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Ian William Murison Smith. 15 June 1937—8 November 2016

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IAN WILLIAM MURISON SMITH

15 June 1937 — 8 November 2016



Jan W. Smith



IAN WILLIAM MURISON SMITH

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Elected FRS 1995

BY GUS HANCOCK*

Department of Chemistry, Oxford University, Oxford OX1 3QZ, UK

Ian Smith was one of the world-wide leading researchers into reaction kinetics, energy transfer and molecular dynamics in gas phase systems. He was able to span all of these aspects of collisional behaviour, and to form connections and insights that allowed him to make advances in all of them, advances which have stood the tests of time. His graduate work at the University of Cambridge was followed by academic positions in Cambridge and in Birmingham. He provided new insights into molecular energy transfer by systematically measuring how vibrational frequencies and multipole moments influenced the magnitude of the energy transfer cross sections. In reaction kinetics his detailed work on the OH radical has led to an understanding of the importance of its reactions not only in applied areas such as atmospheric and combustion chemistry, but also in fundamental dynamical studies of radical recombination and the effect of reagent energies on reactive processes. Of particular significance has been his development of both cryogenic and nozzle expansion methods of studying collisional processes at temperatures down to 10 K, with the discovery that reactions without activation barriers can get faster as the temperature decreases. The impact of this work upon astrochemistry has been profound, and has stimulated theoretical explanations of the effect. He was one of the first pioneers in the UK of the use of laser techniques to study collisional processes, using laser-induced fluorescence as a sensitive detection tool, UV laser photolysis to form reactive species and laser pumping to create excited state populations in order to observe their effect upon reaction pathways and vibrational relaxation.

Ian was devoted to his family—his wife Sue, their four children and 11 grandchildren. His research collaborators will always remember his scholarship, his unending suggestions of interesting problems to study, his deep integrity and humanity. His legacy lives on with his personal and academic families.

* gus.hancock@chem.ox.ac.uk

EARLY YEARS

Ian William Murison Smith was born in Leeds on 15 June 1937, the second of three children of William Murison Smith MB ChB and Margaret Moir Smith, whose maiden name was Forrest. Both his parents were from Aberdeen, so Ian was genetically 100% Scottish, a fact that his father would bring up whenever Scotland played England at rugby. His parents had moved to Farnley, on the outskirts of Leeds, shortly after they had married and his father had graduated in medicine from Aberdeen University. He obtained a partnership in West Leeds in 1929 and he continued to practice in the same partnership, through the conversion of private medicine to the National Health Service, for 37 years until his retirement in 1967. As was a rather general custom in those days, Ian's mother served as unpaid doctor's secretary and receptionist. Ian's elder brother, Bruce (b. 1933), recalls that one of his earliest memories of Ian was when his brother was about 18 months old, perched on the back seat of the family car, and sliding up to the door as a particularly sharp corner was negotiated by their father. The door opened, and Ian was deposited into the road. The absence of traffic and a cushion provided by his nappy meant that no harm was done, but this early manifestation of the motion of bodies under particular forces possibly influenced Ian's later thinking in the area of molecular dynamics. Ian, Bruce, who is a retired consultant paediatrician, and their younger sister, Elaine (b. 1942), who trained as a physiotherapist, all attended Fulneck School, a private Moravian institution on the outskirts of nearby Pudsey, which covered all school years. Ian studied there from 1942 to 1950.

In 1950 he was entered for the scholarship examination at Giggleswick, a boarding school in north-west Yorkshire. To prepare for it, he received some special tuition in mathematics and French. His maths tutor was pushing at an open door, since he had a natural ability and interest in that direction. His French tutor probably had a harder time, though in days when there was less emphasis on the spoken language, he assimilated her teaching rather well. He obtained a scholarship to Giggleswick and entered the school in September 1950. He had not received any special coaching in Latin and was told that his performance in the scholarship examination had shown the greatest variation of any that had been seen: from nearly perfect in mathematics to disastrous in Latin.

