New opportunities and emerging themes of research in microwave spectroscopy

BY NICHOLAS R. WALKER

School of Chemistry, University of Bristol, Bristol BS8 1TS, UK

It is easy to set a frisbee spinning but hard to flip a javelin end-over-end. The properties of a rotating body are determined by its moment of inertia. Changes in the energy associated with the rotation of a single molecule are incremental, or quantized, in contrast with the everyday examples of the frisbee and the javelin. Only photons with energies that correspond to specific discrete frequencies of electromagnetic radiation can be absorbed or emitted to cause transitions between different rotational energy levels. Photons that cause rotational transitions generally have microwave or millimetre-wave frequencies. Microwave spectroscopy thus provides a basis for exploring molecular structure through studies of molecular rotation. The first experiments involving microwave spectroscopy exploited technology developed for radio detection and ranging during the Second World War. Microwave spectroscopy is now being applied to study chemical reactions significant in atmospheric chemistry and to probe superfluidity in He$_n$ clusters. This article reviews the research themes that were the focus of the past 50 years and surveys new opportunities.

Keywords: microwave spectroscopy; spectroscopic techniques; helium clusters; atmospheric chemistry; chirped pulse

1. Introduction

Spectroscopy exploits the emission, absorption and scattering of electromagnetic radiation for the study of molecules and materials. Emission takes place when a molecule loses energy by radiating light. Absorption is the reverse process. In each case, the energy of the photon involved is coincident or ‘resonant’ with the difference between two energy levels predicted by quantum mechanics. In general terms, photons from visible and ultraviolet regions of the electromagnetic spectrum induce transitions between electronic energy levels and infrared light excites transitions between vibrational levels. Microwave frequencies (between 3 and 300 GHz) are associated with changes in the rotational energy of molecules. These are intimately related to the geometrical structure of molecules. Microwave spectroscopy thus provides the opportunity to measure precisely the structure of isolated, gas-phase species. This article will provide a brief introduction to the experimental methods and essential concepts that underpin this powerful technique. Several themes of current research will be explained and new emerging opportunities will be discussed. An overview of the historical development of the field is provided to set the scene.

*nick.walker@bristol.ac.uk

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Landmarks in microwave spectroscopy

The earliest experiment where microwave frequencies were used to interrogate a molecule was performed by Cleeton & Williams (1934). This group constructed custom-made magnetron oscillators to perform a study of the inversion vibrational mode of NH\textsubscript{3}. The construction of more powerful sources of microwave radiation was essential to the development of radio detection and ranging (RADAR) equipment during the Second World War. Early equipment tests illustrated starkly the significance of molecular resonances at microwave frequencies. Townes (2002) recalls how atmospheric water vapour completely absorbed the microwave radiation from one source limiting the range to eight miles in RADAR applications. Gordy (1983) describes how a boat transporting garbage released ammonia that absorbed the radiation from another device. Experiments were necessarily halted when the boat was passing. The development of the klystron source had been intended to allow the construction of superior RADAR equipment but it had proved unsuited to the purpose. Instead, it provided a boost to the new field of microwave spectroscopy.

The initial post-war surge of experiments, in 1946, all involved studies of the inversion vibration of ammonia. Microwave emission from a klystron source was coupled into a cell using a waveguide and the molecular absorption of microwaves was measured. Bleaney & Penrose (1946) identified ‘rotational structure’ in the vibrational band of NH\textsubscript{3}. This was evidence of transitions between different rotational energy levels. Good (1946) confirmed the presence of ‘hyperfine’ structure, later attributed to coupling between the electric quadrupole moment of a nucleus and the electric field gradient within the molecule (Dailey et al. 1946). Townes (1946) reported on the effects of power saturation on line shapes. Dakin et al. (1946) reported the splitting of a spectral transition by an external electric field. This first measurement of the ‘Stark effect’ allowed the group to determine the dipole moment of a molecule from spectroscopic data for the first time. Gordy (1948) was able to prepare a review of the results contained in approximately 100 research papers. The results obtained from approximately 25 different molecules were included. These ranged in size from a single diatomic, ICl, to species as large as CF\textsubscript{3}CH\textsubscript{3}. Microwave spectroscopy had become a powerful means of determining the molecular structure of isolated gas-phase molecules.

