Infrared Laser and Microwave Spectroscopy of Electric Discharges

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1 Introduction and Historical Background

The use of the electric discharge as a spectroscopic source in the laboratory goes back to the early part of this century. However, until twenty years ago most high resolution spectroscopy of molecules in discharges, particularly of short-lived species like free radicals and ions created and destroyed within the discharge itself, was confined to the optical region. Emission and absorption spectra were recorded with large grating spectrometers with resolving powers of $> 5 \times 10^5$. Accurate structural parameters for ground and excited electronic states were obtained for many diatomic and triatomic species in this way. For example, Lew[1] measured the electronic emission spectrum of H_2O^+ using water vapour at low pressure in a multi filament hot cathode discharge source. Analysis of bands in the $\tilde{A}^2A_1$–$\tilde{X}^2B_1$ system of H_2O^+ yielded accurate rotational constants of both states for the first time. The development of optical spectroscopy for studying ions and free radicals, not only from discharges but also in flames and photolytic sources, has been described by several authors.[2]

In contrast to the wealth of optical spectroscopy there were relatively few complementary infrared or microwave results. Some free radicals, *e.g.*, ClO, OH, CH, had been detected using highly sensitive resonance spectroscopy, either with microwaves (electron paramagnetic resonance, EPR[3]) or with far infrared and mid infrared lasers (laser magnetic resonance, LMR[4]). In almost all cases, however, EPR and LMR experiments concentrated on the type of reactive species which could be formed either chemically in a flow system or detected outside an electric discharge. The problem of electrical noise frustrated attempts to detect absorption spectra in the discharge itself. The first successful attempt to record a microwave absorption spectrum within the discharge was achieved by Dixon and Woods in 1974.[5] They overcame the problems of microwave attenuation and noise generation and recorded the lowest rotational transition of the cation $CO^+(X^2\Sigma^+)$ in a liquid nitrogen cooled d.c. glow discharge cell. The basic features of this experiment were subsequently extended to the successful detection of many other ions and free radicals by microwave and sub mm spectroscopy. In 1980 Oka[6] reported the first infrared laser absorption spectrum of a molecular ion (H_3^+, ν_2 fundamental) in a cooled glow discharge. This experiment, too, led to many successful studies of the IR absorption spectra of ions and free radicals in discharges.

The author has developed several high resolution spectroscopic techniques for studying the spectra of short-lived molecules.

These include far infrared laser magnetic resonance, tunable far infrared laser spectroscopy, and diode laser spectroscopy. His current interests include the infrared laser spectroscopy of free radicals, moleculer ions, Rydberg states, and Van der Waals complexes. Most of these are studied using diode laser spectroscopy. He is currently a Reader in the University of Cambridge and a Fellow of Corpus Christi College.

The remainder of this article will describe how the electric discharge source has been developed and modified for spectroscopy. While much higher concentrations of short-lived molecules exist within rather than outside the discharge, these concentrations are still very small (10^9—10^{12} cm^{-3}), and different modulation techniques have therefore been developed to improve selectivity and sensitivity, which will be described in Section 3. A few examples, illustrating the widely different types of transient molecules now studied in discharges are described in Section 4. Lastly, the practical uses of spectroscopy in probing and understanding the mechanisms of chemically reactive plasmas are mentioned in Section 5.

2 Spectroscopic Discharge Sources

2.1 DC Glow Discharge

Although many types of electric discharge have been developed not all are suitable as sources for microwave or infrared spectroscopy. The most frequently used is the d.c. glow discharge which in its simplest form consists of two metal electrodes at the ends of a glass cylindrical cell. The cell used by Dixon and Woods was 3.5 m long and 15 cm in diameter and cooled with liquid nitrogen. The d.c. glow discharge can produce a large variety of atoms, radicals, and ions from molecular gases. These species may be in excited as well as in ground electronic states. The behaviour and distribution of positive and negative charge carriers along the axis of glow discharges have been studied extensively and are described in the literature.[7] Plasma diagnostic techniques like Langmuir probe measurements yield information about the concentrations of ions without being molecularly specific. The distribution of ions in glow discharges is both axially and radially non-uniform. The electric field and other properties of the discharge depend on gas composition, pressure, cell dimensions, and other factors but it is possible to generalize about behaviour in the 'normal' glow discharge.