Although he missed his parents, his years at Giggleswick were happy ones and he made friendships that lasted a lifetime. He excelled at sports, particularly cricket (figure 1), and this love of the game as an active participant (a fearsome fast bowler) and a spectator was to last for his lifetime. He saw every ball of the Headingley test against Australia in 1948 when Bradman scored 173 in the second innings. One peculiarity of his school education was that he attained only two O levels, in English Language and French. For a brief period at that time, educational theory had it that youngsters should not take these examinations before they were 16, and the result for many bright pupils was that they proceeded to sixth form studies without any official O levels. At the end of their first year in the sixth form, they took only the O levels that they needed for university entry or matriculation, and then A levels were taken in their chosen specialist subjects a year after that. As Ian had decided to try for entrance to the University of Cambridge, he took a special Latin paper set by Cambridge (then a peculiar requirement of that institution for admission to read any subject), along with four A levels in maths, further maths, physics and chemistry. He stayed at Giggleswick for a third sixth form year (during which he was Head Boy), took the Cambridge Entrance Examination and was admitted to Christ's College to read natural sciences.



Figure 1. Ian in typical forward defensive pose. (Reproduced with kind permission of the Smith family.)

At that time, National Service was still in operation in the UK—it would be 1960 before it ended. Cambridge insisted that, apart from College Scholars and Exhibitioners, undergraduates were only admitted *after* their two-year period of National Service. As a result, in September 1955, Ian was enlisted into the Royal Artillery (figure 2). In the army, as at school, he found plenty of opportunity for, and encouragement of, games playing, and managed to avoid a number of kit parades and sessions of square-bashing using the excuse that they coincided with net practices for the cricket team. In the second of his two years, he was posted, as a second lieutenant, to one of the Royal Artillery regiments stationed in Oswestry and was responsible for receiving new recruits. The official duties were apparently not demanding and left plenty of time for relaxation. At that time, the army camp at Oswestry was almost next door to the Robert Jones and Agnes Hunt Orthopaedic Hospital, which among other things, trained orthopaedic physiotherapists. And here a most important event occurred in Ian's life—he met Sue Morrish, who was training to be a physiotherapist and who was to become his wife in 1961. Her father, John Eric Morrish, like Ian's, was in general practice,



Figure 2. National Service. (Reproduced with kind permission of the Smith family.)

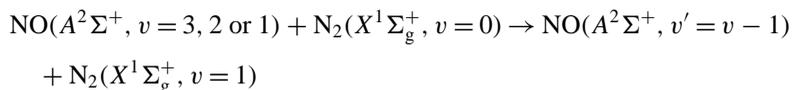
in his case in Altrincham. Sue's grandfather, William John Morrish, had been a distinguished general practitioner in south London and had conducted research in pathology in a laboratory in his own house.

CAMBRIDGE AND TORONTO UNIVERSITIES: UNDERGRADUATE, GRADUATE AND POST-DOC

As an undergraduate, Ian was one of many Cambridge students who benefited from the flexibility of the Tripos system; in particular, that one is admitted to read natural sciences, so that only later in the course does one concentrate on one particular science. In his first year, Ian took physics, chemistry, mathematics and metallurgy, and in his second year he was placed in the First Class of the Natural Sciences Part 1 Tripos, and awarded a College Scholarship. In that year, he was supervised (given tutorials) in physical chemistry by Dr A. B. (Tony) Callear, who had recently been appointed to the staff of the Department of Physical Chemistry headed by R. G. W. Norrish FRS (Nobel Laureate for Chemistry 1967). In his final year, Ian determined to do a PhD under Tony Callear's supervision if his final examination results were

good enough. They were. He graduated in 1960 with a First Class BA in Part II of the Natural Sciences Tripos, was awarded a College Graduate Studentship and was assured of funding for a PhD with the award of a studentship from the DSIR (Department of Scientific and Industrial Research, the precursor to the Science Research Council). In October 1960, he started research with Tony Callear on ‘The fluorescence of nitric oxide’.

The major components of the equipment in those early days were a high intensity xenon arc lamp and a quartz spectrograph. As with most Cambridge Physical Chemistry students at that time, Ian had to learn glassblowing to a level adequate for the construction of a Pyrex gas line. This proved enjoyable and gradually the apparatus took shape. Ian commented later in life that it was really during these years that his enthusiasm for science and being a scientist was generated. The studies that he did with Tony Callear on the electronically excited states of NO led to a number of findings that have stood the test of time. However, it was probably those involving vibrational energy transfer which had the greatest influence on experiments that he pioneered later in his independent research career. A notable example was the discovery that the vibrational frequencies of ground state N₂ and of NO in its excited A²Σ⁺ state were almost identical. As a result, he was able to study for the first time the collisional exchange of vibrational energy between two molecules in almost exact resonance (1, 2)*:



Ian became a convinced ‘nitroscopist’ and continued in his later career with innovative experiments on energy transfer in the molecule, now using elegant double resonance techniques with laser preparation and probing quantum resolved ground state NO.

