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# Microwaves in Chemistry

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**ABSTRACT** The unique properties of microwaves make them useful in many diverse applications across a wide range of fields, spanning much of engineering and science. In the chemical sciences, microwaves provide a toolkit of electric and magnetic effects with which, at high power, unconventional heating modes can be used to produce new materials not obtainable by conventional heating. At low power, unique microwave properties can be used to make revealing spectroscopic measurements. In this review, we consider the current outlook for microwaves in chemistry beginning with the theoretical framework for our understanding of microwaves interactions and the causes of results observed. We then survey major application areas including in synthesis and emerging areas in catalysis, energy, and environmental applications. Finally, we review new concepts in dielectric and magnetic spectroscopy at microwave frequencies with a focus upon dielectric property measurement and electron paramagnetic resonance. This nonexhaustive review seeks to highlight important and emerging areas in the chemical sciences and put into context recent developments and advances in our understanding of microwave applications in this diverse area of science and engineering.

**INDEX TERMS** Catalysis, chemical analysis, microwave catalysis, microwave chemistry, microwave heating, microwave measurement, microwave spectroscopy, microwave synthesis, microwaves, synthesis.

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## I. INTRODUCTION AND BACKGROUND

Microwaves have a long history in the chemical sciences. Since microwaves were first generated in the 19<sup>th</sup> century, they have been used in a wide range of experiments, to measure and heat, stimulating many different phenomena from magnetic resonance to cyclotron resonance, from catalysis to sintering and synthesis. The breadth of applications is matched only by their multidisciplinary nature. Microwave science transcends traditional discipline boundaries and is still growing in relevance, continuously finding many new applications. In microwave chemistry, at low power, measurements using the microwave electric field have been able to sensitively measure changes in charge dynamics resulting from phenomena as varied as catalyst deactivation to adsorption of ammonia in zeolites [1], [2], whilst measurements with high frequency magnetic fields are commonly used in magnetic resonance imaging, nuclear magnetic resonance and electron paramagnetic resonance [3]. More recently, microwave magnetic field effects have been used to produce quantum

images of current flow in graphene and even measure pulses in neurons [4], [5].

At high power, microwaves have been used in many organic reactions, synthesis and catalysis. The different mechanisms in microwave heating lead to dramatically different results from conventional heating in chemical processes such as catalysis, which has been the subject of much debate in the literature. The rapid and highly selective heating of microwaves, in which heat is generated locally in regions with differing complex permittivity, activates different chemical processes than conventional heat. In addition, the microwave-electric field and the microwave-magnetic field interact very differently with chemical species, and when field strengths are increased, field ionization can take place, which further shifts the reaction away from the expected result from conventional chemistry. Over the past 20 years and more, further understanding of how microwaves interact with chemical species has developed and has led to theoretical frameworks, within which we can understand microwave enhanced chemical

reactions, for example in microwave heating of powders for heterogeneous catalysis [6].

This review begins with a discussion of our fundamental understanding of microwaves in chemistry. We identify themes in microwave driven reactions and frameworks for understanding the causes of common observations and associated challenges. We review microwave effects in chemistry such as enhanced reaction rates and changed product distributions, before considering the challenges associated with accurate measurement and control of reaction conditions and temperature. This is then followed by an exploration of microwave heating applications in key areas of chemistry, including synthesis and catalysis, before looking at emerging applications in dielectric and magnetic spectroscopy.

Whilst the focus of this review is on microwaves in chemistry, the breadth of applications and opportunities in the field are too large to cover in a short review. This review also seeks to demonstrate the multidisciplinary nature of microwave chemistry, where much of the work interfaces with engineering, physics and the biological sciences. Indeed, it is difficult to find a field of science or engineering in which microwaves are not currently finding new applications.

## II. THEORETICAL FRAMEWORK

In the chemical sciences, microwaves have for some time been recognized as producing useful and often unexpected results. But how do we begin to understand the enhanced reaction rates, lower reaction temperatures and higher yields often observed in microwave assisted reactions? New results obtained using microwaves in chemistry (and indeed other sciences and engineering) often precede the theoretical foundation upon which our understanding of them is based, and unsurprisingly, major questions remain open in many areas of microwave chemistry. In recent times this has led to robust debate in the literature, but also great steps in our understanding of microwave interactions with complex chemical systems. Fundamentally, the theories of electromagnetism in materials differ between disciplines only by convention and notation, but in Chemistry, complex chemical mixtures present scientific challenges to our understanding on a) the microscopic scale, compounded by competing reaction pathways and additional complexities at b) the macroscopic scale.

In work describing reactions in organic synthesis, research groups in the US and Europe provided contrary results to determine whether there is some ‘specific microwave effect’ responsible for different results obtained by conventional heating [7]–[10]. The consensus in the microwave chemistry community is that – clearly – microwave ‘quanta’ are not energetic enough to interact with chemical bonds directly, there must be some other energy exchange, most likely through heat, which leads to the activation of chemical mechanisms. In addition, the highly localized heating caused by microwaves in heterogeneous mixtures can cause hot spots on the scale of features such as polycrystalline particles, which when heated can lead to a local thermal runaway. Higher order effects can also take

place. As field strengths increase, the fields can become ionizing, further complicating the chemical reaction pathways. Microwave dielectric and magnetic chemical spectroscopy make use of frequency and temperature dependent polarization and absorption to measure a range of material properties (see section V of this review), but for applications such as synthesis and catalysis (see sections III and IV), one often starts with a heterogeneous mixture comprising polycrystalline materials that have many active surface species and associated complex permittivities. To construct a framework to understand the interaction, we can separate the problem into macroscopic and microscopic effects. One can make use of the vast literature on mixing theories (which we shall not cover here) to determine effective permittivities, but such theories say nothing of the molecular interaction or local reaction conditions.