The highest concentration of ions is found in the negative glow region (up to 100 times that in the positive column for cations) where the electrons have enough energy to ionize in a single collision. In most of the early studies using glow discharges no attempts were made to address the problem of inhomogeneous distribution of ions, *i.e.* the microwave or laser radiation passed along the whole length of the discharge. While using discharges in this way is no longer the case, as will be described later, there have been only a few studies to determine quantitatively how specific molecules or ions distribute themselves within the discharge. For example, Pan and Oka[8] determined the radial distribution of H_3^+ and ArH^+ in the positive column of a d.c. glow discharge under various conditions of current, pressure, *etc.* They used infrared laser absorption of resolved rovibrational transitions of the ions and found, for example, that at higher currents the concentration of ArH^+ was depleted at the centre of the discharge tube due to ambipolar diffusion. In spite of these very interesting findings there has been relatively little work published since then on plasma diagnostics in axial or cylindrical discharges.

2.2 Hollow Cathodes

The hollow cathode source has been widely used in optical spectroscopy. The motivation for using it in high resolution infrared and microwave absorption spectroscopy is that it enables the absorption to be detected in the regions where the ion concentration is known to be highest, namely in the negative glow The design of hollow cathode absorption cell now used almost universally is that due to van den Heuvel and Dymanus [9] The main feature of their discharge cell is a 0 7 m long, 50 mm diameter cooled copper cathode The small anode is symmetrically placed in a side-arm off the cathode The positive column is established in the small space between the side arm and the cathode whilst, by suitable choice of voltage, the negative glow can be made to fill the large volume within the cathode This design of cathode has proven to be highly versatile and has also been used in FTIR absorption spectroscopy (mentioned later)

Since the negative glow region is so important for detecting ion spectra other methods of enhancing this region have been tried One successful approach has been to enclose a d c glow discharge in a solenoidal field This has the effect of extending the negative glow by confining the electrons from the cathode to the axis of the tube thus increasing the number of ionizing collisions Bowman *et al* [10] found concentrations of HCO$^+$, HN$_2^+$, and CO$^+$ were enhanced by a factor of 100 by applying fields of 200 Gauss

2.3 Nozzle Electric Discharges

Although the glow discharge remains the most common source for free radicals and ions there is increasing spectroscopic interest in ion clusters, which are best produced and studied in molecular beams The d c glow discharge is not easy to adapt for this purpose The first successful experimental solution seems to have been arrived at by Droege and Engelking[11] who combined a high pressure corona discharge with a supersonic expansion In their design the discharge strikes from a pointed electrode close to a nozzle orifice (diameter 25—100 μm) The transient species formed in the discharge are rapidly expanded into a near collision-free environment They observed emission from rotationally cold ($T_R \sim 10$ K) OH radicals in the A$^2\Sigma^+$ state in this way

In a more sophisticated version of this experiment, developed for infrared laser spectroscopy of clusters containing hydrogen bonded neutrals and cations, Crofton *et al* [12] combined the corona discharge–supersonic expansion arrangement with mass selection The ion cluster of interest is mass selected after leaving the ion source and held in an octopole ion trap where it interacts with an infrared laser beam A second ion detector collects fragment ions after absorption and vibrational predissociation of the cluster ion The sensitivity of the technique is extremely high since in principle it can detect absorption and dissociation of a single ion Crofton and co-workers estimated the minimum detectable absorption was 10^{-12}, about 10^5 times better than in the best direct absorption technique Examples of species detected with the method include water clusters of the general formula $H_3O^+(H_2O)_x, x = 3—8$

However, both the corona discharge experiments described above use c w nozzle sources, and in many experiments pulsed nozzle sources are more desirable Several designs which combine a pulsed valve with an electric discharge have appeared in the literature Generally they all rely on the discharge striking on the downstream side of a nozzle orifice when a pulse of gas passes A schematic representation of a pulsed jet discharge is shown in Figure 1 The performance of such a discharge, used to study OH and N$_2^+$, has been described by Bramble and Hamilton [13] Most of the pulsed nozzle discharge sources have been used for optical spectroscopy,[14] but applications in microwave spectroscopy have begun to appear and some results will be described later

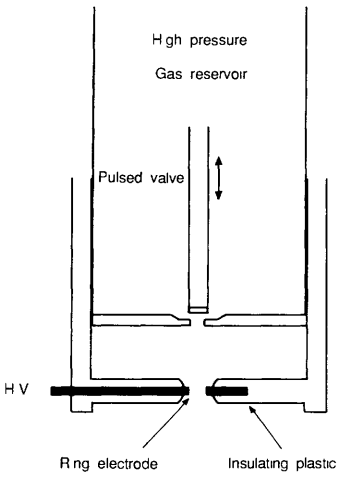


Figure 1 Supersonic jet electric discharge source Spectroscopic measurements are made as close as possible to the discharge In this case a ring electrode is used and the discharge strikes to the walls of the vacuum chamber

