with 10 min integration time. Although Fourier transform spectroscopy is a powerful and sensitive technique for microwave absorption measurements, the equipment required is undeniably complex and its operation for routine chemical analysis probably not practical at the present state of development of the technique. Much work is, however, in progress with Fourier transform techniques, particularly the work of Baker *et al.* in Manchester, applied to pulsed microwave–microwave double resonance techniques (Andrews & Baker 1987). The use of double resonance methods imparts very great selectivity to the already specific microwave spectroscopic technique and there is a large body of work published on various combinations of radio-, infrared-, optical- and microwave-frequency double resonance spectrometry. Some particularly elegant experiments have recently been carried out by Vogelsanger *et al.* (1988), working in ETH Zurich, applying two-dimensional correlation techniques to microwave Fourier transfer spectroscopy. Working with 1-chloro 1-fluoroethene as model, in the 8–18 GHz region, three pulse, and two pulse autocorrelation experiments were carried out. The detail revealed in the two-dimensional correlation spectra, shown in this paper, clearly indicate the attraction of this complex but rewarding technique for analytical applications. Hitherto these have always been applied to diagnostic investigations studying generally intramolecular or intermolecular processes, but the potential for quantitative analytical spectroscopy of very high specificity has not been truly exploited.

Most quantitative analytical work was carried out in long-path-length waveguide cells, which have the significant advantage of broad frequency bandwidth, but the serious disadvantages of large size and high wall-area : cell volume ratio, with all the problems these features entail. One of few recent developments in this area has been the design of a helical groove absorption cell by Longo (1989), which guides the microwave radiation around a helical groove machined on the outer surface of the inner cylinder of a coaxial tube arrangement 146 mm diameter and 300 mm long. The outer tube is plain and the annular gap is 3 mm, the groove is more than 5 m long. A Stark field is maintained between the inner and outer tube, and radiation between 18 and 26.5 GHz is coupled into and out of the structure by two pieces of waveguide tangential to the slot and at 87° to the longitudinal axis (i.e. the helix angle). Although full-band operation requires tuning of the structure by rotating the inner cylinder to overcome impedance mismatches. Overall, sensitivity of the order $10^{-9}\ \mathrm{cm}^{-1}$ can be achieved using this device, which makes it comparable with a practical Fabry–Perot cavity spectrometer in this respect, while having rather better broadband characteristics than the cavity device. The surface-area : volume ratio is, however, rather large, so adsorption and memory effects may be a nuisance, although the cell can be baked to 150 °C. The helical groove cell may be improved by refinements in the design and may have useful applications for broadband routine analytical work in conjunction with a synthesized frequency generator.

Fabry–Perot semiconfocal microwave cavities have been known for two decades and more as very useful, compact and structurally simple spectrometers. The high quality factor of the cavity produces an apparent path length much greater than the geometrical dimensions, yielding high sensitivity at the expense of spectral bandwidth. These devices have often been applied to quantitative analysis where only one analyte gas is to be determined at one spectral line, as changing the resonant frequency more than a few tens of megahertz (in the 20–30 GHz region) would require significant mechanical adjustments to optimize the cavity at the new setting. Current work has been aimed towards a fully automatic Fabry–Perot spectrometer capable of working anywhere in the 18–40 GHz region. The goal is an instrument that can be adjusted under computer control to step between frequencies within a 1 GHz bandwidth. The spectral source in this design is a Gunn oscillator, critically coupled to the microwave cavity. The dimensions of the cavity define its resonant frequency and the Gunn oscillator is locked so that frequency for a range of cavity dimensions. Currently we have achieved stable working bandwidths of 350 MHz around 25.65 GHz before the Gunn oscillator jumps to a different frequency. This has been achieved by optimizing the design and position of the coupling iris, Gunn oscillator cavity and the electrical coupling. Computer control of the mirror position now permits automatic tuning of the spectrometer to within about 20 MHz of predetermined frequencies in the range 18–26 GHz, before locking the Gunn oscillator frequency to that of the spectral line through the second-order Stark effect. This has already been demonstrated using a manual locking procedure (Thirup *et al.* 1986) and is now being made automatic.