Ian and Sue married in 1961 in the University Church of Great St Mary’s. In his final year as a research student, he made the decision to start an academic research career. In 1963 he was awarded a Junior Research Fellowship at Christ’s College, where he had been an undergraduate and graduate student. A characteristic career move for young aspiring academics at the time was to gain further experience abroad in research, and in 1964 Ian and Sue moved to Toronto where Ian worked with John Polanyi (FRS 1971, Nobel Laureate for Chemistry 1986), whom he had met earlier in Cambridge. Polanyi was at the time developing new experiments designed to examine the partitioning of energy in chemical reactions by recording infrared chemiluminescence from the reaction products. For the academic year 1964–65, Ian worked on two problems in John Polanyi’s laboratory at the University of Toronto. The first involved the observation of infrared emission from CO and NO excited by quenching Hg*(³P) atoms (3); in the second series of experiments infrared emission from I*(²P_{1/2}) was observed when HI was photolysed at 254 nm (4). Both sets of experiments employed very powerful mercury lamps, so-called Toronto arcs.

During this period with John Polanyi, Ian made plans for the type of research that he would conduct when he returned to Cambridge. It was a time when the creation and employment of infrared gas lasers, especially chemical lasers, was a hot topic. The experiments that he had in mind were to use lasers to promote molecules to vibrationally excited states in order to measure the rates of their relaxation with different collision partners: such experiments were to play an important role in his subsequent career. In the end, he submitted a proposal to DSIR

* Numbers in this form refer to the bibliography at the end of the text.

to construct an infrared chemiluminescence experiment—initially to study emission from NO formed in reactions of N atoms. The idea was that excess N atoms would rapidly react with NO and thereby ‘freeze in’ the initial distribution over vibrational states of the NO formed in the primary reaction. In fact, this idea only came to fruition about 25 years later in laser-induced fluorescence experiments on the NO formed in the reaction between N(⁴S) atoms and OH radicals (27).

INDEPENDENT RESEARCH: CAMBRIDGE 1965–1985

Sue and Ian returned to Cambridge in September 1965. After some discussions with Tony Callear, Ian undertook some flash photolysis experiments principally designed to examine the reaction between O(³P) atoms and CS₂. Among other publications, this work led to a paper given at a Faraday Discussion in Toronto in 1967 (5). It reported the vibrational state distributions of the CS and SO products, as well as his first venture into classical trajectory calculations that were intended to provide some more dynamical information on this four-atom reaction.

In 1966, he was appointed as a University Demonstrator in the Department of Physical Chemistry, the first step on the Cambridge academic ladder. By this time, he had received his first research grant, from DSIR, to support infrared chemiluminescence experiments. The flash photolysis work that he was doing convinced him that it would be possible and interesting to observe emission from vibrationally excited CO from a mixture of O atoms and CS₂, and this was able to get going with the arrival of his first graduate student in September 1967. Here, I declare a personal interest—I was that student, freshly arrived from a degree in chemistry from Trinity College, Dublin. I had been introduced to Ian’s work through the kind offices of Jack Linnett, then Professor of Physical Chemistry in Cambridge, whom I had met when he came to give a talk in Dublin, and who sang the praises of this extremely bright young Demonstrator who was working on the dynamics of gas phase reactions. Now that topic did not feature heavily in the Irish chemistry curriculum, and when Ian sent me a letter about what he thought I might do, and a few references to read on the topic of infrared chemiluminescence, my heart sank at the utter incomprehensibility of it all. My desire to go to Cambridge and work with Ian won over my profound ignorance of the subject, our academic marriage was arranged, and first-time supervisor met up with first-time supervisee in the autumn of 1967.