3 Molecular Modulation

3.1 Zeeman Effects

In order to improve sensitivity and selectivity for measuring the spectra of low concentrations of transient species in discharges, various modulation techniques have been used Frequency modulation or amplitude modulation of the microwave source or infrared laser are the oldest methods but lack molecular selectivity For this reason a number of modulation methods which depend directly on the absorbing molecule of interest (molecular modulation) have been developed In their pioneering study of the methyl radical, Yamada *et al* [15] used Zeeman modulation of the discharge cell to identify the infrared absorption lines arising from the ν_2 mode of the methyl radical Magnetic fields, usually applied through a solenoid wound around the absorption cell, have been widely used to discriminate between paramagnetic and non-paramagnetic molecules

As well as the a c magnetic fields used for modulation, d c magnetic fields have been used to discriminate between the different species present in discharges An axial d c field, as mentioned earlier, can be used to enhance the concentrations of ions in microwave spectroscopy [10] Lemoine and Destombes[16] have also reported that the infrared laser spectra of H$_3$O$^+$ were greatly enhanced in the presence of an axial field The same workers also used magnetic field effects to distinguish between paramagnetic and non-paramagnetic species giving rise to microwave spectra At low fields rotational lines of paramagnetic molecules are less intense than at zero field due to the sharing of intensity among several Zeeman components At higher fields (100—300 Gauss) the neutral paramagnetic spectra have almost disappeared Conversely, at higher fields ion spectra increase in intensity due to the electron confinement effect

3.2 Optogalvanic Spectroscopy

Laser optogalvanic spectroscopy (LOG) detects the change in impedance of an electrical discharge which occurs when a (tunable) laser frequency coincides with an atomic or molecular transition The technique was first developed for visible spectroscopy where the optogalvanic effect is larger, partly due to the availability of higher power lasers and partly because differences in impedances between electronic states are larger than between rovibrational levels Nevertheless, LOG using infrared lasers has been successfully demonstrated for both atoms and molecules

Saykally and co-workers[17] used LOG to measure low lying Rydberg–Rydberg transitions in H, He, Li, Ne, and Ar excited in a hollow cathode discharge The reader is referred to the articles by Begemann and Saykally,[18] and by Webster and Menzies[19] for a full description of the experimental arrangements and interpretation of the LOG signal Interpretation of the LOG signal is not straightforward and it depends in a complicated way on discharge conditions and this may explain why there seems to have been little progress recently in exploiting the technique

3.3 Velocity Modulation Spectroscopy

This is the most commonly used modulation technique for detecting the infrared laser spectra of molecular ions It necessitates using an alternating current discharge Both sinusoidal and square waveforms have been used The technique has its origin in the observation of small but measurable Doppler shifts ($\Delta\nu/\nu \sim 10^{-6}$) in the absorption frequencies of molecular ions in d c glow discharges These were first observed[20] in the $J = 1 \leftarrow 0$ rotational frequency of HCO^+, and later in higher rotational transitions of HCO^+, NO^+, CO^+, and HN_2^+ ions[21] The observation of Doppler shifts in infrared spectra was first reported by Haese, Pan, and Oka[22] who measured the effect in vibration–rotation lines of ArH^+ The shifts themselves provide a non-invasive method of investigating ion mobilities and electric fields in discharges Woods and co-workers also used them to distinguish between neutrals and ions It was this characteristic which was ingeniously exploited by Gudeman and Saykally[23] when they devised the technique called Velocity Modulation They realized that in an a c discharge the ion absorption frequencies would be undergoing significant blue and red Doppler shifts as the electrode polarity switched These shifts would occur at the frequency of the discharge and when the detection system was referenced to the discharge frequency the demodulated signal would consist only of velocity modulated lines The initial velocity modulation spectrometer employed a color center laser but subsequently both difference frequency lasers and diode lasers have been used for velocity modulation ion spectroscopy An impressive array of anions and cations have been studied this way, including such fundamental species as OH^+, OH^-, H_2O^+, and H_3O^+ The important discriminatory feature of velocity modulation is most relevant when investigating discharges in large precursor molecules like hydrocarbons These discharges are potentially a source of many different neutral species which are likely to be much more abundant than the molecular ions Using velocity modulation, Oka and co-workers have accumulated a large body of spectroscopic and chemical information on simple carbo-ions, *e g* CH_2^+, CH_3^+, $C_2H_2^+$, and $C_2H_3^+$[24] generated in a c hydrocarbon discharges