4. Recent advances in quantitative analysis

Whereas there are many reports of structure determination and studies of molecular spectroscopy in the literature, the number of quantitative analytical applications is miniscule. The book by Varma & Hrubesh (1979) contains much information about quantitative aspects of microwave spectrometry but there is only a little detailed practical information on how to undertake proper method development using this technique, either in that book or elsewhere. In the late 1970s, the Mitsubishi Petrochemical Company in Japan had introduced a microwave spectrometer using a resonant waveguide cavity 90 cm long, with Stark modulation and reported a noise level corresponding to 0.08 p.p.m. ammonia (Uehara *et al.* 1980) and later reported work on determination of ammonia in waters after alkaline hydrolysis and gasification of the ammonia (Hirose *et al.* 1982). Later the same authors applied the technique to the determination of urea in serum using urease (Hirose *et al.* 1983). The reason for the very few papers on quantitative analysis of real mixtures after 1980 must lie in part with there being few, if any, commercial microwave spectrometers anywhere in common use outside the physical spectroscopy research laboratories. Probably the most important paper to appear in the last decade dealing with the quantitative analysis of real atmospheres was by Kolbe & Leskovar (1983). They reported calculated line intensities for carbon monoxide, sulphur dioxide, formaldehyde, ozone, water, hydrogen sulphide, carbonyl sulphide, nitrogenmonoxide and the radicals OH, SO and CS. All their results pointed to higher frequencies for greater sensitivity in terms of absorption coefficient, but the optimum signal:noise ratio obtainable is probably limited by the detector noise at the higher microwave frequencies. In a later paper (Kolbe & Leskovar 1985) they described a 140 GHz Fabry–Perot spectrometer with 30 MHz frequency modulation signal recovery. The cavity had a loaded quality factor of about 109000. They used a heterodyne Alpha/TRG F9640 receiver (Alpha Industries, Maidenhead) with a 12 dB noise figure at 141 GHz, which mixed the 141 GHz frequency modulated carrier with the source frequency, and the 30 MHz intermediate frequency was amplified and recovered using conventional radio techniques. With this system they obtained limits of detection for sulphur dioxide of around 0.21 p.p.m. at 143.047 GHz and formaldehyde about 0.13 p.p.m. at 140.839 GHz. One notes the absorption coefficient of 0.0099 cm^{-1} for sulphur dioxide and 0.018 cm^{-1} for formaldehyde at these frequencies.

Baker (1990) has designed and constructed a millimetre wave spectrometer for gas analysis comprising a compact and portable all-solid-state system. Based on a Gunn oscillator operating between 71.5 and 81.0 GHz, it uses a frequency doubler to study spectra in the 140–160 GHz region. He reports detection of OCS isotopes down to 1 p.p.m. at 145 GHz using a Fabry–Perot cavity which could be employed between 24 and 150 GHz having quality factors of 10000 at the lower frequency end of the spectrum and 50000 at the upper limit. The design of the electronic hardware was rather different to that of Kolbe & Leskovar (1985). They used an InSb (50 GHz–20 THz) detector (QMC Type ULN207, helium cooled). This has the advantage of no $1/f$ noise at modulation frequencies down to as low as 20 Hz and broadband sensitivity. This good low-frequency characteristic was exploited by using a low-frequency modulation (0.5–4 kHz) and cavity profile background subtraction. A resonant cavity of quality factor 50000 at 145 GHz has a full-width-half-height bandwidth of about 3 MHz, which is of the same order as that of the spectral line. Source frequency modulation therefore extracts a background signal due to the cavity which has to be removed from the spectral signal. Thus Baker has achieved using a computer-controlled pulsed sample introduction system to the cavity which permits sweeps of the frequency across an empty cavity and then one containing the sample gas. Subtraction of the signal then yields the unperturbed spectrum. Significant enhancement of the spectral information was achieved using correlation with the second derivative of a gaussian function to treat the data (figure 2). Baker (1990) has also used a cavity tuning system similar to Thirup *et al.* (1986) to scan the cavity profile in phase with the source frequency modulation to minimize the background due to the cavity. The work of Baker (1990) read in the context of that by Kolbe & Leskovar (1983, 1985) clearly demonstrates the trade-off between working at high frequency to benefit from the higher absorption coefficients of transitions, and the sacrifice to be made in signal : background noise ratio, design complexity and cost.