Macroscopically, the rapid, volumetric and selective heating caused by microwaves is the result of many competing mechanisms. A general understanding of such heating considers the effective complex permittivity or loss tangent of the sample based upon a time-dependent polarization of the material. This has been described in numerous textbooks [11], [12] and is summarized in the general form in equation (1).

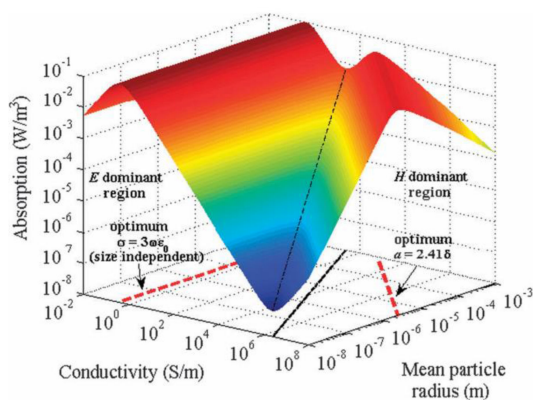
$$P = \frac{1}{2} \int_V \sigma |\vec{E}|^2 dV + \frac{\omega}{2} \int_V (\epsilon_2 |\vec{E}|^2 + \mu_2 |\vec{H}|^2) dV \quad (1)$$

Equation (1) describes the time-averaged power dissipation and accounts for contributions from conductivity, dielectric and magnetic losses, where  $\sigma$  is the electrical conductivity,  $V$  is the sample volume,  $\vec{E}$  is the vector electric field,  $\omega$  is the angular frequency,  $\epsilon_2$  is the imaginary permittivity,  $\mu_2$  is the imaginary permeability and  $\vec{H}$  is the vector magnetic field.

Standard approaches to the measurement of these properties are well-established [11]–[15].

For dielectrics, though the microscopic contributions to the real and imaginary permittivity from dielectric coupling with transverse optical phonons, charge carriers, direct and rotational polarization can be identified, the quantitative characterization and prediction of them remains elusive. In complex, heterogeneous media, effects such as field redistributions caused by depolarization and screening, and the impact of polycrystallinity and grain boundaries, create unpredictable electromagnetic fields.

A model of electromagnetic absorption in powders of small conducting particles was developed by Porch *et al.* in 2012 [6], which is based upon full analytic solutions for the electric and magnetic dipole absorption of small conducting spheres. The model was used to develop guidelines on the efficiency of microwave heating based upon the particle size and conductivity of powder particles. Small, highly conducting particles were shown to not heat effectively when placed in a microwave electric field because of screening of the field from within the particle. Instead, magnetic absorption associated with induction was shown to cause the large experimental heating rates observed for small metal particles. Figure 1 shows that at low conductivities, absorption in the macroscopic particle is predominantly due to electric dipole



**FIGURE 1.** Heating rates in powders of different particle radius and conductivity [6].

absorption (driven by a microwave electric field), which is maximized when the conductivity is approximately  $\sigma \approx \omega\epsilon_0$ . For highly conducting particles, magnetic dipole absorption dominates over the full range of particle radii, with the maximum magnetic dipole absorption (for non-magnetic powders) occurring at  $a \approx 2.41\delta$ , where  $\delta$  is the skin depth. This is a remarkable result, meaning that for a metal of any given conductivity, maximum microwave magnetic absorption can be assured by simple selection of the mean particle radius.

Microscopically, the theoretical framework underpinning our understanding of microwaves in solids is complex: in conductors, causing phenomena such as cyclotron resonance, and in magnetic materials, causing electron paramagnetic resonance and ferromagnetic resonance. The microscopic contributions to the complex permittivity under different reaction conditions are not trivial to predict from first principles. Computational approaches have been developed and proven to predict the properties of some relevant oxide materials at high temperature. Using density functional theory to calculate harmonic properties of oxide lattice phonons and introducing anharmonic effects using quantum field theory, a robust approach has recently been introduced [16]. A fundamental microscopic model of the temperature dependence of metal oxides and other materials may be particularly useful in microwave heating of solids in synthesis and catalysis, since our ability to predict observed results is significantly diminished by the lack of data available on high temperature permittivities of relevant materials. Current models are often oversimplifications based upon room temperature dielectric properties and can lead to erroneous conclusions.

### III. MICROWAVE SYNTHESIS

The advantageous effects of microwave heating have found a great deal of use in chemical synthesis. Rapid and localized microwave heating can produce materials and phases difficult to achieve under normal reaction conditions in solid state, organic synthesis and solution phase chemistry [17]–[20]. In the solid state, microwave heating can be used to make novel materials that are inaccessible by other routes [21] or materials

with properties that are improved compared with when heated conventionally.

In the solid state (more so than in solution), the mechanisms of microwave heating are made more complex by the structure and interfaces at varying length scales throughout the sample.

Our understanding of these mechanisms continues to develop, but there are major challenges associated with verifying processes and temperatures inside the sample, as discussed in section II above. This lack of temperature data has often led to claims of ‘non-thermal’ effects caused by microwave electric or magnetic fields, which are difficult to prove [22], [23]. There has often been contention in the literature as a result and claims of such effects are commonly treated with skepticism [7]–[10].

Simple mechanical mixtures of solids can form effective reaction mixtures for solid state synthesis. High permittivity materials can lead to regions within the mixture and dramatically different reaction conditions throughout. For effective solid-state synthesis in microwaves, reagents should have a high enough imaginary permittivity for the microwaves to couple well enough and provide the required rapid heating of the reagents. In many cases, reagents used may have a small imaginary permittivity and synthetic chemists must search for alternative precursors, or use a susceptor material that will heat well such as silicon carbide or carbon, either mixed into the reaction mixture or forming a vessel (or vessel coating) in which the mixture sits. This will transfer heat energy to the reaction mixture and is an indirect form of heating that is closer to the conventional heating approach. One must also ensure that susceptors in direct contact with reaction mixtures are not able to influence the reaction and contaminate the products. Another approach for samples with low imaginary permittivity is the use of microwave plasma processing [24], though the reaction conditions in this regime will be even more complex with the plasma itself often acting as a source of reactive species.

