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MOLECULAR SPECTROSCOPY: Some Personal Reminiscences¹

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EARLY YEARS 1943–1949

My career as a molecular spectroscopist began at the end of my final undergraduate year at Cambridge University when Dr. GBBM Sutherland approached me to see if I would be willing to work with him on some problems in infrared spectroscopy. I agreed, provided that the work was largely experimental and did not involve too much high-powered mathematics. I subsequently learned that this struck a sympathetic chord in him.

There were two main schools of infrared spectroscopy in the UK at that time, one at Oxford and one at Cambridge. Both were working on problems connected with the war effort. One of their main activities concerned the analysis of enemy aviation fuel, and infrared spectroscopy provided a means for identifying the components of this fuel. First, however, a catalog of hydrocarbon spectra had to be established. Thus, the work was divided so that hydrocarbons that boiled at less than 120°C were assigned to Oxford while those that boiled at 120°C or more were studied at Cambridge.

Although several people were already working on this project, I was asked to study some problems connected with polymers. I was given a Hilger infrared spectrometer equipped with a rock salt prism and a

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Schwarz thermocouple. I soon discovered that even a background spectrum contained many lines in addition to the well-known water lines. These additional lines originated in a thin film of pyroxylin that had been used to coat and protect the rock salt prism. I, therefore, repeatedly dried and distilled a sample of amyl acetate and one day, with much trepidation, proceeded to wash the rock salt prism. After successfully completing this operation, I inquired if I should also wash the KBr window on the thermocouple. Assured that this was a reasonable thing to do, I washed the window and reassembled the apparatus. Nothing worked, so I took the apparatus apart again and found that the amyl acetate had loosened the cement that held the KBr window in what was originally a vacuum thermocouple.

Finding the spectra of substances like polystyrene and cellulose acetate difficult to interpret, I decided to study the spectra of a series of sugars. To simplify the problem further, I studied the series cyclohexane, tetrahydropyran, 1, 4-dioxane and trioxane in an attempt to understand the ring frequencies. There was interest as to whether these compounds existed in a chair or boat configuration. Because these structures belong to different symmetry groups with different numbers of infrared and Raman active fundamentals, they can usually be distinguished by the numbers of fundamentals observed. Unfortunately, the standard textbooks on group theory and normal vibrations had not yet been published, but the article by Rosenthal & Murphy in the *Reviews of Modern Physics* (1) was very helpful.

Upon completion of my doctorate, I found no shortage of jobs, in contrast to the present-day situation. I was offered appointments in Australia, Canada, Sweden, the USA, and even Bahrein, but decided to go to Canada. This decision was based partly on the advice of my undergraduate supervisor, FS Dainton, who had the highest regard for EWR Steacie, who was, at that time, the Director of the Chemistry Division of the National Research Council (NRC) at Ottawa. I had married Nancy Brayshaw in June 1946, and together we set sail for Canada in July 1947 on the first post-war voyage of the Empress of Canada. Our cabin had not been completely renovated after wartime use, so our fare was reduced to £15 each—the best travel bargain we are ever likely to get.

In Ottawa, I first worked with R Norman Jones who was interested in the infrared spectra of steroids. He was working in collaboration with Konrad Dobriner of the Memorial Hospital in New York in an attempt to find a clue as to the origin of cancer. Together they had compiled a catalog of the infrared spectra of a large number of ketosteroids and had made interesting correlations between the frequency of the carbonyl group and its position in the ketosteroid framework (2). I decided to see if

intensities could add any useful information and made a study of methods for measuring the intensities of bands with spectrometers of limited resolving power, such as were available at that time (3). This paper subsequently became a Citation Classic, but I do not regard it as my most significant contribution.

I was looking for an opportunity to enlarge my spectroscopic horizon when, fortunately, Dr. G Herzberg came to the Physics Division of the National Research Council in 1948. I applied for a transfer and commenced working with him in July 1949. Further details of this early period are given in an article that I was recently asked to write for the *Canadian Journal of Chemistry* (4).

DIVISION OF (PURE) PHYSICS 1949–1976

Free Radical Studies

The first objective on arriving in the Physics Division was to try to get a spectrum of the CH_2 free radical. We decided to try to produce the radical by the flash photolysis of ketene and to photograph the spectrum in absorption by using a Lyman-type flash lamp to provide a source of continuum radiation. We also decided to use a grating spectrograph to aid our search because for sensitive detection one ideally needs an instrument with a resolution comparable to the Doppler widths of the lines.

I found a paper by Murphy & Edgerton (5) on the characteristics of flash lamps extremely helpful. With the assistance of George Ensell, a highly skilled glass (and quartz) blower, I proceeded to build a flash photolysis apparatus. Norrish & Porter (6) published their first article on flash photolysis around this time, but no experimental details were available until the second paper appeared in 1950 (7). I subsequently learned that Norman Davidson and coworkers (8) at Cal. Tech. were also using flash lamps at this time in their study of the recombination of iodine atoms.