3.4 Population Modulation Spectroscopy

The a c discharge has a second modulation advantage which has been almost as heavily exploited as velocity modulation itself[23] Since the concentration or state population of transient species in the discharge follows the on and off periods of the discharge these transients are in principle modulated at twice the discharge frequency If the signal processed by the lock-in detector is now demodulated at this frequency (2*f*) then spectra arising from transient species – neutral or ionic – can be observed The population modulation method applies to all transient molecules and also for stable molecules in excited states The signals appear as zero-order line shapes, *i e* as simple absorption (or occasionally emission) lines Population modulation is analogous to mechanically chopping the laser beam (using a d c discharge source) and demodulating the laser absorption signal at the chopping frequency The frequency selected for population modulation depends on the lifetime of the free radical or transient to be studied Too high a frequency for a long-lived molecule would result in negligible decay during the off period of the discharge, which in turn would mean small modulation depth For molecular ions this is unlikely to be a problem since they are so short-lived that their concentrations will decay to zero almost instantaneously when the discharge is extinguished, even at frequencies as high as 50 kHz, *i e* they will be fully modulated

In addition to its widespread use for conventional glow discharges, a variation of population modulation has been used in conjunction with hollow cathode discharges Foster and McKellar[25] used discharged modulation at 9 kHz to enhance sensitivity and discriminate in favour of ions in a liquid nitrogen cooled hollow cathode A high voltage (9 kHz) square wave signal was applied to the anode only The cell only supported a discharge during the half cycle when the anode had positive polarity, *i e* the cell acted as a rectifier, and population modulation occurred at a frequency of 9 kHz Although all transient species generated in a c discharges undergo population modulation to some extent, the widely different lifetimes of ions and neutrals means that it is possible to discriminate between them by varying the discharge frequency This in turn affects the amplitude and phase of the signals[23]

Given the choice of modulation methods now available it is interesting to surmise which might be the best In fact very few direct comparisons have been published Figure 2 shows a spectrum of H_3O^+ recorded near 521 cm $^{-1}$ using velocity modulation in a glow discharge and population modulation in a hollow cathode cell[26] There seems little difference in the measured signal to noise ratios In practice the different modulation schemes and different discharge configurations lead to almost unique distributions within the discharges for each species and the best experimental approach is to use both 1*f* and 2*f* detection methods From an experimental point of view, being able to change from 1*f* to 2*f* detection is highly convenient since the same discharge cell can be used Figure 3 shows one design of discharge tube which has been used primarily for velocity modulation but in which population modulation spectra can also be detected

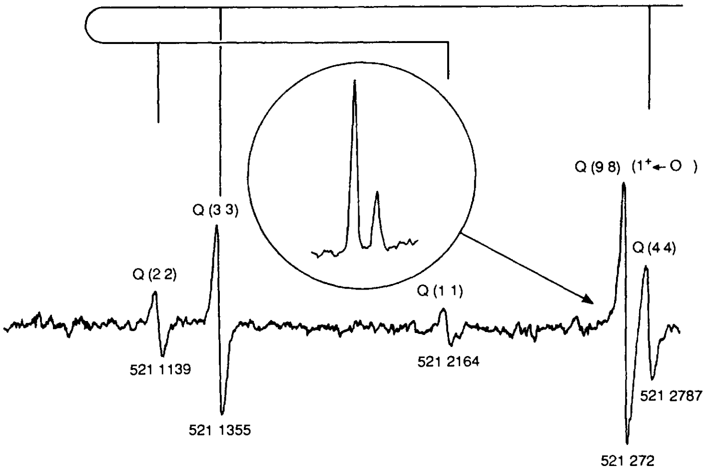


Figure 2 Diode laser spectrum of lines in the ν_2 (1^+—0^-) band of H_3O^+ The main spectrum was recorded with velocity modulation detection in a discharge tube such as that shown in Figure 3 The inset shows a population modulation spectrum recorded in a hollow cathode cell

4 Examples

It would require a review of enormous length to describe all the transient molecules which have now been investigated by the two types of spectroscopy selected for this article Instead, representative example will be described in more detail, which should give an indication of the variety of species detected and the quantitative results obtained from their spectra

4.1 Molecules Relevant to Astronomy

Extended chain hydrocarbons belonging to the isovalent families HC_nO and HC_nS are of considerable interest to spectroscopists, both for structural reasons and for their potential importance in interstellar chemistry Members of the oxygen series with $n = 1$—4 are all bent in their ground electronic states These states correspond to the lower of the two components which