The difficulty involved with using microwave spectra in the determination of geometrical structure increases with the size and complexity of a molecule. It was logical for the first microwave spectroscopists to perform experiments on those small molecules that were most amenable to study. Later experiments extended the range of systems. High-temperature ovens (Stitch et al. 1952) were used to generate gas-phase species containing refractory metals. Organic molecules of increasing complexity were studied as researchers became interested in measuring the energetic barriers to internal rotation about the axes of C–C bonds (Wilson 1951). Rotational transition frequencies could be measured with high precision but researchers were unable to provide structural information of corresponding accuracy. This situation was improved through advances in the numerical methods used to obtain molecular structure from rotational constants (Costain 1958). Even today, rotational constants are determined experimentally to higher precision than the molecular structures that are calculated from them. Microwave amplification by stimulated emission of radiation (MASER) was...
reported by Gordon et al. (1955). Their experiment proved that microwave amplification by stimulated emission could be achieved and principles were established which later guided the design and construction of laser instruments. The invention of the MASER ultimately stimulated the development of the modern lasers used in applications as diverse as compact disc recorders, surgical instruments and bar code readers.

Research into molecular structure remained the central theme in microwave spectroscopy between 1960 and 1970. The related technique of molecular beam electric resonance was providing new details of molecular structure, dipole moments and hyperfine interactions (Dyke et al. 1972). Research was gradually evolving towards experiments that probed the intermediates of chemical reactions and their mechanisms. Researchers began to explore reactive complexes and free radicals. Dixon & Woods (1975) completed the first assignment of the microwave spectrum of a molecular ion, CO\(^+\). The identification of molecules in the interstellar medium was another highlight of the 1960s. Microwave transitions were measured in the laboratory and matched to emissions from the interstellar medium using a radiotelescope. NH\(_3\) was the first stable polyatomic molecule to be identified in the interstellar medium (Cheung et al. 1968). H\(_2\)O (Cheung et al. 1969) and H\(_2\)CO (Snyder et al. 1969) were detected during the following year. Many molecules of varying size and complexity have since been identified through radioastronomy. Recent studies confirm that molecules as large as HC\(_{11}\)N are present in interstellar nebulae (Thaddeus 2006). Studies that investigate the extent of prebiotic chemistry in the interstellar medium have become the sustaining activity of many researchers.

Improvements to electronic instrumentation and vacuum equipment brought new opportunities after 1970. It was found that molecules generated or stabilized within a supersonically expanding gas sample could be effectively probed through spectroscopic experiments. Ekkers & Flygare (1976) reported the use of high-power pulse trains of microwaves of single selected frequency to excite transitions in preference to the more conventional, continuously swept sources. The transient emission signal was collected and Fourier transformed using a computer. A major advantage of this method was that individual measurements (taken after each pulse) could be readily summed to improve the signal/noise ratio of the final result. Pulsed spectroscopic techniques were increasing in popularity at this time owing to the increased availability of pulsed lasers, ability to control and synchronize experiments through fast electronics and the growing importance of experiments performed under high vacuum.

Supersonic expansion maximizes the population of low energy rotational levels such that transitions between those levels can be observed with greatest intensity. The cold temperatures in a supersonic jet allow the formation of molecules and complexes that are unstable against decomposition at room temperature and atmospheric pressure. A pulsed injection of sample gas offers several advantages in the context of spectroscopic experiments: (i) the necessary experimental conditions can be established with lower total gas throughput and smaller, slower, less expensive vacuum pumps, and (ii) pulsed sources are highly compatible with methods that involve the pulsed irradiation of a sample. Balle et al. (1979) implemented these advantages in their design of the cavity Fourier transform microwave spectrometer. The development of a spectrometer employing a cavity
and ‘free-space’ cell opened up a vast range of weakly bound molecules and complexes to first study by microwave spectroscopy (Legon 1983). It provided the basis for an instrument that was ultimately exploited throughout the world. A description of this design of spectrometer will provide a suitable introduction to the experimental methods used by the microwave spectroscopists whose work is featured in §4.