Although the initial search for CH_2 was not successful, I did find spectra of SH (9) and NH_2 (10). The latter was particularly interesting because we were able to show that some of the features observed in absorption coincided with features in the emission spectrum of an oxy-ammonia flame. Before this, no definitive proof had existed that the latter spectrum, known as the α -bands of ammonia, was produced by the NH_2 free radical. We were able to establish the presence of N and H atoms through experiments with $^{15}\text{NH}_3$ and ND_3 (11).

The spectrum of $^{15}\text{NH}_2$ was so similar to that of $^{14}\text{NH}_2$ that, even in the absence of any detailed analysis, we could identify corresponding features. The $^{14}\text{NH}_2 - ^{15}$

the origin of the system was near $10,000\text{ cm}^{-1}$ and that the angle in the excited state was about 160° . However, because quasilinear molecules were unknown at that time and because the band types alternated in the spectrum, we decided that the excited state was probably linear.

There was some excitement in the lab when a report came through from Belgium that Monfils & Rosen (12) had obtained the spectrum of the 4050 Å bands in a discharge through CH_4 and found no isotopic shifts when they substituted CD_4 . This system of bands, which were originally found in the spectra of comets, had been tentatively assigned to CH_2 by Herzberg (13). Alex Douglas was asked to repeat the experiments using $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ and mixtures thereof. From the number of band heads he was able to observe, and from a rotational analysis of the bands, he established that the spectrum was produced by the linear C_3 molecule (14, 15).

The second polyatomic free radical that I was able to find was HCO . A system of bands in the near ultraviolet, known as the hydrocarbon flame bands, was known at the time and was tentatively attributed to the HCO free radical (16), but confirmation did not come for several years (17, 18). I found a series of bands in the visible (19), and from isotopic shifts between HCO and DCO I established that the origin lay in the near infrared. The bands have a very simple rotational structure consisting of a P, Q, and R branch. Lying approximately halfway in between is a series of diffuse bands. The sharp bands were interpreted on the basis of a $K_a' = 0 - K_a'' = 1$ transition from a ground state with a nonlinear structure to an excited state with a linear configuration (20).

It is interesting to reflect that prior to 1950, the only example of a molecule that undergoes a change of shape in an electronic transition was CS_2 (21). In the early 1950s, Ingold & King (22) and Innes (23) showed that the ultraviolet bands of acetylene lead to a *trans*-bent configuration in the excited state while Herzberg & Innes (24) showed that the ultraviolet bands of HCN lead to a bent configuration in the excited state, with a H-C-N bond angle of 125° . The situation in HCO is almost exactly the reverse; in the ground state, the angle is 125° , while in the excited state, the molecule is linear (25).

In 1952 I had an interesting meeting with AD Walsh at Leeds University. I listened while he expounded his theories on AH_2 , HAB , and BAC molecules, which were subsequently published in a series of papers in the *Journal of the Chemical Society* (26). At first I was highly skeptical that anything based on such simple premises could have any widespread application, but over the years I found that many of his predictions were confirmed by experiment, and I developed a great admiration for his work. Walsh diagrams still find a place in the literature, though nowadays they tend to be superseded by ab initio calculations.

The rotational analysis of the NH_2 bands provided a considerable challenge, but after a few years, I was able to find three bands with similar rotational structures in different regions of the spectrum and with ground-state combination differences that agreed. Computers were not then available, so to calculate rotational term values for an asymmetric top molecule, I had to interpolate in the tables published by King, Hainer & Cross (27). I established the geometry of the ground state of NH_2 and showed that the angle was very similar to that in the ground state of water (28).

The spectrum consists of a long progression of bands with alternating band types. Some sub-bands were of the type $K_a' = 0 - K_a'' = 1$ (Σ -sub-bands), while others were of the type $K_a' = 1 - K_a'' = 0$ (Π -sub-bands). The question remained, where are the other sub-bands? Eventually I found some $K_a' = 2 - K_a'' = 1$ sub-bands (Δ -sub-bands) lying about 100 cm^{-1} below the corresponding Σ -sub-bands and, later, some $K_a' = 3 - K_a'' = 2$ sub-bands (Φ -sub-bands) lying about 200 cm^{-1} below the corresponding Π -sub-bands. Remembering that the splittings between the various l -components for the bending vibrations of a linear molecule vary as gl^2 , where g is normally of the order of 1 cm^{-1} , I invoked a similar dependence, gK^2 , where $g \sim -27 \text{ cm}^{-1}$, to explain the large separations found in the NH_2 spectrum. In this way, I also found some higher sub-bands (Γ , H , etc).

I wondered why there were such large splittings in the NH_2 spectrum and eventually came across a clue in one of Mulliken's papers (21) in which he referred to a paper by Renner (30), who was a student of Teller. Renner (30) showed that, in a molecule with electronic angular momentum, there can be considerable interaction between this angular momentum and the vibrational angular momentum associated with the bending vibrations of the molecule. He gave specific examples for a molecule in an electronic Π state.