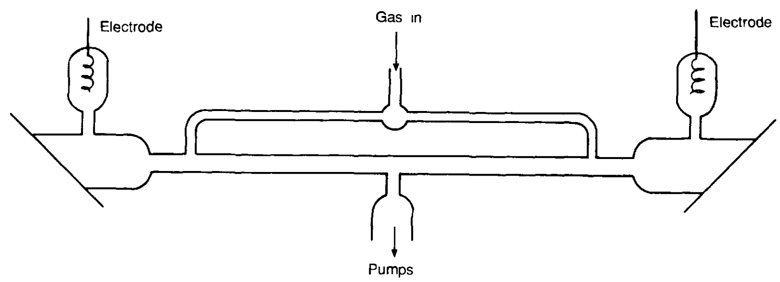
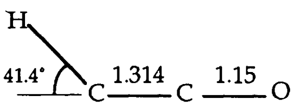


Figure 3 Discharge tube used for velocity modulation spectroscopy of molecular ions. The gas flow is split equally between the two identical arms of the discharge. Typical dimensions for a velocity modulation cell are length 1 m, internal diameter 7—10 mm.

correlate with a $^2\Pi$ electronic state in the linear configuration. The microwave spectrum of the HC_2O radical is a good example of the detailed structural information that can be derived from a rotational spectrum with resolved hyperfine structure.[27] From the Fermi contact coupling constant [$-54.030(24)$ MHz] the spin density on the carbon atom adjacent to the proton was calculated to be 86%, so the radical is well represented by the valence structure $H{-}\dot{C}{=}C{=}O$. A combination of rotational and hyperfine data leads to a geometrical structure for the radical, as shown below. (In arriving at this structure the C=O bond distance (Å) has been fixed at an *ab initio* value and the C=C=O angle is assumed to be 180°.)



The sulfur analogue of HC_2O was first detected by optical spectroscopy[28] and more recently has been detected by pure rotational spectroscopy.[29] Hirahara and co-workers[30] have now observed spectra of HC_3S and HC_4S using Fourier transform microwave spectroscopy with a pulsed discharge supersonic nozzle free radical source. In their experiment the microwave frequency, swept in small steps of a few MHz, is fed to a Fabry Perot cavity which is maintained at the resonance frequency by synchronous length adjustment. In this way the high Q of the cavity is retained as the microwave frequency is changed – an essential feature of this high sensitivity experiment. This is an extremely tedious procedure when large frequency searches are required, since the cavity length has to be adjusted after each 1—2 MHz scan. A second experimental feature of this type of spectrometer is that the scan has to be carefully synchronized with the transient burst of molecules from the discharge nozzle. Nevertheless, the cooling to rotational temperatures ~1—2 K from the expansion greatly enhances the populations of the lower states, and hence the signal to noise ratios of the lowest rotational transitions. In addition, the simplification of the spectrum by rotational and vibrational cooling is an aid to assignment, particularly useful when there is no ancillary detection system to independently identify the carrier.

Probably the most important result from this study is the finding that both HC_3S and HC_4S are linear in their ground states, in contrast to their oxygen analogues. Along with HC_2S all three radicals have $^2\Pi_i$ $(n = 2, 4)$ or $^2\Pi_r$ $(n = 3)$ ground states. It appears that in the oxygen analogues the strong Renner–Teller interaction lifts the degeneracy of the $^2\Pi$ state. This raises a further interesting question about the simplest member of the sulfur series, HCS, for which no high resolution spectra have yet been analysed. An *ab initio* calculation[31] has predicted a bent ground-state configuration. As in the case of HC_2O the hyperfine structure is highly important for understanding the electron distribution in HC_3S, for example. The spin density on the carbon atom next to the proton is much lower in this case, suggesting a hybrid structure: $H{-}\dot{C}{=}C{=}C{=}S \leftrightarrow H{-}C{\equiv}C{-}\dot{C}{=}S$. The high resolution rotational spectra, both line positions and intensities, are highly important in searches for these radicals in the interstellar medium.

4.2 Exotic Molecules and Novel Species

Discharges in polyatomic molecules often produce a wide range of species and usually there is little chemical control over what these are. While posing a problem for assigning spectra to a particular carrier it can also turn out to be a great bonus, *i.e.* unexpected molecules can be discovered in this way. Such species are invariably reactive and highly transient, automatically requiring high sensitivity techniques for their detection. One of the best recent examples of a novel species discovered in this way is the molecule Si_2H_2. This was detected in a silane/argon low power plasma using submillimeter-wave spectroscopy.[32] Its subsequent identification and characterization provides a model example of the combined power of high resolution rotational spectroscopy and precision *ab initio* calculations.