The work proved successful. The experiments demonstrated clearly that vibrationally excited CO was formed in the secondary reactions of O atoms with CS and that this reaction channelled an extraordinarily high fraction of its exothermicity into the vibration of the newly formed molecule. These observations also unequivocally defined the ‘pumping’ reaction in the CO chemical laser (6). In addition, we devised a novel method of studying vibrational energy transfer from CO in a wide range of vibrational levels to a large number of collision partners (7). These measurements defined how the collisional probability of vibrational energy exchange depended on the magnitude of the vibrational quantum number v and on the discrepancy between the vibrational transition energies in the partners. It also provided strong circumstantial evidence that such exchange often occurred under the influence of long-range attractive forces, with the result that collisional probabilities could be related to the radiative transition probabilities of the partners. The paper describing the totality of these measurements (7) became a Citation Classic in 1981 (19).

By the early 1970s, the work of Ian's group had strong connections with the mechanisms of molecular gas lasers. They used a homemade CO laser to investigate absorption/gain in the products of chemical reactions and in measurements extending the range of energy transfer processes to 'low' (*ca* 100 K) temperatures (9). This feature was to play a very important role in Ian's future work on reactions down to a few tens of K, experiments which at that time seemed beyond experimental possibilities. More chemical laser work came with the extension of laser action on the O + CS reaction to O + CSe (10). Although reaction exothermicities are different in the two cases, the energy distributions were identical when plotted as a function of the fraction of energy appearing in vibration, showing the similarity of the highly attractive potential energy surfaces controlling the reactions involving two members of the group 16 elements. Thankfully, the logical extension to CTe was not attempted: those who have worked with the precursors CS₂ and CSe₂ know the increase in stench of the compounds as group 16 is descended, and the preparation of CSe₂ on the roof of the Chemistry Department in Cambridge did not go unnoticed in the local surroundings.

Starting in the early 1970s, Ian began a lifelong interest in the kinetics and dynamics of the atmospherically important OH radical. First experiments used time-resolved absorption from an OH resonance lamp (8) to study the kinetic behaviour with a variety of reagents, including those involving the formation of an internally excited adduct which could undergo redissociation, stabilization or further disproportionation. Of particular (and continuing) interest is the reaction with CO, first studied by Ian in 1973 (12). Some four years later he proposed that the temperature and pressure dependence that he (and others) had studied pointed to the reaction occurring via an HOCO intermediate (13). HOCO has since been the subject of many further investigations, for example by molecular beam spectroscopy, and its formation via the photolysis of hydrogen halides complexed to CO₂. Ian's further work after he left Cambridge for Birmingham used tunable diode laser absorption to measure the energy distribution in the CO₂ product of the OH + CO reaction. He found very little vibrational excitation, suggesting that the O–C–O structure in the transition state was very similar to that in ground state CO₂ (25). Further ideas that Ian proposed which are pertinent to such association reactions concerned the vibrational relaxation of OH/D(*v* = 1) by CO, which he argued gave a measure of the formation rate of the H/DOCO complex (23), as the pathway to redissociation of the complex into the same (vibrationally excited) reagents is likely to be minor in comparison with redissociation to ground state reagents (by vibrational deactivation). These important ideas (initially proposed by Ian some years earlier in Cambridge for vibrational relaxation of NO(*v* = 1) with O atoms, again forming a complex (16), led the way to a clearer route for the calculation of rate constants for reactions proceeding through transition states and involving bound complexes.

Although he was not involved in the development of techniques using crossed molecular beams, Ian was becoming an influential member of the rapidly expanding reaction dynamics community led by his post-doctoral supervisor John Polanyi at Toronto, Dudley Herschbach at Harvard and Y. T. Lee at Berkeley, who would jointly win the Nobel Prize for Chemistry in 1986. The Faraday Discussion on State-Selected Species, held at Birmingham in 1979, featured papers by all of these pioneers and Ian made several contributions at that meeting, including an influential review with Bradley Moore on the chemical reactions of vibrationally excited molecules (15) and his time-resolved study on the OH(*v* = 1) relaxation by NO, NO₂ and O₂ (14).

Further work on OH reactions with atoms paved the way for his future experiments at low temperatures. The $N + OH$ and $O + OH$ reactions were found to show a negative temperature dependence when measured between 250 and 515 K (18). This was one of the first experimental studies to suggest that chemical reactions between some neutral species can go faster as you cool them down. This result had significance for understanding the chemical reaction networks in cold interstellar clouds, an area that was soon to be a major interest for Ian.