From the work of Walsh (26) and others, I realized that both the ground state and excited state of NH_2 are components of a $^2\Pi$ state in the linear configuration. By extrapolating the behavior calculated by Renner (30), I could explain the structure found in the excited state of NH_2 and, thus, provide the first example of this type of interaction in an electronic spectrum (31, 32).

In the summer of 1957, I made an extensive visit to Europe and established many valuable contacts. At Cambridge, I gave a seminar to the Theoretical Chemistry Group about my NH_2 work, and this resulted in the paper by Pople & Longuet-Higgins (33). I met DWG Style at King's College in London, and he showed me some of the emission spectra he and his colleagues had taken of the fluorescence obtained from molecules excited by vacuum ultraviolet radiation. The energy of this radiation

was sufficient to dissociate the molecules and excite one or more of the fragments, which then fluoresced. From energetic considerations it was highly likely that fluorescence would involve the ground state of the fragment. Although the spectra were taken with very low resolution, the spectral region and the possible carrier were still of great interest because it might be possible to obtain high-resolution spectra in absorption using flash photolysis. Indeed, on my return, my colleagues and I did obtain absorption spectra of two of the radicals, NCO and NCS, which we published jointly with Style & Holland (34).

In Uppsala, I met Stig Claesson and we spent two days exchanging our experiences with flash photolysis. He had carried out considerable work on the construction and performance of flash tubes (35), and we later adopted his method of sealing electrodes to flash lamps with araldite. I was interested in his experiments on the breaking strengths of flash tubes and was pleased that we could be spared this activity. I made many subsequent visits to his laboratory.

Soon after my return I built a larger flash photolysis apparatus with an absorption cell 2 m in length. The absorption path length could be increased up to 80 m with a multiple reflection mirror system. This apparatus has remained in use to the present day. We observed the NH_2 spectrum down to the first vibronic level at 9000 Å (36). Later we were able to observe the HCO bands with sufficient intensity that H^{13}CO bands could be seen in natural abundance (25). In the same spectra, weak axis-switching lines (37) were also observed, and analyzing them resulted in a refined ground-state geometry.

Many workers in the Spectroscopy Group at NRC have used the flash photolysis technique over the years. A brief list of the polyatomic free radicals that have been studied under high resolution and yielded information on the geometries and vibration frequencies of these species follows: BH_2 (38), CH_2 (39–43), NH_2 (32, 36, 44), AlH_2 (G Herzberg & JWC Johns, quoted in 45, p. 583), SiH_2 (46, 47), PH_2 (48, 49), CH_3 (39, 50), HCO (20, 25, 51), HNO (52, 53), HCF (54), HNF (55), HCCl (56), HSiCl (57), HSiBr (57), HSiI (58), C_3 (59, 60), CCN (61), CNC (62), NCN (63, 64), CCO (65) NCO (66–68), CNO (69), N_3 (70) BO_2 (71), NCS (72), HNCH (73), and HCCS (74). Other species that have been studied include the C_3H_2 (75), C_5H_5 (76), vinoxy (77, and references therein), allyl (78), and propargyl radicals (79).

Some unusual structural rearrangements were discovered during the course of these photochemical studies. For example, during the flash photolysis of straight-chain pentadiene, the spectrum of cyclic C_5H_5 was obtained (CL Currie & DA Ramsay, unpublished data). Porter & Ward (81) obtained a similar result in the flash photolysis of anisole, which is a

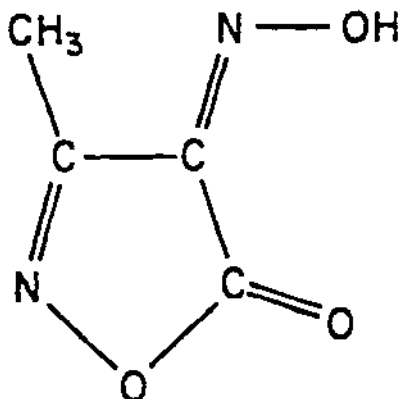


Figure 1 The 3-methyl-4-oximinoisoxazol-5(4H)-one molecule.

six-membered ring compound. The flash photolysis of thiophene, a five-membered ring compound, yielded the spectrum of SH and a new spectrum, which was originally assigned to C_4H_3 (82). A high-resolution study showed, however, that the carrier was the linear HCCS radical (74). Finally, the flash photolysis of 3-methyl-4-oximinoisoxazol-5(4H)-one (Figure 1) yielded spectra of NH, OH, CN, NCN, NCO, HNCN, and a new spectrum, which was assigned to CNO (69).

H + NO Reaction

With a summer visitor in 1961, we decided to look at the emission produced by reacting H atoms with NO. The initial spectra were photographed using a prism instrument and showed strong bands with a series of line-like features (83). These features were identified as R-heads of sub-bands of the $\tilde{A}^1A'' - \tilde{X}^1A'$ system of HNO. The sub-bands involve much higher values of K' than are seen in the absorption spectrum (52) and come to an abrupt halt after $K' = 13$ for the 000 level. This phenomenon is reminiscent of the well-known breaking-off in the rotational structures of diatomic molecules (84) and is caused by predissociation in the upper state. After more than 30 years, this is still the only example of breaking-off in the rotational structure of a polyatomic molecule.