Important applications of solid-state microwave synthesis include in the production of oxides, carbides, silicides, chalcogenides and nitrides. Perhaps most important amongst these is oxides, since they have an extremely wide range of applications and their synthesis is common in microwave chemistry. Oxides are often straightforward experimentally to synthesize and in microwaves, large numbers of experiments have shown faster reactions with significantly lower reaction temperatures reported [25]–[27]. Metal oxides can exhibit a reasonable microwave imaginary permittivity, which often increases dramatically at higher temperatures, leading to a potential thermal runaway effect. In addition, reduced oxides in which some oxygen has been removed from the crystal lattice can have higher microwave absorbing properties because of the extra charge carriers generated by the oxygen vacancies. Reduced oxides such as  $\text{TiO}_{2-x}$  have been used to increase heating rates [28], and more recently to help activate catalytic processes, which will be covered in the next section of this review.

Microwave solid state inorganic reactions have become more popular in the last two decades and a comprehensive

review has been provided by Kitchen *et al.* [29]. Even before this, microwaves were growing in popularity in microwave assisted organic synthesis (MAOS). Microwave devices are now commonplace in the laboratories of organic synthetic chemists and MAOS is well-established as a tool in academia and industry. The first reports of the use of microwave heating to accelerate organic chemical transformations were in 1986 [30], [31]. Early experiments used simple, modified domestic microwave ovens, and suffered from a lack of controllability and reproducibility. There was also a general lack of understanding of microwave heating in the field of organic synthesis. Safety concerns were also an issue, with flammable organic solvents placed in a microwave electric field and at the time, there were few adequate temperature and pressure controls. Microwave heating of organic synthetic reactions was commonly enabling a reduction in chemical reaction times from hours to minutes, whilst also reducing side reactions that lead to unwanted products. There are a large number of organic chemical reactions that can be enhanced using microwave irradiation, though it should not be expected that this should be the case for all organic synthetic reactions since microwaves generally cause high temperatures unsuitable for some reagents and for reactions that rely upon a kinetically controlled pathway.

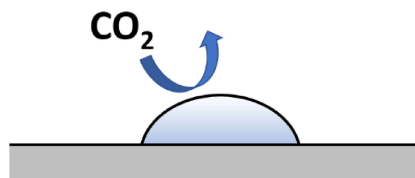
Commercial microwave reactors are often designed with organic synthesis in mind, and a large market now exists for benchtop laboratory equipment. Using these devices, controlled microwave heating of samples in sealed-vessel systems can produce dramatically reduced reaction times and higher yields. An authoritative review of many synthetic reactions in MAOS has been produced by C. O. Kappe [32].

#### IV. MICROWAVE CATALYSIS

The benefits of microwave heating in catalysis have been known for some time, with early work recognizing enhanced reaction rates and product selectivity in some reactions when microwaves were used instead of conventional heating [33]–[35]. As in other fields of microwave chemistry, this led to discussions about the causes of the enhancements and early speculation on the existence of non-thermal effects [36]–[38], followed by a number of studies concluding that such effects do not exist [22], [23]. At high field strengths, higher order processes such as plasma generation can influence reactions and lead to unexpected results, which are sometimes attributed to non-thermal effects. However, the discussion can become mired in semantic questions since plasmas are generated by high electric fields (non-thermal) and microwave plasmas at atmospheric pressure can be extremely hot (thermal). Microwave plasmas are being used in their own right in catalytic reactions such as CO<sub>2</sub> conversion [39], but to conclusively demonstrate the influence of microplasmas in heterogeneous catalytic reactions is difficult. For normal reactions without plasmas, rate enhancements and shifts in product selectivity are generally attributed to thermal effects and highly localized heating at sites of high complex permittivity contrast. Such

**TABLE 1. Three Cases for Microwave Heterogeneous Catalysis**

	Catalyst particle	Support material	Gaseous reagents
I	High T	High T	Bulk T
II	High T	Bulk T	Bulk T
III	Bulk T	High T	Bulk T



**FIGURE 2. Schematic diagram of a heterogeneous catalytic system, with CO<sub>2</sub> gas passing over a metal catalyst particle (commonly tens of nanometers in diameter) on the surface of a support, such as a zeolite or alumina.**

thermal effects can create large differences between the observed temperature and effective real reaction temperature at active sites and in the majority of microwave assisted reactions reported in the literature, temperatures far lower than those in conventionally heated reactions are reported.

A common problem faced by microwave chemists is how to measure temperature accurately. The bulk temperature of samples cannot be measured using thermocouples in high microwave fields, and so fiber-optics or infra-red pyrometry must be used. Though this can lead to accurate determination of the bulk temperature, the question remains about the effective real reaction temperature at reaction sites. Zhang, Hayward and Mingos [40] considered three cases for a gas/solid heterogeneous catalytic system exposed to microwaves in which catalyst particles are supported on a dielectric material with gaseous reagents. Table 1 shows the cases where microwave irradiation leads to a significant temperature gradient between the catalyst, the support, and the bulk temperature of the sample. Figure 2 shows a schematic diagram of the typical supported catalyst particle exposed to microwaves.

Zhang *et al.* concluded from experimental results and a heat transfer model that a significant temperature difference between the catalyst and the bulk gas, and between the catalyst particle and the support could not be possible. Though they acknowledge that X-ray diffraction measurements on the catalyst before and after microwave heating demonstrated local phase changes characteristic of temperatures >200 K higher than the bulk temperature, confirming the presence of hotspots. This behavior is difficult to predict in catalyst systems and results not only in rate enhancements, but also in apparent shifts in the equilibrium constant. However, many of the assumptions in these calculations lead to a highly simplified and inaccurate model. Most notably, there is a lack of published data detailing the high temperature complex microwave permittivities of many of the oxide or zeolite support materials used in these reactions. For example, alumina is known to exhibit a dramatically increased imaginary permittivity at



high temperatures. And with some heterogeneous catalytic reactions reaching  $>1000$  K, the heat transfer models become vastly more complex, with support materials potentially becoming involved in the catalytic reaction themselves.