The assignment to Si_2H_2 was based primarily on spectroscopic considerations. However, prior to its sub mm-wave discovery mass spectrometric results indicated that Si_2H_2 $(^m/_e = 58)$ was predominant in a SiH_4/Ar plasma. The rotational lines detected by Bogey *et al.*[32] were found to be unaffected by a confining magnetic field, *i.e.* they showed neither the Zeeman splitting nor the enhancement expected for a paramagnetic or ionic species. In addition they corresponded to the pattern expected for a near prolate symmetric top with $(B + C)/2 \sim 7.2$ GHz. A rotational constant of this magnitude is close to that expected for a molecule containing two heavy atoms, in this case two Si atoms. Adjacent rotational lines exhibited a 3:1 intensity alternation, the nuclear spin intensity statistics expected for two equivalent protons. Putting this and other evidence together Bogey *et al.* deduced the double H-atom bridged butterfly structure shown in Figure 4. This non-classical structure is in complete contrast to that expected from acetylene. Confirmation of the structure was provided by concurrent, independent *ab initio* calculations of Colegrove and Schaefer[33] which showed that the lowest energy conformer of Si_2H_2 was indeed (I). With its high symmetry, only three independent geometrical parameters are required to define the structure of (I) and these were readily derived from the three rotational constants given in Table 1. The r_0 parameters are shown on the structure, while Table 1 shows the very satisfactory agreement between experimental and *ab initio* rotational constants.

The *ab initio* calculations also yielded another important result, namely the prediction of other stable conformers of Si_2H_2 including a monobridged structure (II) (Figure 4) only 8.7 kcal mol^{-1} higher in energy than the ground state (I). Cordonnier *et al.*[34] have succeeded in detecting and analysing the rotational spectra of this conformer in a SiH_4/Ar discharge under similar conditions to those used to produce (I). Tests with a confinement magnetic field indicated a closed-shell electronic structure. The rotational pattern again corresponded to a near prolate symmetric top structure but with different rotational constants (particularly the A constant) from those of the dibridged conformer. The absence of nuclear spin effects, similarity to *ab initio*

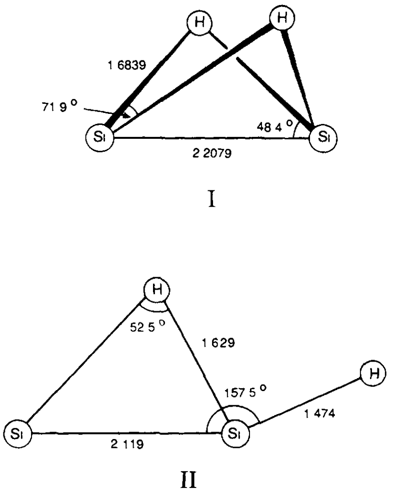


Figure 4 Ground (I) and excited state (II) conformers of Si_2H_2 Bond distances are given in Å, details of the structures are given in references 32—34

Table 1 Experimental[32 34] and calculated[33] rotational constants for conformers of Si_2H_2 (MHz)

		A	*B*	*C*
(I)	Spectroscopic	157160 54	7157 94	7079 14
	Ab initio	163446	7236	7154
(II)	Spectroscopic	262091	7362	7162
	Ab initio	264170	7258	7064

predictions, and other factors led the spectroscopists to structure (II) Once again there was satisfactory agreement between *ab initio* and experimental rotational constants (Table 1)

Much spectroscopic work remains to be done on Si_2H_2 and its conformers For example, no high resolution infrared spectroscopy of the molecule has yet been reported although Colegrove and Schaefer[33] have produced *ab initio* harmonic vibrational frequencies for the molecule The ground state (I), for example, is predicted to have a very intense transition of b_1 symmetry near 1220 cm^{-1}