The C_2 Molecule

We tried to observe the infrared spectra of free radicals that are produced by rapidly passing gases, e.g. CH_4 , through a carbon furnace and found, even with an evacuated furnace, an emission band in the region of 5600 cm^{-1} . Analysis showed it to be the 0-0 band of a $^3\Sigma_g^- - ^3\Pi_u$ system of C_2 (85). One line involving an upper-state F_1 level with $J = 52$ was found to

be displaced by 0.15 cm^{-1} . The level that caused this small perturbation was eventually identified as the $J = 52, v = 3$ level in the lower state of the Phillips bands ($^1\Pi_u - ^1\Sigma_g^+$) (86). With this information, we discovered that the $^1\Sigma_g^+$ state is the ground state of the C_2 molecule and not the $^3\Pi_u$ state as was formerly thought. We confirmed this result after observing six small singlet-triplet perturbations; the separation between the $^1\Sigma_g^+$ and $^3\Pi_u$ levels is $610 \pm 5\text{ cm}^{-1}$ (85). Interestingly, the controversy concerning the ground state of CH_2 was also eventually settled by the observation of small perturbations between the lowest singlet and triplet states (87).

One reason the $^3\Pi_u$ state had been considered the ground state of the C_2 molecule is that the Swan bands ($^3\Pi_g - ^3\Pi_u$) are prominent in the spectra of comets, although the Phillips bands ($^1\Pi_u - ^1\Sigma_g^+$) have also been observed. No satisfactory reason has been given for the strength of the Swan bands, but it seems reasonable that an optical pumping mechanism is involved and that molecules pass from the singlet to the triplet manifolds via singlet-triplet perturbations.

Spectrographs

In 1961, I constructed a 7.3-m over-and-under Ebert spectrograph with the able assistance of Werner Goetz. I had a valuable discussion with Bill Fastie at Johns Hopkins University concerning the best arrangement for the slit, mirror, plane grating, and plate holder to produce a flat focal plane. The instrument gave a resolution of about 600,000 over an 18-inch plate length, which was sufficient to resolve the rotational structure of many molecules down to the Doppler widths of the lines. The grating was a Bausch & Lomb replica of an original Harrison (MIT) grating and was blazed at approximately 63° . The grating was used in high orders, which were separated by a foreprism placed before the entrance slit. The dispersion ranged from $0.20\text{ \AA/mm}$ at $6000\text{ \AA}$ to $0.10\text{ \AA/mm}$ at $3000\text{ \AA}$.

For survey work, e.g. in flash photolysis experiments, we also built a 21-foot Eagle spectrograph with the same entrance slit and with the concave grating located in front of the Ebert mirror. The curved plateholder could accommodate two 18-inch plates. The instrument was used in low orders of the grating, from 1 to 4, and the region from $9000\text{ \AA}$ to $2500\text{ \AA}$ could be covered in four settings, which was very convenient when searching for new spectra. When new features were observed, they could be investigated at higher resolution by switching from the Eagle to the Ebert spectrograph. It is interesting to reflect that the photographic plate is still the only detector that permits the simultaneous recording of spectra

over a wide spectral region in periods of time as short as a few tens of microseconds.

Glyoxal

Apart from the time devoted to finding new free radical spectra, we made a detailed study of the spectrum of glyoxal and its isotopic derivatives. This molecule has C_{2h} symmetry and is a near symmetric top. It has one small moment of inertia about an axis that lies between the oxygen and carbon atoms in the direction of the O-C-C-O framework. The first transition, which involves a $\pi^* - n$ excitation, has its 0-0 band at 4550 Å. The selection rules involve $\Delta K_a = \pm 1$, so that the band consists of a series of sub-bands that are well separated at the high frequency end of the band but that overlap extensively at the low frequency end. King (88) had carried out an analysis of the symmetric top portions of the band, but Paldus and I were able to analyze the asymmetric top part of the band as well (89).

ASYROT Computers were becoming available about this time, and I had the good fortune to meet Fraser Birss, a theoretical chemist at the University of Alberta at Edmonton. He was working on problems that by their very nature were only asymptotically convergent and relished the opportunity to work on a problem that, though large, was nevertheless bounded. He developed the program ASYROT, which calculates eigenvalues and eigenvectors for an asymmetric top molecule, produces frequencies and intensities of lines according to selection rules provided, accepts frequencies of assigned lines, and performs a least squares adjustment to produce improved values of the molecular constants (90). This program has proved to be invaluable in our analyses of molecular spectra, and one important feature is the calculation of the line intensities, which are an important guide in making assignments.

ASYROT was used extensively to assist in the rotational analysis of many bands of glyoxal and its isotopic derivatives (91–93). Birss et al (93) obtained sufficient data to deduce the geometry of the molecule in its ground and excited states (93). This work provided the basis for subsequent photochemical studies. Glyoxal is a molecule of intermediate size and an ideal prototype for studies of dissociation, internal conversion, and intersystem crossing. Parmenter (94) and others have carried out extensive work in this area by using tunable lasers to excite specific rovibronic levels.