In the mid to late 1970s, Ian purchased the first commercial lasers to be employed in his group, namely a flashlamp-pumped tunable dye laser from Chromatix and (very bravely at the time) an optical parametric oscillator (OPO), which could produce tunable pulses of infrared radiation between about 1.45 and 3.6 μm . His group used the latter equipment to fulfil the wish that he had at the start of his career, of pumping molecules such as HCN and C_2H_2 to selected vibrational levels and observing their time-resolved decay by infrared fluorescence in the presence of various quenching molecules. The tunable dye laser allowed electronic levels to be pumped in the UV, and again the OH radical kinetics featured heavily in the laser-induced fluorescence (LIF) studies that he carried out. The mechanism of OH association reactions was one of the first sets of experiments carried out with the laser, and included measurements up to a total pressure of over eight atmospheres (20), showing for example that the $OH + NO_2$ reaction had not reached its limiting high pressure rate, despite the magnitude of the rate constant at the highest pressure being larger than other previously published values. Another study of the behaviour of $OH(v = 1)$ showed intriguingly that vibrational excitation of OH did not enhance its reaction with HCl and HBr (21) and this was linked again to these fast reactions of neutral radicals having no activation energy.

Ian was now equipped to carry out a variety of measurements of vibrational deactivation and radical kinetics. At the same time as using what were then state of the art methods for determining such rate processes, Ian managed to find time to write important theoretical papers, including semiclassical trajectory calculations carried out as early as 1973 (11) and an intriguing proposal and development of the angle-dependent line-of-centres model for bimolecular reactions. The second of these areas of theory appeared in his outstanding book on gas phase processes, *Kinetics and dynamics of elementary gas reactions* (17), published in 1980. Ian's writing style immediately comes across to the reader in this monograph: he was concise, clear, logical and highly readable. His list of publications shows that he was always being asked to write authoritative reviews of collisional processes, and his graduate students will treasure the handwritten descriptions of what was interesting him about their present research: 'Some notes on ...' would encapsulate their current progress and provide suggestions for at least another PhD's worth of work to be carried out.

Ian and Sue had a growing family at this time: Fraser (b. 1967), Andrew (b. 1968), Katie (b. 1972) and Tracey (b. 1973). They moved from their original Cambridge home in Cherry Hinton to a beautiful spacious house in Glisson Road in the centre of Cambridge. Many of his group and friends will remember the wonderful hospitality of the Smiths at their homes, with the children encouraging participation in various games and activities, and Smith senior recruiting burly group members to help him replace the engine in his aging Mini. He was a dedicated Director of Studies for Natural Sciences at Christ's College, and as a tutor there he also had responsibility for the welfare of students studying many subjects. Sue was delighted to recall how they often entertained these students to dinner at home.

BIRMINGHAM: 1985–2002

Gas phase reaction kinetics had been a major interest in the Cambridge Physical Chemistry Department for many years and this was connected with the pioneering work of a previous Head of Department, Ronald Norrish FRS. In 1984, Ian was offered, and accepted, the Chair of Physical Chemistry at the University of Birmingham. Although he was very happy with his situation in Cambridge, he saw a move to Birmingham as one that would present new challenges—not least the re-shaping of a department that had a distinguished past record for research in chemistry, but whose fortune had reached a rather low ebb. For family reasons, he delayed his move to Birmingham until July 1985, and the Smith family moved to a huge house in Olton, a suburb of Solihull. The proximity to Edgbaston was a delight for Ian, and the garden was large enough for serious ball games to be played. Members of Ian's group were regularly entertained to dinner cooked by the effervescent Sue.

Ian's initial work at Birmingham continued the studies of the kinetics and dynamics of elementary reactions, particularly those of atoms and free radicals. By then, Ian had acquired or built a number of lasers so that photolytic methods could be used to form atoms and radicals such as O, H, CN and OH, with LIF used to determine removal rate constants and energy distributions in the products. In addition, a narrow band OPO allowed infrared pumping of molecules to rotationally and vibrationally excited state selected levels, with the subsequent fate of these followed by LIF. An example indicating the range of insights available from these double resonance experiments is in the kinetic behaviour of the $v = 2$ level of ground electronic state nitric oxide: the temperature and rotational state dependence of self relaxation (to form two NO molecules in $v = 1$) was used to suggest the importance of long-range attractive forces in determining the kinetic behaviour (29) and pointed the direction of many other future publications on the detailed quenching mechanisms involving NO.