Despite the complexities of the mechanisms of microwave interaction, strategies to harness the advantageous effects of microwave heating have been used to great effect. In the field of catalysis, the use of microwaves has become increasingly popular and is now being applied to a vast range of reactions and applications, often under the banner of ‘process intensification’. New applications are emerging in microwave catalysis, applied to global challenges in energy and environmental science. Our recent results have demonstrated the use of microwaves for effective monitoring of catalyst deactivation [1], production of highly pure hydrogen from fossil fuels and the destruction of plastic waste [42]–[44]. Palma *et al.* [45] have given a recent and extensive review of many fields of application, including preparation of catalyst materials and applications in oil and gas processing such as hydrocarbon conversion processes, partial oxidation reactions, production of syngas and water-gas shift reactions, desulfurization, and dehydrogenation of hydrocarbons.

## V. MICROWAVE SPECTROSCOPY

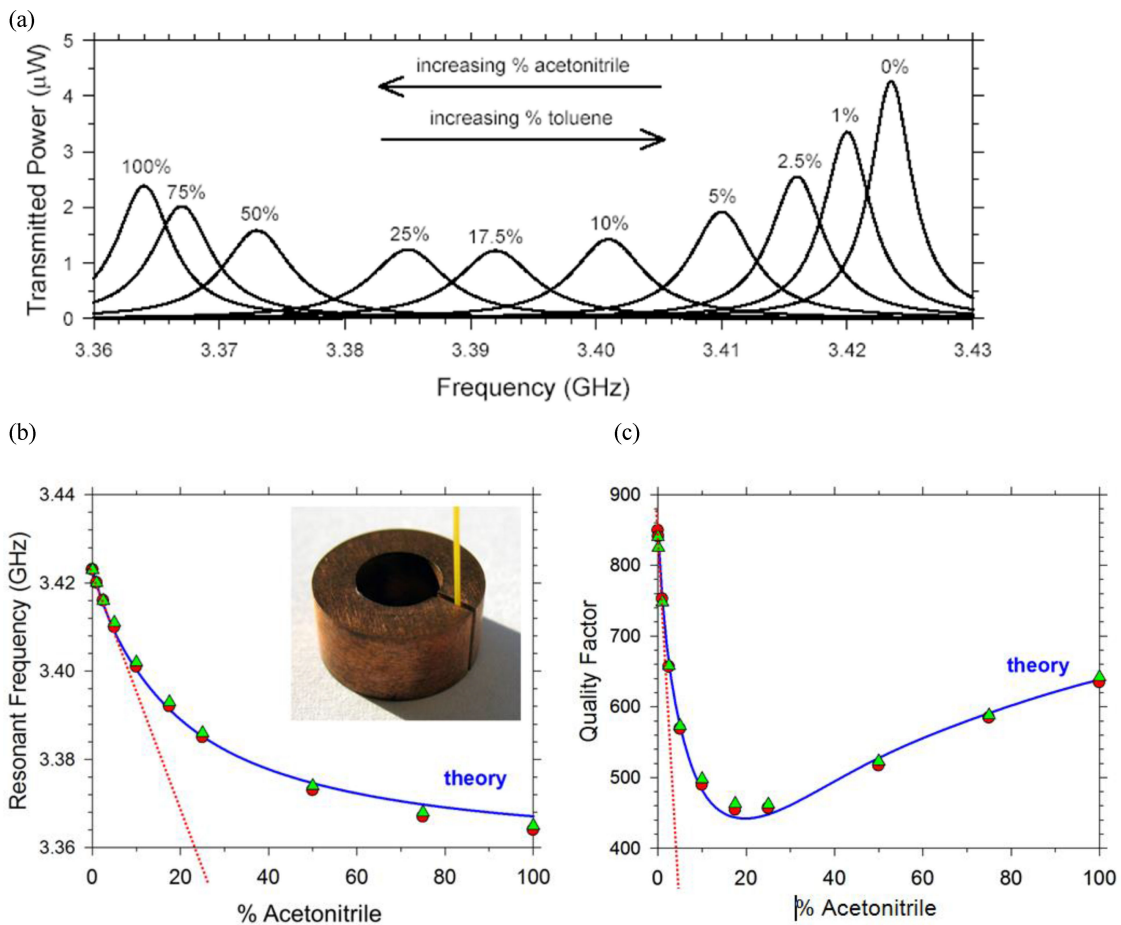
Spectroscopy is the study of the interaction of a specimen with electromagnetic radiation as a function of the frequency of the radiation. Here, this definition will be generalized to include interactions at discrete frequencies, and we will focus on case studies in dielectric property measurement [46] and electron paramagnetic resonance (EPR) [47], both of which have proven to be essential tools in the Chemist’s inventory for the fundamental understanding of materials and material interactions, and both of which benefit from innovations in microwave engineering.