Later, we studied the emission from glyoxal excited by the various lines of an argon ion laser. The fluorescence bands were readily assigned except for a series of bands excited by the 4880 Å line (95). Looking at the

absorption spectrum, we noticed that the rotational structure, while similar to that of glyoxal, showed about twice the number of sub-bands. Rotational analysis showed that the band was produced by a *cis*-isomer of the molecule (96). The molecule in this configuration has a dipole moment and the microwave spectrum was subsequently found.

Electric Field Studies

David Buckingham was a regular visitor to the lab in the late 1960s and early 1970s and inspired us to carry out some work with electric and magnetic fields. We constructed a 2-m Stark cell equipped with multiple reflection mirrors and studied formaldehyde. Freeman & Klemperer (97) had measured the dipole moment of the first singlet-excited state so we decided to make a measurement on the corresponding triplet state (98). In the course of this work, we found that we had to revise the spin constants for the triplet state, and this prompted Birss to write another program (STROT) for the analysis of triplet-singlet bands. This program was tested on formaldehyde (99) and subsequently used to analyze additional triplet-singlet bands of formaldehyde (100), propynal (101), and other molecules.

One interesting experience involved the Stark effect on the near ultraviolet bands of CS_2 . Because the molecule is linear in its ground state and nonlinear in its excited state, no first-order Stark effect is expected. When we looked at the simple Σ -type band near 3775 Å, however, we found that the $R(26)$ and $P(28)$ lines showed a marked Stark effect, indicating a pseudo-first order Stark effect in the excited state. The reason is that the $27_{0,27}$ and $26_{1,26}$ levels in the excited state are nearly degenerate and are coupled by the electric field. By analyzing the Stark shifts, we determined the dipole moment of the molecule in the excited state and the zero-field separation between the two levels (102).

Magnetic Field Studies

In 1970, we built a magnetic rotation apparatus and used this to identify triplet-singlet transitions in various molecules (103–105). Excellent spectra could be photographed at high resolution with exposure times on the order of 1 h by using modest field strengths in the range 1–3 kG. We carried out a detailed study of the magnetic optical activity in the $\tilde{a}^3A_2 - \tilde{X}^1A_1$ system of formaldehyde and devised methods for measuring separately the magnetic circular dichroism and magnetic circular birefringence (105). This study paralleled a similar earlier study of the Kerr effect in the same transition (106).

Later, several groups interested in the photochemistry of formaldehyde began working on measurements of lifetimes and fluorescence quantum efficiencies of specific rovibronic levels in the $\tilde{A}^1A_2 - \tilde{X}^1A_1$ system. Because

fluorescence quantum yields are usually less than unity, the question arises: Where does the energy go? Does it go into high rovibronic levels of the ground state—internal conversion—or to levels of the $\tilde{a}^3A_2$ state—intersystem crossing? The magnetic rotation spectrum of formaldehyde in the near ultraviolet shows many irregularly spaced lines with widely different intensities. Because high resolution spectra can be obtained with low field strengths, the Zeeman shifts of the lines are small. By comparing the magnetic rotation lines with an absorption spectrum, one can usually decide which rotation line corresponds to a given absorption line. In this way, we determined which rotational levels in the excited singlet state were mixed with triplet levels. The pattern that emerged was that strong ${}^{\prime}R$ and ${}^{\prime}P$ lines and medium intensity ${}^{\prime}P$ and ${}^{\prime}R$ lines that correspond to perturbed levels can be seen in the magnetic rotation spectrum, but ${}^{\prime}Q$ and ${}^{\prime}Q$ lines, which are strong in the absorption spectrum, are rarely seen in the magnetic rotation spectrum. In this way, singlet-triplet perturbed levels were identified in many vibrational levels of the excited singlet state (107–110). We now know that intersystem crossing plays only a minor role in formaldehyde and that internal conversion and predissociation are mainly responsible for the low quantum efficiencies found for most excited-state rovibronic levels.

33-Meter Absorption Tube

In the mid-1960s, with the able assistance of Werner Goetz, we built a 33-m absorption tube and equipped it with multiple reflection mirrors. In one of our early experiments, we searched for the triplet-singlet bands of ethylene in the gas phase. In 1950 Reid (111) had studied the absorption spectrum of liquid ethylene with path lengths up to 2.5 m and found a series of bands in the region 3350–2600 Å, which he assigned as triplet-singlet bands. Gavin Currie and I filled the long tube with ethylene at pressures of up to 2 atm but were unable to find any bands in the region studied by Reid, even with up to 64 traversals of the multiple-reflection mirror system. Therefore, we built a cell for studying liquid ethylene, but with path lengths up to 3 m and with the same spectrograph used by Reid, we were unable to observe any bands. Our cell was closed while his was open to the atmosphere; hence, we concluded that his bands were probably caused by the well-known enhancement of triplet-singlet transitions by oxygen. We did not think it prudent to add oxygen to the ethylene in our long tube.