One of the drawbacks of working at the lower microwave frequencies is that for many molecules, one is working with transitions between high J levels and there is a distribution of the molecular population amongst all the J levels as their energy is less than kT at ambient temperatures. To overcome this a number of workers have used supersonic nozzles to inject gas into cavity spectrometers to lower the rotational temperature into the 3–10 K region reducing therefore the population of higher J levels, and minimizing Doppler broadening. The loss of molecular density resulting from the reduced solid angle of the sample stream in the supersonic jet, is more than compensated in sensitivity terms by the hundred-fold reduction in temperature. The reduced line widths, less than 30 kHz, in the cooled gas also yield a sensitivity

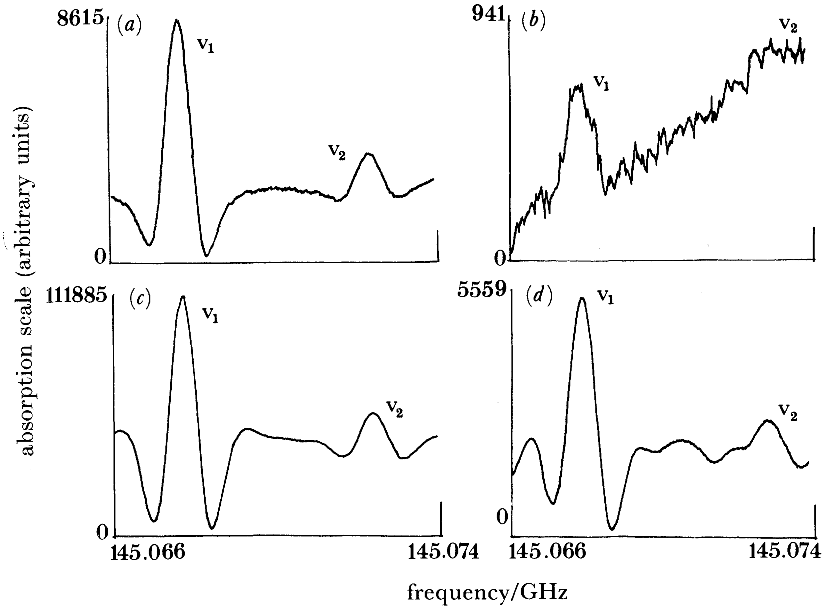

Figure 2. 145 GHz frequency modulated spectral scans of OCS using a 2 m waveguide cell, after background subtraction. (The two transitions are from vibrational states v_1 (populated 200 p.p.m.) and v_2 (populated 38 p.p.m.) at 300 K.) (*a*) Signal due to pure OCS; ν_1 (2, 0, 0), 859 cm^{-1}, 200 p.p.m.; ν_2 (0, 0, 1), 2070 cm^{-1}, 38 p.p.m. (*b*) Signal due to 20-fold diluted OCS; ν_1, 10 p.p.m.; ν_2, 1.9 p.p.m. (*c*), (*d*) Gaussian correlations of signals in (*a*), (*b*) respectively.

advantage. Thus Brown *et al.* (1988), working at around 60–64 GHz with a Stark modulated cavity spectrometer, reported data for glycine and thymine, and refer to other work on uracil, although there are as yet no reported data on analytical sensitivity.