Microwave spectroscopy in the typical frequency range 1–10 GHz (often centered on the ISM frequency of 2.45 GHz) has been applied diversely across the industrial, scientific and biomedical sectors [48]–[51]. Its usefulness is based on the low cost and high robustness of instrumentation, high measurement accuracy, high sensitivity, high penetration in dielectrics (i.e. for volumetric sensing), fast data rates and non-invasive nature for evaluating material properties and processes; it has been shown to be applicable to the study of all states of matter [52]–[56]. Microwave sensors for spectroscopy are based on resonant and non-resonant methods [46], [48]. Whilst the former operate only at discrete frequencies, they offer much higher resolution and exquisite sensitivity, especially when small changes in material property are being measured, and can be operated over a broader bandwidth by using multiple resonant modes [58]. Another advantage of using resonant sensors is that the antinodes of electric and magnetic fields become spatially separated, meaning that electric and magnetic properties of samples can be evaluated independently [59]. Recently, there has been much effort in developing miniaturized, planar microwave sensors using metamaterial-inspired methods driven by the demands

of Internet of Things [60] and lab-on-chip applications [55], [61], the latter having the potential to revolutionize point-of-care, label-free biosensors [51]. The same fundamental field interactions for sample sensing and diagnostics at low field amplitudes are also responsible for sample heating at high amplitudes, so microwave test fixtures have dual roles as both sensors and applicators, opening up the possibility of simultaneous heating and materials characterization.

The principle of operation of microwave resonant sensors and applicators is based on the fact that any sample exposed to an oscillating EM field will develop an oscillating electric  $p$  and/or magnetic dipole moment  $m$ , which will depend on both its material properties and geometry. The generation of a dipole moment increases the stored EM energy of the system, which is the fundamental origin of the measurement. For maximum sensitivity in such a diagnostic we must ensure the maximum dipole moment per applied field. This means suppressing the effects of depolarization, ideally making the samples thin perpendicular to the direction of the applied field, thus minimizing the effect of any polarization charges induced on surfaces perpendicular to the field. A striking example is that of a thin, water-filled capillary, whose induced electric dipole moment is around  $\times 80$  larger for an electric field applied parallel to the capillary, compared with when applied perpendicular [62]. In terms of the electric field  $E$  within a material, we express the material’s polarization as  $P = p/V = \epsilon_0(\epsilon - 1)E$ , where  $V$  is the sample volume, within which we assume that  $P$  is uniform. The relative permittivity  $\epsilon$  of the material (or, more precisely,  $\epsilon - 1$ ) determines its polarisation per unit internal electric field; its real (i.e. in-phase) part  $\epsilon_1$  quantifies energy storage, whilst its imaginary part  $\epsilon_2$  quantifies energy loss. The resulting dielectric response function  $\epsilon(\omega, T) = \epsilon_1(\omega, T) - j\epsilon_2(\omega, T)$  depends on both frequency  $\omega$  and temperature  $T$  and is a result of conduction, relaxation and resonant phenomena. Conductive behavior tends to dominate at lower frequencies ( $<1$  MHz), associated with the transport of free electrons or ions. Resonant behavior is associated with inter and intra molecular vibrations and occurs at infrared frequencies and above ( $>1$  THz). At RF and microwave frequencies (between about 0.1 to 10 GHz), both conductive and relaxation effects dominate the dielectric response. Polar liquids (such as water) are well-described by the Debye theory of dielectric relaxation, which can be appended to include ionic conduction [46].

Some examples now follow on the application of microwave resonators, together with resonator (cavity) perturbation theory [63]–[66], to measure the dielectric properties of samples. The polarization is found from the shift downwards in resonant frequency, whereas the loss is found from the decrease in resonator quality factor (Q). Most resonators are designed to have very high Q factors when empty, typically in the range 1000 to up to 10000 at room temperature, depending on the volume occupied by the stored EM energy within the resonator, with more compact resonators having lower Q owing to their smaller volume to surface area ratio. A compact, high Q cavity, in which the sample is placed at an



**FIGURE 3.** (a) Resonant traces of a copper 3.5 GHz split ring resonator for a sample made up of a mix of acetonitrile in toluene; (b) the shift in resonant frequency as a function of acetonitrile in toluene mixture, taken from Fig. 3(a); (c) the corresponding quality (Q) factor. The data shows three repeats and also the theoretically predicted trend based on cavity perturbation theory. The SRR is shown in the inset; the diameter of the inner hole is 5 mm, the outer diameter is 13 mm, the length is 5 mm and the gap is 0.5 mm. The SRR is housed in an outer radiation shield (not shown) and the solvent mix is contained in a PEEK capillary of 0.3 mm inner diameter [69]. The dotted red lines show the high sensitivity for detecting trace quantities of the highly polar component.

electric field antinode, will enable a highly sensitive measurement of dielectric properties. Since we deal exclusively with differences in frequency in the cavity perturbation technique, in principle changes in resonant frequency and bandwidth are easily measured to a resolution of around 100 Hz, leading to resolutions of about 1 part in  $10^4$  and 1 part in  $10^3$  for the real  $\epsilon_1$  and imaginary  $\epsilon_2$  parts, respectively, of the sample's complex permittivity. This is a much higher resolution (by up to two orders of magnitude) than can be achieved with non-resonant approaches (e.g. the open-ended coaxial probe) [67], [68], but with the drawback of measurements only being possible at spot frequencies.

Figure 3 shows resonant traces (i.e. plots of transmitted power  $|S_{21}|^2$  as a function of frequency) for a 2-port split ring resonator (SRR), with Q of 1200 and resonant frequency 3.5 GHz when empty [69], measured using an Agilent E5071B vector network analyzer. For resonant measurements we fit the transmission spectra for each mode to a Lorentzian function and extract the required resonator parameters (i.e. frequency and Q) using non-linear least squares fitting. A