With McKellar we filled the long tube with HD at 1 atm pressure and with path lengths up to 3 km we observed vibrational overtone spectra from the 3-0 to the 6-0 band (112). The 5-0 and 6-0 bands were new and particularly interesting because lines seen in the spectra of Jupiter and

other planets had been tentatively assigned as the $R(0)$ lines of these two bands. Our measurements confirmed the assignments and, using intensity measurements, we were able to revise the value for the D/H ratio in Jupiter. These bands have since been observed with much shorter path lengths in laser cavity experiments, but the latter do not give such accurate intensity measurements.

We also filled the tube with methane and, using path lengths up to 5.3 km and pressures up to 1.6 atm, we found lines in the near infrared that showed many coincidences with spectra of Uranus taken by Lutz. The presence of methane in this planetary atmosphere was thereby confirmed (113).

The long tube was filled with oxygen, and several new bands of the Herzberg I, II, and III systems were found and analyzed (114–116). The absorption spectrum of water vapor was studied and features observed as far as 4000 Å (117). Experiments were also carried out with carefully purified pyridine and bands found in the region 3000–3400 Å, which were tentatively assigned to two triplet-singlet transitions (118).

HERZBERG INSTITUTE OF ASTROPHYSICS 1976 TO PRESENT DAY

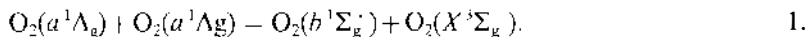
The formation of the new Institute did not involve any move, but it did bring the astronomers into closer daily contact with the spectroscopists. Otherwise, activities continued as usual.

Infrared Chemiluminescence

High-resolution Fourier transform spectrometers became available in the early 1980s and now produce enormous quantities of data in the infrared and, to a lesser extent, in the electronic regions of the spectrum. I became involved in a collaboration with Professor Ewald Fink of the Universität Wuppertal, Germany on studies of near infrared chemiluminescence excited by metastable $a\ ^1\Delta_g$ oxygen molecules. At first sight, it might be thought that the intensity of the chemiluminescence would be insufficient for the recording of high-resolution spectra and that the number of systems would be severely limited, but experience has shown that high-resolution spectra of many molecules can be obtained. Because the excitation energy available in $^1\Delta_g$ oxygen molecules is about 8000 cm^{-1} , most of the spectra recorded lie in a region below this frequency. This is a region that lies beyond the limit of photographic plates and one that had been relatively unexplored by infrared spectroscopists.

The first system studied was the $b\ ^1\Sigma_g^+ - a\ ^1\Delta_g$ system of oxygen, which

Noxon (119) first found in the spectrum of the night sky. The molecules in the $b\ ^1\Sigma_g^+$ state are produced by an energy-pooling mechanism:



The transition is electric quadrupole in nature as is evidenced by the observation of S, R, Q, P, and O branches (120). The radiative lifetime for the transition is calculated to be 720 s (121). With added gases, or at higher pressures of oxygen, at a total pressure of a few torr, a broad band emission was observed underneath the discrete rotational structure. This emission was assigned to $O_2(b):M$ collision complexes (122).

All Group VI–Group VI diatomic molecules have low-lying energy levels similar to those of oxygen, and all $b-X$ and some $a-X$ transitions have been studied using this technique (123). The present limitation on the observation of the $a-X$ transitions is experimental and dependent on the availability of suitable detectors. The transitions in the homonuclear diatomic molecules are magnetic dipole in character (124) while those for the heteronuclear diatomic molecules are electric dipole. The $b\ ^1\Sigma_g^+ - X\ ^3\Sigma_g^+$ system of SeS proved to be particularly interesting (125). The signal-to-noise ratio, of the strong lines was ~ 1000 and 4 of the expected electric dipole branches were observed. The 1R_0 branch was not observed. Another R branch was found in a similar region and was found to be magnetic dipole. Two other weak magnetic dipole branches were also found. This is the first example of a band in which both electric and magnetic dipole branches are observed. The reason for the absence of the 1R_0 electric dipole branch is given by Watson's theory of intensities in triplet-singlet transitions (126). The matrix elements contain two terms, one dependent on a transition moment along the internuclear axis and the other on a transition moment perpendicular to this axis. For the 1R_0 branch in SeS, these matrix elements are very nearly equal, though opposite in sign; hence, the calculated intensity is below the noise level of the experiment. The ratios of the parallel and perpendicular transition moments and of the magnetic transition moment were obtained from the relative intensities of the observed branches. Bielefeld et al (127) had measured the radiative lifetime of the transition; thus, we were able to obtain absolute values for these transition moments.

Molecules with large spin-orbit splittings in their ground states were also studied using this technique. The $^2\Pi_{1/2} - ^2\Pi_{3/2}$ transition of TeH (128) and the $X_{21} - X_{10}^+$ transition of BiH (129) have both been analysed and spectra of the corresponding halides have been obtained. High-resolution spectra of the $\tilde{A}\ ^2A' - \tilde{X}\ ^2A''$ systems of HO_2 , HS_2 , HSe_2 , and HTe_2 have also been recorded.