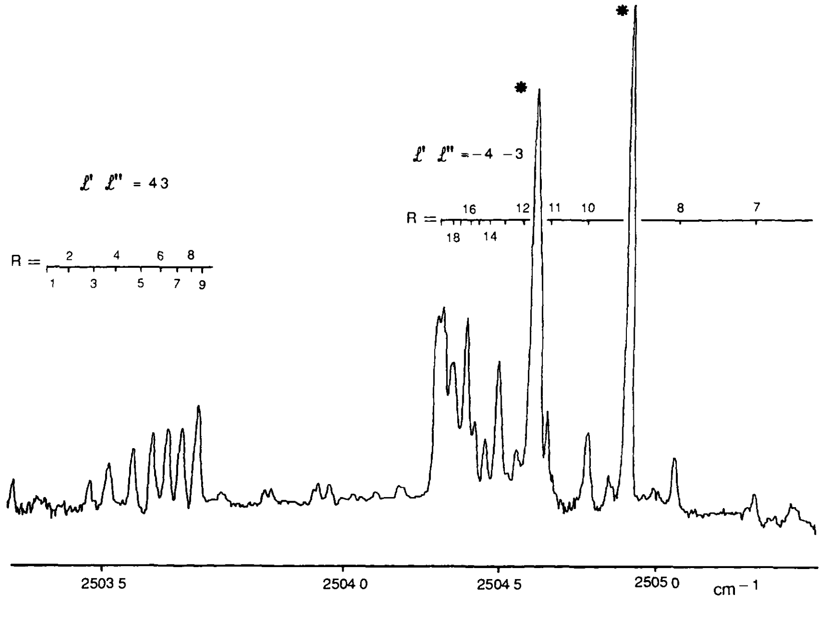
4.3 Rydberg States and Rydberg–Rydberg Spectroscopy

A great deal of structural information on the Rydberg states of hydrogen has been deduced from recent high resolution infrared spectroscopy Both emission FTIR[35] and laser absorption spectroscopy[36] have been used The increasing interest in the experimental spectroscopy of these molecules is that they provide model systems for *ab initio* calculations of Rydberg state rovibronic levels This is particularly true for H_2 There are two theoretical approaches to calculating energy levels multichannel quantum defect theory[37] and multipole polarization theory [38] In the case of hydrogen, both theories give excellent agreement with experiment although the latter method is restricted to high orbital angular momentum (high l) states From an experimental viewpoint the a c discharge is a copious source of Rydberg states In H_2, for example, it has been possible to detect 3d, 4d, 4f, 5f, 6g, 6h, 7h, 7i, and 8i states In addition, the discharge provides a convenient means of population modulation for detecting infrared Rydberg–Rydberg transitions

Infrared laser Rydberg–Rydberg spectroscopy of other diatomic molecules is now being developed, *e g* of nitric oxide An emission spectrum from air at $4\mu m$ is now known to arise from the 4f–5g system of nitric oxide [39] Recently, Martin *et al* [40] examined this band in an a c discharge using diode laser spectroscopy A representative spectrum is shown in Figure 5 The non-penetrating Rydberg states (*i e* 4f and 5g) are best described by Hund's case (d) coupling In this coupling scheme the rotational angular momentum $\boldsymbol{R}$ of the NO$^+$ ($^1\Sigma^+$) core is coupled to the orbital angular momentum $\boldsymbol{l}$ of the Rydberg electron to yield a total momentum $\boldsymbol{N}$ It is convenient when describing these states to introduce a new quantum number $\mathscr{L}$ defined as $\mathscr{L} = (N-R)$ $\mathscr{L}$ takes values from $+l$ to $-l$ (At high values of R, levels with the same $|(N-R)|$ converge) The most prominent features of the spectrum, such as that shown in Figure 5, are those having constant $\mathscr{L}'$, $\mathscr{L}''$ and R

The Rydberg energy levels of the 4f, 5g states of NO have been calculated using the multipole-polarization method Unfortunately this is not as straightforward to apply as it is for H_2 because the *ab initio* properties of the NO$^+$ core are less well known In their analysis of the NO 4f—5g Rydberg spectra Martin *et al* [40] therefore adopted a different approach, using four variable molecular parameters These were the Quadrupole moment (Q_{zz}) and the polarizabilities (α_s, α_t) of the core and a parameter

Figure 5 Part of the diode laser absorption spectrum of the 4f—5g Rydberg–Rydberg transition in NO recorded with population modulation in a 10 kHz electric discharge Lines indicated * are atomic transitions



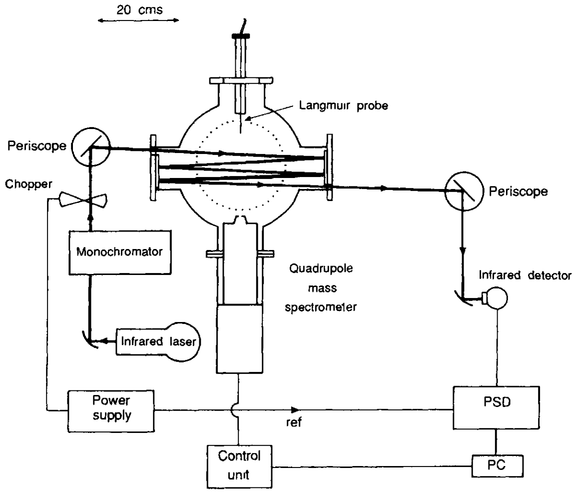


Figure 6 A parallel plate discharge cell used for CVD studies equipped with infrared diode laser, mass spectroscopy, and Langmuir probe diagnostics.[44]