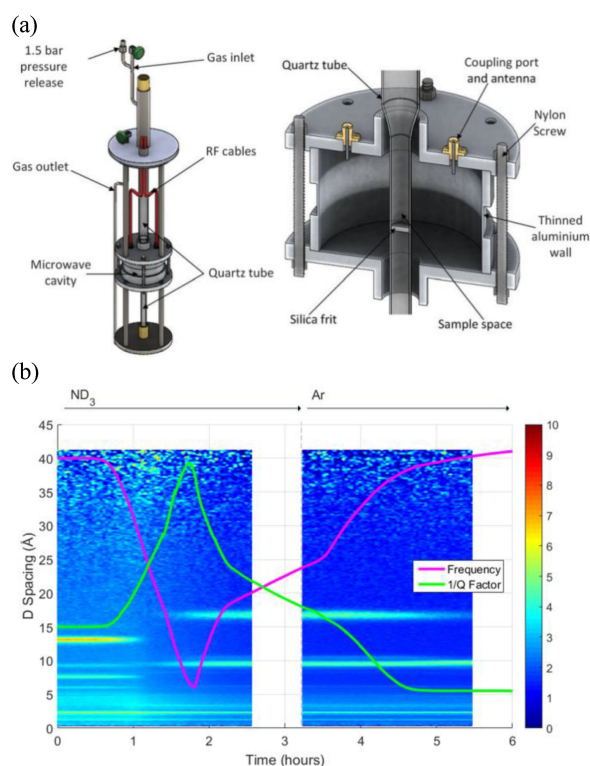
solvent mix of acetonitrile and toluene has been chosen here since they are totally miscible and have high dielectric contrast between the two pure phase components (the real part of the relative permittivity of toluene is about 2.4 and acetonitrile about 38). As can be seen, there is a monotonic decrease in the resonant frequency of the SRR as the solvent mix was changed from pure toluene to pure acetonitrile, owing to increased polarization, but a prominent maximum in the microwave loss (i.e. a minimum in Q) for an acetonitrile concentration of about 20%. This can be entirely understood using the concept of depolarization mentioned above, since in these experiments the electric field is applied perpendicular to the sample, which resides in a PEEK (polyether ether ketone) capillary of 0.3 mm inner diameter and sits in the SRR's gap. As the concentration of acetonitrile increases so too does  $\epsilon_2$  of the solution, but at the same time the electric field  $E$  within the sample reduces owing to depolarization. Since the microwave loss is proportional to the product  $\epsilon_2|E|^2$ , the loss initially increases for small increases in the concentration of acetonitrile, then has a maximum at about 20% concentration, then reduces as

the concentration tends to 100%. Despite this multi-valued behavior, this SRR is capable of determining composition of the mix (to an accuracy of about 0.1%) for fluid volumes of 10 nl based on frequency shift alone. Note that it is ultra-sensitive to low concentrations of acetonitrile in toluene, and therefore for detecting trace amounts of highly polar liquid in a low polar host (e.g. water contamination of oil).

One of the experimental drawbacks of microwave resonator techniques is their sensitivity to changes in ambient temperature, as thermal expansion affects resonant frequencies via size changes, but also the permittivity of samples (especially polar liquids) are highly temperature sensitive. We can stabilize the ambient temperature to  $\pm 0.1$  °C by inserting the resonator equipment into a temperature-controlled oven, which is the best we can hope to achieve, yielding changes in the fractional change in complex permittivity values for typical polar solvents of around  $\pm 0.5\%$ . We make great efforts to correct for long term temperature drifts by using reference resonant modes which do not couple the sample [66], [70], which have been shown to be very effective for calculating relative permittivities of standard materials that compare favorably with accepted, precision values (e.g. quartz).

Recently we have developed instrumentation for the ISIS POLARIS neutron diffractometer at the UK's Science and Technology Facilities Council's Rutherford Appleton Laboratory, for real-time, simultaneous dielectric (microwave) and structural (neutron diffraction) characterization of absorption processes in solids [71], [72]. The aluminum cylindrical host cavity operates in its  $TM_{010}$  mode at 2.45 GHz (internal diameter 92 mm, internal length 40 mm), with high electric field on its axis, where the sample is placed. This system illustrates the additional functionality that can be built into microwave cavity approaches to dielectric spectroscopy, simply as a result of the non-invasive nature of the approach. One compromise in this instance is that the curved aluminum wall of the cavity has to be as thin as possible to have as little effect as possible on the diffracted neutron beam; this dictates the choice of aluminum over more conductive metals such as copper, owing to its much smaller neutron scattering cross section. For our cavity, this wall is about 1 mm thick, which has worked well in practice since it does not compromise the structural integrity of the cavity.

The system has been applied to the real-time measurement of ammonia storage in halide salts [71] and in metal-organic frameworks (MOFs) [72]. Ammonia is well known as a potential hydrogen storage material owing to its very high gravimetric (17.8 wt%) and volumetric ( $121 \text{ kg/m}^3$ )  $\text{H}_2$  density [73]. MOFs are multi-dimensional network structures comprising metal ions or clusters connected by organic links. They have high surface areas and pore volumes and are capable of storing a number of gases, such as hydrogen [74] and ammonia [75]. Ammonia has a very high electric dipole moment owing to the shape and electrochemistry of the  $\text{NH}_3$  molecule (1.46D, not far off water at 1.85D) so we are able to track the absorption and desorption of ammonia via cavity perturbation, as the sample changes its dipole moment accordingly. The flow of



**FIGURE 4.** (a) Schematic of the beam insert for the POLARIS neutron diffractometer, with an expanded, cross-sectional view of the bespoke microwave cavity; (b) Superimposition of the surface plot of Bragg diffraction and dielectric data at 2.45 GHz during ammonia absorption and desorption within the metal-organic framework (MOF) HKUST-1 under deuterated ammonia ( $\text{ND}_3$ ) and argon (Ar) flows. [72].

ammonia is interchanged with that of dry argon to remove the absorbed ammonia. The dielectric and diffraction data shown in Fig. 4 is for the MOF HKUST-1. In these experiments the cavity data were measured using a Copper Mountain S5085 network analyzer, which is both rugged and portable; the whole microwave system consisted of just the analyzer, the cavity and laptop computer to collect data, so there are few constraints to taking measurements in challenging environments. The changes measured are instantaneous and at the sample interface, not at some time later downstream using a more standard technique such as mass spectrometry. We have shown in separate experiments of ammonia absorption by zeolites [2] an almost perfect correlation between changes in resonant frequency and Q factor with downstream  $\text{NH}_3$  mass spectrometry data. Furthermore, features in the microwave loss data can be traced to order-disorder transitions within the coordinated network of bound ammonia molecules. Therefore, the combined methodology of diffraction and dielectric spectroscopy provides a valuable tool to interpret complex ammonia absorption and desorption behavior, providing insights that are not available from the use of these techniques individually. The system is currently being adapted to study the absorption dynamics of other polar molecules of interest, e.g. sulfur dioxide  $\text{SO}_2$ .