Experiments with Thioformaldehyde

In 1980 we started a series of experiments on thioformaldehyde that have continued to the present day. Thioformaldehyde is an ideal molecule in many respects because the $\tilde{A}^1A_2 - \tilde{X}^1A_1$ and $\tilde{a}^3A_2 - \tilde{X}^1A_1$ ($\pi^* - n$) transitions both lie in the region of lasers that use Rhodamine dyes. Furthermore, the spectroscopy of some of the singlet and triplet levels is well understood (130).

THE $v' = 0$ PERTURBATIONS The $v = 0$ level of the $\tilde{A}^1A_2$ state shows many perturbations in the levels with $K_a = 0$ to 6, and magnetic rotation studies show that these perturbations are magnetically sensitive. An analysis of the problem showed that all of the perturbations could be explained by interactions with the rotational levels of a single vibrational level of the $\tilde{a}^3A_2$ state. Sufficient information was available to determine the mechanism of the triplet-singlet interaction. Stevens & Brand (131) had given the matrix elements for two possible mechanisms, viz. spin-orbit orbital-rotation and vibronic spin-orbit interactions. A vibronic spin-orbit mechanism with a matrix element of $0.651(7) \text{ cm}^{-1}$ times the appropriate J and K factors explained all the observed perturbations (132).

INTERMODULATED FLUORESCENCE Intermodulated fluorescence experiments with a resolution of a few MHz showed that the K -type doublings observed in various branches, e.g. 1R_3 , differed from the calculated splittings in a seemingly random manner; some of the discrepancies were as large as a few hundred MHz. This result led us to suggest "that in the spectra of polyatomic molecules numerous perturbations exist between the higher rovibronic levels of the ground state and the corresponding levels of electronically excited states" (133, p.397). Confirmation of these results was obtained by direct measurement of the K -type splittings by radiofrequency-optical double resonance (134). Similar small perturbations in the $\tilde{A}^1A''(000)$ states of HNO and DNO have also been found by microwave-optical double resonance (135, 136). More recently, Adam et al (137) have found similar behavior in the $\tilde{A}^2\Pi_u$ state of BO_2 .

MICROWAVE-OPTICAL DOUBLE RESONANCE We have carried out many experiments involving microwave-optical double resonance. Originally we had hoped to determine rotational constants for molecules in electronically excited states with the same precision as is normally obtained for ground states. The high rovibronic levels of the ground state cause numerous small perturbations in the excited-state levels, however, which thwarts this objective.

High rovibronic levels of the ground state Our work thus far has been

limited to the 8–12 GHz region and, in general, to the $v_4 = 1$ level of the $\tilde{A}^1A_2$ state of thioformaldehyde. In this region, only four microwave transitions are expected in the excited state. Numerous microwave-optical signals have been found, however, and are accompanied by a decrease in the fluorescence signal from the excited state. These signals are interpreted as microwave transitions from rovibronic levels of the excited state to high rovibronic levels of the ground state (138, 139). The density of the vibrational levels of the ground state in the region of the electronically excited state is ~ 1 to 2 levels per cm^{-1} .

Collisional Processes Some of the above transitions are strong (signal-to-noise ratio > 100) and provide a convenient way for monitoring specific rovibronic levels in the excited state. By fixing the microwave frequency on one of these transitions and scanning the laser, the relative efficiencies for rotational relaxation from excited-state levels to a specific level are readily obtained. We found changes of J up to ± 12 and of $K_a = \pm 2$ (140). The selection rule symmetric $\leftrightarrow$ antisymmetric has never been violated. These experiments should be repeated with time resolution.

Magnetic studies Experiments carried out in the presence of a magnetic field result in well-resolved Zeeman patterns. By measuring the Zeeman shifts in parallel and perpendicular polarisations, rotational g -factors can be obtained for the excited state level and for the high rovibronic level of the ground state (141). Whether the high rovibronic level of the ground state lies higher or lower in energy than the excited-state level can be determined by using circularly polarized light (142). Some anticrossings have been observed and assigned to rovibronic levels of the $\tilde{a}^3A_2$ state and high rovibronic levels of the ground state (143).

Comets Halley and Wilson

In 1986 I was fortunate to obtain time on the Anglo-Australian telescope to observe Comet Halley. On the first night, I recorded spectra in the region 3500–6000 Å using the Image Photon Counting System; the dispersions ranged from 3–5 Å/mm. On the second night, I recorded spectra in the region 6000–9250 Å at dispersions of 10–20 Å/mm using a Charge Carrier Device as detector. The weather was cooperative. Many well-known molecular spectra were observed, including the red ($A^2\Pi - X^2\Sigma^+$) and violet ($B^2\Sigma^+ - X^2\Sigma^+$) systems of CN, the Swan ($d^3\Pi_g - a^3\Pi_u$) and Phillips ($A^1\Pi_u - X^1\Sigma_g^+$) systems of C_2 , the $A^2\Delta - X^2\Pi$ system of CH, the $A^1\Pi - X^1\Sigma_g^+$ system of CH^+ , and bands of the $\tilde{A}^2A_1 - \tilde{X}^2B_1$ systems of NH_2 and H_2O^+ . In addition the 6302 Å line of atomic oxygen was seen both in the comet and in the night sky.