My present work has been directed towards the design, construction and application of simple, low-cost spectrometer designs to routine gas analysis. Using a semiconfocal Fabry–Perot cavity operating in the 18–26 GHz region using sinusoidal Stark field modulation, calibration curves for ammonia (Thirup *et al.* 1986), water (Davis *et al.* 1987) and acrylonitrile (Wang *et al.* 1990) have been obtained. The limits of detection obtained: ammonia, 2 p.p.m., 23.870 GHz; water 130 p.p.m., 22.235 GHz and acrylonitrile, 470 p.p.m., 18.967 GHz, compare reasonably well with the theoretical calculations based upon the calculated line strengths and the calculated sensitivity of the overall spectrometer systems. In the study on ammonia a practical sensitivity, based upon the limit of observed detection and the known line strength for the ammonia transition, yielded a sensitivity of about $2 \times 10^{-9}\ \mathrm{cm}^{-1}$. Based on this figure, one would expect a limit of detection for water of the order 300 p.p.m., and for acrylonitrile 440 p.p.m. The theoretical sensitivity of the spectrometer $\alpha_{\min}$ can be calculated from the equation:

$$\alpha_{\min} = (2\pi/Q_{\mathrm{L}}\,\lambda)\,(4kTN_{\mathrm{F}}\,\Delta f/P_0)^{\frac{1}{2}}, \tag{1}$$

where π, k and T have their usual meanings, Q_{L} is the loaded quality factor of the cavity (measured as 3700 at 19 GHz). N_{F} is the ratio between the noise output of the actual system and the noise output caused by thermal noise of the microwave circuit if the detector and amplifier were noiseless. The value of N_{F} for the spectrometer described above has been measured by us as 24 Δf is the bandwidth over which the measurements are made. With the lock-in amplifiers used in this work, that figure is of the order 1 Hz. P_0 is the microwave power reflected from the cavity. In earlier work that was about 0.8 mW, in more recent work it was of the order 4 mW.

The calculated value for $a_{\min}$ is therefore of the order 6×10^{-12} cm^{-1} depending upon the exact frequency of operation and value of the various factors involved. The discrepancy between theoretical and measured sensitivity for the spectrometer system may well lie with inefficient coupling between the various parts of the microwave system and hitherto unidentified sources of noise in the system. Discrepancy between the measured noise figure on the detector–amplifier train and the observed value when it is coupled into the system could also be a contribution, as indeed could experimental error in the calibration procedures. None the less, both figures are in reasonable agreement with those of others in the field using Fabry–Perot cavity spectrometers, and give an indication of what may be achievable in practice.

The calibration curve for the ammonia and acrylonitrile were convex to the gas concentration axis from the origin, although the water calibration plot was near linear. The log (instrument response) against log (concentration) plot having gradients of 0.39 for acrylonitrile 0.87 for ammonia and near unity for water over their working range. The exact reasons for the curvature are not known, but it is certain that there are both spectroscopic and instrumental contributions to the effect.

5. Microwave spectroscopy and trace analysis

Study of many papers on microwave spectroscopy, some of them referenced herein, reveals sensitivities achieved in practice of around 10^{-9} cm^{-1}. This figure is about average for cavity spectrometers over the range 18–140 GHz. Fourier transform techniques may gain an order of magnitude over this, at best. The trade-off between cost, complexity, operational ease and maintenance mitigates against the use of Fourier transform techniques at the present time. The increase in absorption coefficients in working at the higher frequencies makes that spectral region more attractive, but the theoretical increased sensitivity in terms of limits of detection rarely seems to be achieved, due to increased detector and source noise and complexity in spectrometer design. Taken together with the greatly increased cost involved in work above 40 GHz at present, the practicality of doing the work rapidly dampens the enthusiasm for the higher frequencies. Exactly where the cost/benefit plateau is achieved is of course debatable; I believe it comes at around 100 GHz. At these frequencies and below, expected limits of detection are in the 1–10 p.p.m. region with reasonable cost and complexity penalties. If one can tolerate loss of an order of magnitude in sensitivity then work in the 20–60 GHz range is really quite attractive offering a compact, sensitive and selective method of gas phase chemical analysis. No doubt the tremendous advances that are still being made will modify these comments in the years to come.

I am indebted to my colleagues and mentors Gunnar Thirup and John G. Baker, to my many sponsors over the years and to my research group, past and present, for all their contributions and help.

References

Andrews, D. A. & Baker, J. G. 1987 Application of pulsed microwave–microwave double resonance. I. Relaxation studies in gases. *J. Phys.* B **20**, 5675–5704; II. Broadband Fourier spectroscopy. *J. Phys.* B **20**, 5705–5722.