2. The Balle–Flygare Fourier transform microwave spectrometer

The parallel configuration of the Balle–Flygare Fourier transform microwave (FTMW) spectrometer is shown in figure 1. Antennae allow introduction of the microwave excitation pulse and detection of the molecular emission. A pulsed nozzle is used for introduction of the gas sample. The two concave, aluminium mirrors comprise a Fabry–Perot cavity that can be tuned into resonance with the microwave excitation pulse.

Each individual experiment involves the same basic sequence of activities: (i) a gas sample is introduced through the orifice of the pulsed nozzle. Opening times
of 200–400 μs are typical, (ii) on resonance with a rotational transition, a ‘pump’ microwave excitation pulse of 0.3–3 μs in duration rotationally excites the absorbing species, (iii) the pump pulse is deactivated and the molecular emission is measured, and (iv) the molecular emission is Fourier transformed to yield a plot of transition intensity against frequency. The above scheme describes a ‘single’ resonance experiment (i.e. one microwave pulse). Double resonance experiments are particularly useful in assigning complex spectra. One example of a double resonance experiment is described by Suma et al. (2004). An initial microwave pulse was used to increase the population of a selected rotational energy level. The molecular microwave emission from that state was monitored while a millimetre-wave source was scanned. On resonance with a millimetre-wave transition, the state excited initially was depopulated and the depletion of the microwave emission signal was measured. Many other schemes that exploit double resonance are described in the wider literature. Regardless of whether single or double resonance is used for any given experiment, the four stages of the cycle described above can be completed in less than one-tenth of a second. The results obtained over many cycles can be accumulated and averaged in order to improve the signal/noise ratio of measured transitions.

3. Spectroscopic analysis

Transitions between rotational energy levels can be observed in isolation through ‘pure’ rotational spectroscopy. Alternatively, transitions can accompany changes in vibrational and/or electronic energy levels. Microwave spectroscopy is generally concerned with pure rotational spectra and these will be the focus of this work. Generating a particular target molecule for study often requires a gas sample that contains a mixture of different precursors. Many of these will have microwave spectra. A single measurement is therefore insufficient to determine which molecule is responsible for a given rotational transition. Empirical tests can inform the correct assignment. For example, is a transition observed despite the fact that an important precursor has been removed from the gas sample? Ultimately, unambiguous assignment to the correct molecule depends on fitting all observed transitions to a model Hamiltonian for the molecular rotational motion.

The quantum mechanical Hamiltonian of a molecule can be constructed from knowledge of anticipated coupling interactions. Observed transition frequencies are assigned quantum numbers and fit to the predictions of the model Hamiltonian. The value of each parameter in the Hamiltonian is adjusted to obtain better agreement. A spectroscopist can be reasonably confident of success when a fit yields values for parameters that are physically reasonable and within the experimental precision. Assignment is most often challenging where molecules are geometrically complex and non-symmetrical, contain extensive fine or hyperfine structure or yield only weak rotational transitions. The details in such spectra usually allow formidable insight once the assignment has been completed. Simpler molecules can be assigned more readily but the evaluated parameters provide less information about the physics of the species. The methodology necessary to make assignments of the correct transitions to the correct molecule is now well established. There will be very few examples of published rotational spectra that have been assigned to the wrong molecule.

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Quantum mechanics provides the description of molecular rotational motion necessary to interpret microwave spectra. Only species that possess a permanent dipole moment absorb or emit microwave radiation during pure rotational transitions. The rotational constants of a molecule are related to the principal moments of inertia \((I_x, y, z)\) by

\[ B_x = \frac{\hbar^2}{8\pi^2 I_x}, \]

where \(\hbar\) is the Planck constant, and \(B_x\) is the rotational constant associated with the \(x\)-axis. Corresponding expressions apply to the \(y\)- and \(z\)-axes. Microwave spectroscopy involves the experimental measurement of the transition frequencies. The rotational constants can then be used to determine moments of inertia and hence the molecular structure. The determination is simplest for a diatomic molecule for which the moment of inertia, \(I_x\), is related to the internuclear distance, \(R\), by

\[ I_x = \frac{m_1 m_2}{m_1 + m_2} R^2, \]