As a result of the dispersions used to determine the spectra, the

rotational structures of the bands were well resolved. The rotational structures of the Swan bands are similar to those obtained from a carbon furnace at a temperature of $\sim 2500^\circ\text{K}$. However, C_2 is a homonuclear molecule and has no vibrational or rotational transitions in the infrared or microwave regions. Furthermore, temperature is not a meaningful concept in a comet because the pressures are extremely low. The rotational distributions are dependent on the rate of excitation of transitions (primarily electronic) under the influence of the sun's radiation and the rates of emission from the various electronic, vibrational, and rotational levels populated. The latter are of the order of 10^8 , 10^3 , and 10^{-2} s^{-1} , give or take an order of magnitude or two. The rate determining steps in most cases (except C_2) are the rate of excitation by the sun, which may be of the order of 10^{-2} s^{-1} , and the rate of microwave emission from the lowest rotational levels. Because the latter depend on the cube of the frequency of the transition and the square of the dipole moment of the molecule, the slowest process for a molecule in a $X^1\Sigma$ state will be emission from the $J = 1 - J = 0$ transition. For hydrides with large rotational constants the rate will be much larger than for nonhydride molecules. Thus, the spectra observed for CN show rotational structures up to about $J \sim 20$ whereas for the hydride spectra, CH, CH^+ , NH_2 , H_2O^+ , only a few low-lying rotational levels are observed. The simulation of the observed rotational distributions will present a challenge for my future activities.

In 1987 I made a return visit to the Anglo-Australian telescope to observe Comet Wilson, a new Comet on a hyperbolic orbit. Unfortunately, the first night was cloudy, and the second night was restricted to three hours of observation, but some spectra were obtained.

CONCLUDING REMARKS

The most revolutionary development of the last 50 years has been the introduction of the laser in the 1960s. Tunable lasers are now available in most regions of the spectrum from the far infrared to the vacuum ultraviolet. These sources permit not only more sensitive detection of molecular species but also much higher resolution. Computers, which facilitate calculations that would otherwise be impossible, have been another important development.

Apart from these two fundamental developments, there have been several important advances in technique. In the late 1960s, laser magnetic resonance was introduced (144) and has been very successful in detecting transient species both in the far and near infrared. In 1980, the first infrared spectrum of a molecular ion, H_3^+ , was obtained (145), and five years later, the first infrared spectrum of a negative molecular ion was reported (146).

No doubly charged ions have yet been observed in the infrared although several electronic transitions are known, particularly with the use of synchrotron radiation.

The use of supersonic jets has simplified the spectra of many molecules, both in the infrared and electronic regions of the spectrum. Under these conditions, it has been possible to obtain and analyze the spectra of larger molecules and to observe their van der Waals complexes, thus obtaining valuable structural information. Picosecond pulses have been used to stimulate molecules and obtain spectral information by a Fourier transform of the fluorescence from the time to frequency domain (147). In all these techniques, however, it should be remembered that there is a fundamental limitation to any spectroscopic determination, viz. that a rotational analysis yields at most only the three principal moments of inertia of the molecule in the two combining states, and only two moments of inertia in the case of a planar molecule.

Lasers have permitted the observation of two-photon and multiphoton processes and have allowed more information to be obtained for excited states of molecules because different selection rules are operative compared to single-photon processes. The resonance-enhanced multiphoton ionisation (REMPI) technique is an example of a technique with high sensitivity because single ions can be counted. Another interesting development is the zero kinetic energy (ZEKE) technique used to study ionization processes in molecules with much higher resolution (148).

Lasers also permit many types of double-resonance experiments to be carried out. One example is the pump-and-dump technique, which is used to probe the higher vibrational levels in the ground states of molecules (149). Our microwave-optical double-resonance experiments achieve a similar result with higher resolution, but the dump quantum is rather small.

One of the remarkable developments in the last twenty-five years has been the observation of approximately 100 molecular species in the interstellar medium and other astronomical sources with the aid of radio-telescopes (150). Several species, e.g. HCO^+ , N_2H^+ , and HC_9N , have been found prior to their observation in the laboratory.

The development of computers has resulted in high quality *ab initio* calculations. Prior to about 1975, such calculations were of limited value to the experimentalist. I recall a conversation with a theoretician concerning his calculations on pyridine. Failing to follow all the details, I asked how his results agreed with Nature, to which he replied, "That is Nature's problem." Nowadays, it is reasonable to expect that calculations will predict bond lengths to 0.01 Å, bond angles to 1°, vibrational frequencies to 10 cm^{-1} , excited-state energies to 0.1 eV, dipole moments to

10%, and transition moments to 50% or better. Such calculations would be of considerable value to spectroscopists in their searches for new transitions and new molecular species.

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