As a final example of the impact of microwave engineering on chemical spectroscopy, we consider electron paramagnetic resonance (EPR) spectroscopy (also known as ESR, electron spin resonance). This involves the Zeeman splitting of electronic spin states on application of a DC magnetic flux density  $B_0$ . EPR is the electronic equivalent of the more familiar NMR, which involves the splitting of nuclear spin states, and has been used since the 1940s. It is sensitive only to unpaired electrons and their interactions with neighboring magnetic nuclei. This allows the detection and identification of local paramagnetic species, leading to information regarding molecular structure, bonding, motion, concentration and pH [47], [76], [77]. EPR is able to interrogate catalytic processes and to characterize electrochemically active/battery materials and their participation in a number of redox processes, and fixtures for in situ monitoring of Li-ion batteries have been demonstrated [78].

Microwaves are used in EPR to provide the necessary pump energy to flip electrons between their two spin states, via coupling to a microwave magnetic field applied perpendicular to  $B_0$ , usually by means of a resonant cavity. The energy difference between the spin states is given by the well-known Zeeman formula  $\Delta E = g\mu_B B_0$ , where  $g$  is the Landé  $g$  value (used as an identifier for specific paramagnetic species, approximately 2 for free electrons) and  $\mu_B = 9.27 \times 10^{-24}$  J/T is the Bohr magneton. The necessary pump frequency is then  $f = \Delta E/h$  which is approximately 28 GHz/T, referenced to the applied flux density  $B_0$ . Commercial EPR systems operate at X-band (typically at 9.8 GHz and 0.35T), Q-band (34 GHz and 1T) and W-band (94 GHz and 3T), though mm-wave options exist at above 200GHz [79]. Increasing  $B_0$  enhances the resolution of EPR spectra but requires the use of superconducting magnets and more expensive microwave/mm-wave instrumentation, which increases both purchase and operational costs. By far the most common systems in operation worldwide work at X-band and use room temperature electromagnets, which can be water-cooled; this choice is a good compromise between resolution, convenience and cost.

Material samples are placed in the magnetic field antinode in an EPR resonant cavity, which at X-band frequencies is usually of a simple rectangular or cylindrical design. The cavity is critically coupled and excited at resonance. The drive field  $B_0$  is modulated at a typical frequency of 100 kHz and amplitude  $b_1$  to allow for phase sensitive detection of the reflected microwave power. The EPR spectrum is the plot of absorbed microwave power as a function of  $B_0$  as the latter is swept, where the microwaves are usually applied continuously but can be pulsed. The sensitivity of such a system is the product of the cavity Q factor and the effective mode volume, which is the volume occupied by the equivalent uniform microwave magnetic energy. High field, high frequency EPR therefore requires low loss dielectric resonators since the Q factor of metal cavities becomes compromised on miniaturization owing to their reduced volume to surface area ratios. Other subtleties linked to the design of EPR cavities are to ensure microwave field uniformity over the sample volume

and to allow the effective exposure to the sample of the modulation field  $b_1$  (given that the skin depth in copper at 100 kHz is only about 0.2 mm), which has led to the development of lumped-element type resonators such as the split ring (or loop gap) type [80]. Detuning of EPR cavities, with a reduction in Q, is an important factor in the measurement of aqueous samples where the sample can encroach upon the region of finite electric field, leading to large dielectric loss; field separation of electric and magnetic fields is generally better in loop gap resonators compared with distributed (cavity-type) resonators.