where \(m_1\) and \(m_2\) are the masses of the constituent atoms; \(I_x\) and \(I_y\) are equal while \(I_z\) is infinitesimal. A ‘rigid rotor’ model assumes that the diatomic can be represented as two hard spheres connected by an inextensible, incompressible bond. The frequency of light absorbed or emitted during a transition between rotational levels is given by

\[ \Delta E(J) = 2B_e(J + 1), \]

where \(B_e\) is the equilibrium rotational constant associated with an axis perpendicular to the molecular axis of symmetry; \(J\) is the quantum number associated with the lower energy rotational state involved in the transition; \(\Delta E(J)\) is measured in the laboratory through measurements of microwave emission or absorption and then used to determine molecular structure using the expressions provided above. The rigid rotor model provides a useful foundation for studies but does not fully reflect the true nature of molecules. It is possible to assign a distinct rotational constant to every vibrational state within the molecule because bonds extend in response to vibrational excitation. The rotational constant, \(B_v\), is the expectation value of the quantity for a given vibrational state with quantum number, \(v\). It turns out that the energy can still be expressed in a form identical to that of the rigid rotor but with \(B_e\) replaced by \(B_v\). This model is referred to as the ‘effective rigid rotor’.

The above equation is often sufficient to define an effective rigid rotor for a polyatomic linear molecule. More sophisticated equations connect the transition frequencies with rotational constants for polyatomic symmetric and asymmetric top molecules. The methodology involved with assigning spectra is qualitatively the same as for a diatomic, but the assignment is generally more challenging. Data acquired from a series of different isotopologues allow bond lengths and bond angles to be determined. The accuracy of structural determinations is dependent on whether samples containing appropriate isotopic substitutions are available.
(b) Centrifugal distortion

The effective rigid rotor model does not account for the extension of bonds in response to centrifugal force. In reality, all molecules experience ‘centrifugal distortion’ and rapidly rotating molecules are the most severely distorted. This effect can be measured through microwave spectroscopy and used to infer trends in vibrational frequency and bond strength. The effective rigid rotor expression for a diatomic molecule is revised to include a term in $D_v$ quantifying the effects of centrifugal distortion,

$$\Delta E(J) = 2B_v(J + 1) - 4D_v(J + 1)^3.$$  

The second term is small at the low values of $J$ that correspond with low rotational energy; $D_v$ can be measured accurately when higher energy states are probed in millimetre-wave spectroscopy.

(c) Fine and hyperfine structures

Electrons and nucleons can possess spin that couples to the rotational angular momentum of a molecule. This has the effect of ‘splitting’ rotational energy levels into a greater number of components leading to a corresponding increase in the number of observed transitions. The ‘fine’ structure observed in spectra arises from the interaction of individual unpaired electrons with the spins of other electrons, the molecular rotational angular momentum and/or the molecular orbital angular momentum. ‘Hyperfine’ structure is the result of interactions that couple the spin of one or more nuclei with the framework angular momentum. The relative magnitudes of these effects depend on the molecule. The presence of many coupling interactions within a molecule yields spectra that are more challenging to assign, but the effects can provide great insight into charge distribution where they can be thoroughly characterized.

4. Emerging themes

Sources of millimetre wavelengths (approx. 30–300 GHz in frequency) were developed shortly after tuneable microwave generators and are now widely exploited for spectroscopy. Until recently, instruments capable of generating radiation at terahertz frequencies had been unavailable. Sources are now being manufactured and applications appear likely to proliferate (Davies et al. 2004). Descriptions of experiments that exploit millimetre wavelengths and terahertz frequencies are outside the focus of this article. This work will focus instead on results recently achieved by contemporaries using microwave spectroscopy. The purpose is not to provide a complete description of the experiments and motivations of the great number of groups that now use microwave spectroscopy worldwide. The selected examples are only intended to be illustrative of a few themes and their connections with other areas of research. They are intended to demonstrate how workers have adapted to new imperatives and are exploiting emerging opportunities. It is hoped that this snapshot will encourage the reader to seek out further details of research in microwave spectroscopy in the broadest possible sense. Sections 4a–c describe experiments conducted using Balle–Flygare cavity FTMW spectrometers. Section 4d describes the development of an entirely new tool for research.
(a) Atmospheric chemistry and remote sensing