d_Σ to allow for penetration of the core by the Rydberg electron. The spectra could be fitted quite well using these four variable parameters, but not quite to the level of accuracy of the experimental measurements. Improvements in the model have been suggested such as additional corrections for core penetration effects. The high resolution achievable in modern infrared spectroscopy of Rydberg states will hopefully stimulate new *ab initio* calculations of core properties for non-hydrogenic species.

5 Plasma Diagnostics

Apart from the fundamental structural information derived from high resolution spectroscopy, infrared laser spectroscopy has been particularly fruitful for chemical diagnostic studies of discharges. Methane and silane discharges are of practical importance as they are sources of thin surface films. Chemical vapour deposition (CVD) of diamond films from methane and other hydrocarbon plasmas is attracting much experimental[41] and theoretical attention.[42] Several types of discharge have been employed in hydrocarbon CVD studies – microwave, radiofrequency, and d.c. A number of different diagnostic techniques are required even to begin to characterize the complex chemistry of hydrocarbon and similar CVD discharges. These have included mass spectrometry for neutral radicals (CF_2, CF_3), laser induced fluorescence (CH, SiH, Si, CF_2), and infrared laser absorption (CH_3, SiH_2, SiH_3, CF, CF_2). The concentrations of charged species in the plasma have usually been measured with Langmuir probes. Diode laser spectroscopy has been singularly important for methyl radical diagnostics in methane plasmas. It has been proposed that methyl is an important growth species and the radical is incorporated in at least one modelling mechanism.[43] The spatial distribution of methyl in working CVD reactors is therefore of great interest.

A typical parallel plate plasma reactor is shown in Figure 6.[44] It is equipped with diode and other diagnostic techniques. In almost all cases in which IR spectroscopy has been used the methyl radical has been detected using a vibration–rotation transition from its ν_2 out of plane vibrational mode. The Q-branch lines of this parallel type band are conveniently intense and well documentated[45] between 600 and 700 cm^{-1}. There is an increasing body of evidence that the deposition rate of carbon films from methane plasmas is directly proportional to the gas-phase methyl concentration. To gain a better chemical understanding of the plasma processes, kinetic models are being developed which incorporate the large number of atom–molecule and ion–molecule reactions taking place in the discharge.[42,44] The diagnostic results provide essential tests for the validity of these calculations. However, in spite of all the experimental and theoretical effort our understanding of diamond CVD processes is far from complete. The reader is referred to authoritative articles in this field, for example by Bachmann and co-workers[46], for more details.

Similar studies have been carried out with silane plasmas where the important radicals are SiH_3[47] and, to a lesser extent, SiH_2.[48] Diode laser spectroscopy has been used to detect the ν_2 (bending) mode of SiH_2 and the ν_2 and ν_3 fundamental bands of SiH_3. Since SiH_3 has no known optical emission spectrum the diode laser technique is very important for its detection.

6 Concluding Remarks

The types of discharges we can expect to see developed in the near future are now becoming evident. There is increasing interest in studying ion clusters and larger organic-based free radicals. Hydbrid techniques which combine molecular beam and discharge technologies are clearly going to be important. Although this article is primarily concerned with microwave and infrared laser spectroscopy of discharges it is worth commenting that the same types of discharge and modulation methods have been used with other types of spectroscopy. We have already mentioned the use of opto-galvanic detection with visible lasers. Recently, Martin and Guelachvili[49] demonstrated that velocity modulation could be used in conjunction with FTIR to detect ions, *e.g.* ArH^+. In contrast to the great majority of laser experiments this observation was made with emission spectroscopy. Subsequently they showed that population modulation FTIR was also feasible. In velocity modulation FTIR the source emission line is phase-shifted due to the Doppler effect on the emitting ion, whilst in population modulation FTIR the intensity of the emission is amplitude modulated. Nakanaga *et al.*[50] also used FTIR spectroscopy to detect the cations H_3^+ and HN_2^+ in a 1 kHz hollow cathode discharge. (However, they did not mention whether they exploited the a.c. nature of the discharge in their detection scheme.) The ions detected so far by FTIR are amongst the most stable closed-shell species and it remains to be seen whether FTIR will eventually be as fruitful as the microwave and laser techniques.

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