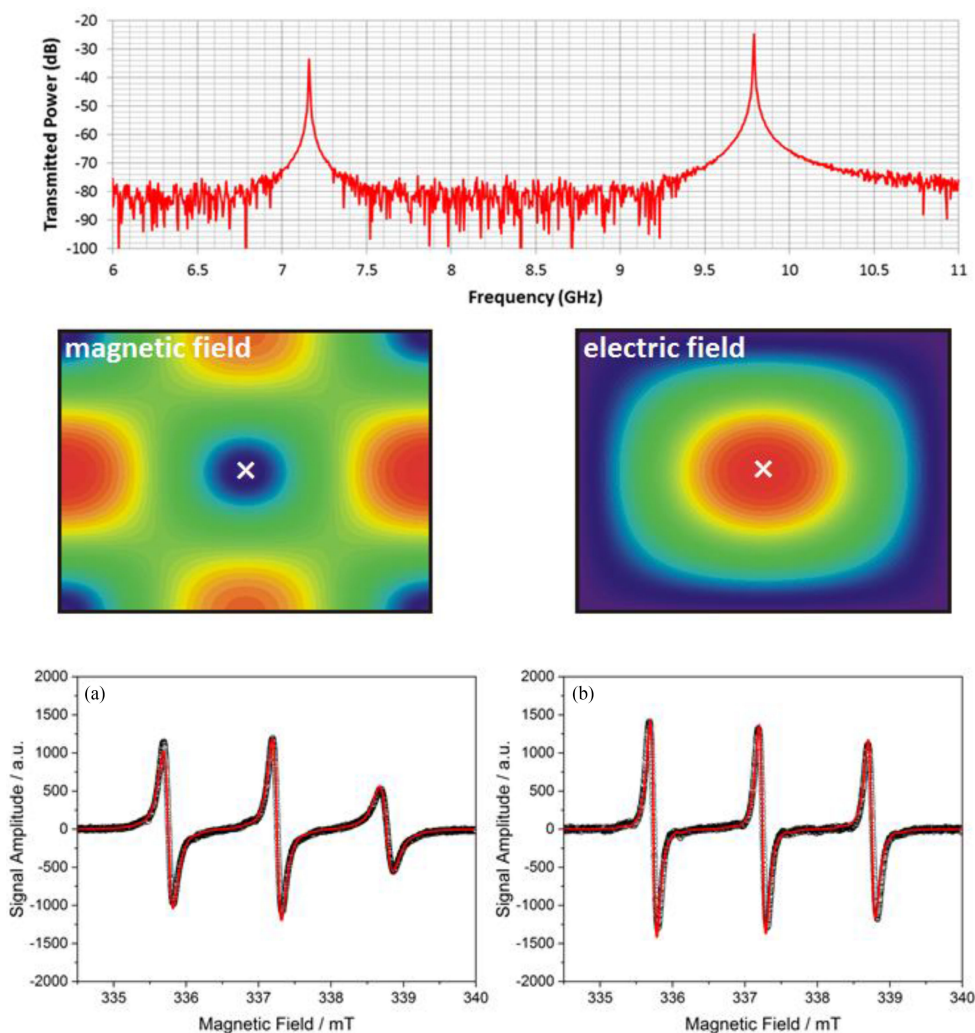
We develop bespoke cavities for X-band systems and have recently introduced a dual mode EPR cavity which allows simultaneous heating and EPR spectroscopy to be performed [3]. Chemical reactions can be perturbed away from thermodynamic equilibrium by imposing a rapid shock to the system, often by a temperature (T) jump, yielding non-equilibrium populations of reactive intermediate states. Most T-jumps are initiated by joule heating or IR lasers. However, since the EPR sample is excited magnetically in a mode such as  $TM_{110}$  for a cylindrical host cavity at about 9.8 GHz, there will be a mode such as  $TM_{010}$  (at 6.2 GHz, for example) in which the sample can be excited by an electric field (for effective heating, if its dielectric loss is high enough). This high-power channel at around 6 GHz will be effectively filtered from the EPR electronics by the X-band waveguide feed to the cavity. We have used this method to induce T-jumps of around 50 °C in a few seconds for a heating input power of 2W. The EPR spectra of spin-labelled SDS (sodium dodecyl sulphate) micelles in water after being subjected to a T-jump are shown in Fig. 5. The spectral changes are associated with an increased rotational diffusion rate owing to decreased viscosity as the temperature increases. We expect the dual mode cavity to enhance the study of the kinetics of paramagnetic intermediate and excited states relevant to catalysis. It will also be possible to introduce this technology with high pressure EPR cells to monitor the kinetic evolution of paramagnetic species and intermediates over wide range of temperature and pressure. This is another example where a relatively straightforward innovation in the context of microwave engineering can have a major impact on chemical diagnostics.

## VI. SUMMARY AND OUTLOOK

The focus of this review has been on the use microwaves in all of chemistry, though the breadth of applications in the field is too large to cover in a short review. We have identified themes in microwave driven reactions and frameworks for understanding the causes of common observations and associated challenges. Unique microwave effects in chemistry were considered, such as enhanced reaction rates and changed product distributions, and the challenges associated with accurate measurement and control of reaction conditions and temperature were reviewed. The field of microwave synthesis, catalysis and spectroscopy were then explored.

Many types of chemical transformation can be carried out using microwave irradiation. Though the conditions do not always lead to enhanced reaction rates or increased yields of





**FIGURE 5.** The dual mode concept for simultaneous EPR/heating. The resonances shown here are for a commercial X-band rectangular cavity, where the relevant modes are  $TE_{101}$  at 7.2 GHz (for heating, sample placed in microwave electric field antinode) and  $TE_{102}$  at 9.8 GHz (for EPR, sample placed in microwave magnetic field antinode). A re-design of this cavity brings the resonant frequency of the heating mode  $TE_{101}$  below the cut-off frequency (6.5 GHz) of the X-band waveguide used as the EPR signal feed. Also shown are some example data of T-jump EPR spectra using the dual mode cavity for spin-labelled SDS (sodium dodecyl sulphate) micelles in water, (a) at 20 °C and (b) at 60 °C. The spectral changes, notably the resonance near to 339 mT, are associated with an increased rotational diffusion rate at higher temperature owing to decreased viscosity.

desired products, basic microwave technology is accessible and convenient to use, and has become a standard tool in chemical laboratories for rapid experimentation. Microwave reactions are carried out routinely in synthetic chemistry and are emerging in microwave catalysis [32], [45].

The field of microwave chemistry is rich with fundamental questions and the literature periodically includes discussions about non-thermal effects [8], [22], [23], [38]. The debate is perpetuated because of the major scientific challenge of verifying real reaction temperatures and conditions at reaction sites as opposed to taking average measurements of bulk materials. This is compounded by the complex and constantly changing environments in microwave heated mixtures. Limited data describing high temperature permittivities lead to more uncertainty and in reactions with many competing pathways, we are firmly in the realm of complexity. Despite this, frameworks and models provide useful tools for

understanding sample behavior and developing strategies with which to harness the advantageous effects of microwave heating [6], [16].

New developments in microwave spectroscopy have been reviewed, including in dielectric measurements using cavity perturbation applied to the real-time measurement of ammonia storage in halide salts [71] and in metal-organic frameworks (MOFs) [72] for hydrogen storage applications. In microwave magnetic spectroscopy we have highlighted developments in electron paramagnetic resonance, with new methods using loop-gap resonators and dual mode cavities for simultaneous microwave heating [3], [80].

We have explored representative examples of microwave applications in chemistry, but the origins of these innovations have often been in unrelated fields of research. Microwave science and engineering has always transcended disciplinary boundaries, and despite the perception of

traditional areas of application for microwave technology, emerging microwave research illustrates a broad and diverse field.

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