A central theme of modern research in chemistry is the study of chemical reactions and processes in the Earth’s atmosphere. The upper stratosphere is cold and sparse compared with conditions in the troposphere near the Earth’s surface. Supersonic expansion of a gas sample provides a local environment where cold, weakly bound molecules can be prepared for study by microwave spectroscopy. Suma et al. (2004) recently probed ClO₂, a radical which may contribute to the depletion of ozone within the polar stratosphere. Studies of HOOO, HOOOH, H₂O–O₂H (Suma et al. 2005a, b, 2006) and H₂O–OH (Ohshima et al. 2004) were also completed by the group. These species are of interest owing to their roles as intermediates in reaction pathways that involve OH radicals. The structure of HOOO, reprinted with permission from Suma et al. (2005a, b) is shown in figure 2. Details of geometric and electronic structure gained through microwave spectroscopy are used to refine our models of atmospheric chemical reactions and processes.

Studies are further useful in providing the spectral ‘signatures’ of molecules that may be detected through remote sensing (Alder 1990). Mass spectrometers are unable to distinguish between different components that have the same atomic mass. Microwave spectra are unambiguous with respect to the identity of a molecule and its structure. A further advantage of microwave spectroscopy is that neutral (rather than ionic) molecules can be probed directly. There is no requirement that sample molecules are ionized before analysis. Successful application of microwave spectroscopy to trace gas detection would require that reliable assignments of transition frequencies were available from laboratory studies beforehand. Bousquet et al. (2005) have described efforts to adapt the techniques of microwave spectroscopy for the detection of chemical warfare agents.

(b) Structure and solvation of amino acids

Microwave spectroscopy can also provide information about the structure and function of different molecules significant in biology. The chemistry of biological systems is fundamentally dependent on the properties of comparatively large organic molecules. These adopt different conformations which may change in...
response to chemical environment or temperature. Species that contain both a carboxylate group and an amine group belong to the class of molecules termed ‘amino acids’. The amine group on one amino acid undergoes a condensation reaction with the carboxylate group on the second during the formation of peptide bonds. The linkage of a large number of amino acid residues leads to the formation of polypeptides and proteins. Amino acids can adopt many different conformations and the number of different possibilities increases with the size of the acid. In biological environments, the propensity of an amino acid to adopt a given conformation can depend on the strength and extent of intramolecular hydrogen bonding and intermolecular bonds that it shares with neighbouring molecules.

Studies by Brown et al. (1978) and Suenram et al. (1980) used ovens to evaporate material and succeeded in characterizing several conformers of glycine, \( \text{NH}_2\text{CH}_2\text{CO}_2\text{H} \) by microwave spectroscopy. Low vapour pressures and a tendency for amino acids to decompose on heating meant that many larger examples could not be prepared for study in this way. Laser vaporization has since provided a more versatile and controllable method of preparing molecules for study. J. L. Alonso and co-workers have applied this technique to generate a wide range of amino acids for study by microwave spectroscopy. In several cases, the molecules studied are possible constituents of the interstellar medium. The obtained transition frequencies provide important benchmarks for astronomical measurements. Leucine (Cocinero et al. 2007) and valine (Lesarri et al. 2004) are among the largest and most conformationally flexible residues studied. Objectives are evolving from the exploration of relatively small species to more complex and flexible molecules. Formamide contains the same functional groups that are present within amino acids. The microwave spectrum of formamide coordinated by \( \text{H}_2\text{O} \) provided a first insight into the structures of solvated amino acids and their coordinating molecules (Blanco et al. 2006). Microwave spectra of glycine attached to water molecules have since been reported (Alonso et al. 2006). Proteins exist as solvated species within the human body and coordination may profoundly affect their shape and function. Studies of more complex and extensively coordinated amino acids can be expected in the future.

\( (c) \) Superfluidity in helium clusters

The cold environment in a supersonic expansion allows extensive aggregation and clustering provided strong intermolecular forces exist between molecules within the expanding gas sample. The intermolecular forces between helium atoms are comparatively weak. The generation of helium ‘nanodroplets’ containing more than 1000 atoms therefore requires a particularly cold expansion. Nanodroplets provide an ideal environment in which to perform ‘matrix isolation’ experiments. Embedded molecules can be probed using spectroscopy and experience minimal perturbations from the surrounding atoms.