Baker, J. G. 1990 Millimetric wave trace analysis of gases. Report to the SERC, Swindon, U.K., on Contract no. GR/E02260.

Brown, R. D., Crofts, J. G., Godfrey, P. D., McNaughton, D. & Pierlot, A. P. 1988 A Stark modulated supersonic nozzle spectrometer for millimetre wave spectroscopy of larger molecules of low volatility. *J. molec. Struct.* **190**, 185–193.

Davis, A. S., Leontakianakos, A. N., Benmakroha, F., Wang, P., Haider, R., Alder, J. F. & Thirup, G. 1987 Microwave spectral emission from a glow discharge filled 18–26 GHz Fabry–Perot cavity spectrometer. *Analyt. chim. Acta* **200**, 593–607.

Dreizler, H. 1986 Experiences with microwave Fourier transform spectroscopy of molecular gases. *Molec. Phys.* **59**, 1–28.

Hirose, S., Hayashi, M., Tamura, N., Kamidate, T., Karube, I. & Suzuki, S. 1982 Determination of ammonia with a Stark microwave cavity. *Analyt. Chem.* **54**, 1690–1692.

Hirose, S., Hayashi, M., Tamura, N., Kamidate, T., Karube, I. & Suzuki, S. 1983 Determination of urea in blood serum with the use of immobilised urease and a microwave cavity ammonia monitor. *Analyt. chim. Acta* **151**, 377–382.

Jones, C. E. & Beers, E. T. 1971 Determination of the number of frequency measurements necessary for the microwave identification of a gas in a mixture. *Analyt. Chem.* **43**, 656–659.

Kolbe, W. F. & Leskovar, B. 1983 Millimetre and submillimetre wave absorption by atmospheric pollutants and constituents. *J. Quant. Spectrosc. Radiat. Transfer* **30**, 463–478.

Kolbe, W. F. & Leskovar, B. 1985 A 140 GHz microwave spectrometer for atmospheric analysis of pollutants. *Int. J. Infrared Millimetre Waves* **4**, 733–749.

Leasure, C. S., Fleischer, M. E., Anderson, G. K. & Eiceman, G. A. 1986 Photoionisation in air with ion mobility spectrometry using a hydrogen discharge lamp. *Analyt. Chem.* **58**, 2142–2147.

Longo, I. 1989 A compact Stark spectrometer of new design for gases at microwave frequencies: the helical groove spectrometer. *J. Phys.* E **22**, 239–241.

Thirup, G., Benmakroha, F., Leontakianakos, A. N. & Alder, J. F. 1986 Analytical microwave spectrometer employing a Gunn oscillator locked to the absorption line. *J. Phys.* E **19**, 823–830.

Uehara, H., Ijuuin, Y., Morino, Y., Kamidate, T., Akiya, N. & Imai, H. 1980 Continuous ammonia monitor using a Stark microwave cavity resonator. *Rev. Sci. Instrum.* **51**, 334–337.

Varma, R. & Hrubesh, L. W. 1979 Chemical analysis by microwave rotational spectroscopy. In *Chemical analysis* (ed. P. J. Elving, J. D. Winefordner & I. M. Kolthoff), vol. 52. Wiley.

Vogelsanger, B., Andrist, M. & Bander, A. 1988 Two-dimensional correlation experiments in microwave Fourier transform spectroscopy. *Chem. Phys. Lett.* **144**, 180–186.

Wang, P., Crouch, J. J., Anstice, P. J. C. & Alder, J. F. 1990 Determination of acrylonitrile in air by microwave rotational spectroscopy. *Analyt. chim. Acta.* (Submitted.)

Discussion

D. Littlejohn (*University of Strathclyde, U.K.*). What difficulties are likely to be encountered when microwave spectroscopy equipment is used in industrial plants for on-line process stream analysis?

J. F. Alder. Undoubtedly the biggest problem will lie with the sampling interface, between high-pressure process streamlines and the vacuum of the spectrometer. This is of course not unique to microwave spectrometry. One must also calibrate the spectrometer for quantitative applications that can be problematic on-line. Plant vibration may also be a nuisance, although real-time system optimization and recalibration would overcome this to a large extent.