The ro-vibrational transitions of OCS embedded in a helium nanodroplet are observed as sharp lines. This suggests that the molecule rotates comparatively freely within the superfluid core of the nanodroplet (Grebenev et al. 1998). Jäger and co-workers performed experiments to explore the transition from the properties of the isolated OCS molecule to those of the species embedded in the nanodroplet. Their first report (Tang et al. 2002) described the microwave
spectra of He–OCS clusters for \( n = 1–8 \). The rotational constant was observed to decrease with increasing size of cluster. This trend is consistent with semi-rigid He–OCS units where each helium atom tracks the motion of the OCS absorber. It was expected to reverse at some higher value for \( n \) where the superfluidity evidenced in the nanodroplet would become important. The data provided in figure 3 have been reprinted with permission from McKellar et al. (2006). Rotational constants of He–OCS were obtained through a combined study that yielded microwave data for clusters from \( n = 1–39 \) and infrared measurements of ro-vibrational transitions for clusters from \( n = 12–72 \).

The addition of a helium atom resulted in an increase in rotational constant where \( 9 < n < 23 \). This trend is a consequence of the motion of the helium atoms becoming decoupled from that of the OCS unit and is associated with the onset of superfluidity. At larger values of \( n \), the magnitude of the measured rotational constant is convergent with that observed for the nanodroplet-embedded OCS. Oscillation around this value is seen throughout the size range from \( n = 10–72 \). This is explained by the formation of solvation shells within the helium cluster and is in agreement with theory. These works have furthered our understanding of the character and extent of superfluidity in finite, microscopic systems. They have provided valuable insight into the localized interactions that give way to the superfluidity observed in bulk samples.

Figure 3. Variation of the rotational constant, \( B' \), of \(^4\text{He}_n\)-OCS with \( n \). Reprinted with permission from McKellar et al. (2006). Copyright © American Physical Society. Filled triangles and filled squares indicate the results of theoretical calculations that are described in more detail in the earlier work. The experimental values of \( B' \) are represented by filled circles. The value observed for \(^3\text{He} \) clusters with \( n = 60 \) is shown as a cross.

\[ B' (\text{MHz}) \]

\[ \begin{array}{c|c|c|c|c|c|c} \hline n & 0 & 1 & 2 & 3 & 4 & 5 \\ \hline B' (\text{MHz}) & 1500 & 2000 & 2500 & 3000 \\ \hline \end{array} \]
Chirped pulse Fourier transform microwave spectroscopy

Microwave spectroscopists have exploited Fourier transform techniques ever since computers able to perform the operation rapidly became available. The burgeoning market for improved telecommunications equipment has helped to ensure that electronic devices and instruments for microwave detection and generation have been continually improved since the advent of the Balle–Flygare design of FTMW spectrometer. New technology has continuously provided new opportunities to innovate.

Over the last 20 years, improvements to the Balle–Flygare spectrometer have increased the frequency range and sensitivity of the device. Automation has brought increased efficiency in data collection. Instruments constructed with the described adaptations continued to employ pulse trains at fixed, selected frequencies to allow the rotational polarization of the sample. The new ‘chirped-pulse’ technique of FTMW spectroscopy (CP-FTMW) avoids this requirement by exploiting a pulse which sweeps over an 11 GHz range of frequencies in a few microseconds (Brown et al. 2006). An oscilloscope with bandwidth greater than 11 GHz is used to resolve the coherent emission signal which is then Fourier transformed to yield the broadband microwave spectrum. All transitions in the spectrum can be measured simultaneously. The performance of the instrument was tested through measurements of lines in the spectrum of epifluorohydrin. These data are reprinted with permission (Brown et al. 2006) in figure 4.

Consistent with the increased bandwidth, the time required to accurately measure all transitions in the spectrum of the molecule was reduced from 14 hours (Balle–Flygare design) to 48 min (CP-FTMW). The line width (full width half maximum) of transitions was 5 kHz using the Balle–Flygare spectrometer and 125 kHz using the CP-FTMW spectrometer. The lower precision achieved in the CP-FTMW spectrometer is much compensated by the increased bandwidth available. The instrument provides data that allows precise structural determinations and the evaluation of hyperfine parameters. Significantly, the need to perform an iterative search for transitions at the outset of an investigation is eliminated. This instrument might be used to great advantage in future studies such as those described in §5.

5. The future

Townes (2002) did not anticipate the applications of today’s laser systems when designing and constructing the first maser. Another microwave spectroscopist, H. W. Kroto, was pleasantly surprised when his interest in the microwave spectra of carbon-containing molecules in space led to his role in the discovery of C_{60} (Kroto et al. 1985). Not all paths will bring research success. Sometimes the most interesting results are obtained unexpectedly or by accident. Attempting to suggest the future of research involves providing a few ‘hostages to fortune’. The reader is encouraged to consider a few possibilities with an open mind.

Molecular units where a metal ion is completely enclosed and coordinated at one or more sites that are all coordinated by a single, much larger molecule are of considerable significance in biochemistry. There is a wide community of researchers currently working to understand molecular recognition in biologically significant species through mass spectrometry. A future role for microwave
spectroscopy may be to provide precise structural information that is relevant to molecular recognition but which cannot be obtained by mass spectrometry. For example, how is the geometry of 12-crown-4 affected by attachment to a metal-containing molecule? How does the conformational landscape change? Crown ethers are cyclic species able to attach to other molecules, particularly metal ions, through coordination of oxygen atoms that are oriented towards the centre of a cyclic structure. As phase transfer catalysts, these molecules facilitate solution-phase chemical reactions even where individual reactants are soluble only in different kinds of solvent. The interface between biology and the work of microwave spectroscopists appears certain to grow. Other opportunities will derive from the increasing need to understand how topology and the nature of surfaces affect the structures of adsorbed species.

The efficiency of industrial platinum catalysts is known to be adversely affected by carbon monoxide poisoning. The reduction in efficiency results from

Figure 4. The 11 GHz rotational spectrum of epifluorohydrin measured by CP-FTMW spectroscopy. (a) A single gas pulse allows the rotational spectrum of one conformer to be observed. (b) Thirty seconds of averaging (100 pulses) are necessary to observe a further two conformers. The inset in each spectrum shows the effect of signal averaging on an expanded scale. The frequency of the $2_{12} - 2_{02}$ rotational transition of the first conformer is indicated in the full-scale spectrum. The transition is also shown in the expanded scale. (c) Approximately 48 min are required to accumulate data from 10 000 gas pulses. This figure was published in Brown et al. (2006). Copyright © Elsevier.
CO binding to surface sites on the metal and reducing the number available to adsorb H2. There is consequently a fundamental need for a greater understanding of the interactions between CO adsorbates and metal catalyst surfaces. Metal-containing clusters provide an excellent opportunity to study these interactions. Their small size permits the acquisition of data that is tractable with theory. Their properties are a strongly varying function of size suggesting that size-selected clusters may ultimately provide promising alternatives to continuous surface catalysts. Ionic clusters can be investigated through mass spectrometry but other forms of spectroscopy are required to explore the properties of neutral species. The assignment of microwave spectra obtained from Ni$_n$–CO clusters would surely present a significant challenge to the experimentalist but Ziurys and co-workers have demonstrated that microwave spectra can be assigned for molecules in high-spin states (Halfen & Ziurys 2005). The prospects for research in this area are encouraging.

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AUTHOR PROFILE

Nicholas R. Walker

Nick Walker applies spectroscopy and mass spectrometry to characterize metal-containing species in the gas phase. He did both undergraduate and postgraduate degrees at the University of Sussex before commencing postdoctoral research in 2000. He completed a postdoctoral appointment at the University of British Columbia with Prof. Michael Gerry and then another at the University of Georgia with Prof. Michael A. Duncan. He started a Royal Society University Research Fellowship at the University of Bristol in 2003 and was awarded the Meldola Medal and Prize of the Royal Society of Chemistry in the same year. He made four short TV programmes in association with ITV (West) in 2004. He also enjoys voluntary work. Acting through ‘Business in the Community’, he organized a team of 32 Bristol postgraduates to redecorate the interior of Weston Park primary school after fund-raising the costs of the project in 2006.