One of the standard ways of obtaining further insights into collisional mechanisms is to observe the dependence of the process as the temperature is changed. At the time temperatures were restricted to a lower limit resulting from cryogenic cooling, i.e. above 77 K. Some temperature-dependent studies have already been mentioned: Ian and his group continued to make important measurements at low temperatures of atmospheric relevance, particularly involving the OH radical (27). Of particular importance, however, was the result for the rate of reaction of $\text{CN} + \text{O}_2$, which was found to increase markedly as the temperature was lowered to 99 K (24) rather than decrease as expected on simple Arrhenius grounds. Temperature played an important role in his future research, and an event in Birmingham not long after Ian's arrival there was to move his temperature-dependent research programme into totally uncharted areas.

THE BIRMINGHAM–RENNES CONNECTION: AN ANGLO-FRENCH
SUCCESS STORY

On arrival in Birmingham, Ian had initiated a series of evening seminars on physical chemistry. On the suggestion of a senior colleague, the first of these was given by Dr Bertrand Rowe from the Laboratoire d'Aérothermique in Meudon, just outside Paris. Rowe had pioneered a novel technique for investigating the kinetics of ion–molecule reactions down to very low temperatures, his record at the time being 8 K. Such low temperatures were achieved by gas expansion through a converging–diverging Laval nozzle such that the rapidly flowing gas was

at a well-defined and measurable temperature. The method is known, then and now, by the French acronym CRESU (for *Cinétique de Réaction en Ecoulement Supersonique Uniforme*). Ian soon realized that this CRESU technique could form the basis for kinetic studies of reactions between neutral species—always supposing that some reactions would remain fast at these very low temperatures. Initial visits to Rowe's laboratory in Meudon were used to carry out preliminary pulsed laser photolysis/laser-induced fluorescence experiments on the very large wind tunnel facility, but were not successful. The collaboration really took off, however, after Rowe had been appointed Director of the CNRS laboratory located at the University of Rennes, and took the decision to construct a CRESU apparatus for the express purpose of studying the kinetics of neutral–neutral reactions. Funding for a collaborative project was obtained from the European Commission and Ian persuaded another Ian, Ian Sims, who had completed a PhD with him in Birmingham in 1989, to take a post-doctoral position in Rennes and to take day-to-day responsibility for these experiments.

At this time, there were no lasers in Rowe's group, and so they were transported, either from Birmingham or from the Engineering and Physical Sciences Research Council (EPSRC) Laser Loan Pool at the Rutherford-Appleton Laboratory, via the cross-channel ferries to Rennes. The Physics Department (where the experiments were to be carried out) was not used to chemists, and needed some persuasion to allow Ian Sims to synthesize the somewhat explosively unstable precursor molecule, NCNO. The first kinetic measurements in the new CRESU apparatus at Rennes were made on the reaction between CN radicals and O₂ on 7 April 1992. Ian spoke excitedly about the date: he was sent the results by fax when he was attending a meeting of the American Chemical Society in San Francisco. Because of the time difference between the West Coast of the USA and France, he was able to announce the results at a local San Francisco time earlier than the French time at which they had been obtained! The initial experiments took the data down to 26 K (26) and a little later this limit was halved to 13 K. In 1994, a new CRESU apparatus was established in Birmingham, and the two groups continued to measure dozens of reaction rates and energy transfer processes.

Chemical kinetics had entered a new experimental domain. The results generated excitement in two communities other than that of gas kineticists: theoreticians and astrochemists. It now seems that the negative temperature dependence of the rate constants for these reactions is attributable to the dependence of the reaction rates on the rotational states of the reagents: low rotational states reacting faster than high. The results have also revised views about how molecules might be synthesized in the cold, dark environment of dense interstellar molecule clouds. Chemical models at the very low temperatures characteristic of this environment emphasized ion–molecule reactions, until the Rennes/Birmingham work demonstrated that potentially many neutral–neutral reactions remain rapid under temperature conditions under which they had been assumed to be irrelevant. In 1997, Ian led a successful application to the European Commission to found a network of European laboratories in England, France, Germany and Italy to carry out investigations that would cast light on processes that could occur at the very low temperatures found in dense interstellar clouds.

ADMINISTRATION AND HONOURS

Although Ian was asked on his appointment in Birmingham if he would wish to become Head of Department, he made it clear that he wanted to establish his research there before

he assumed major managerial responsibilities. He saw such responsibilities as ‘dutiful’, and he expressed no interest at all in progressing up the administrative ladder at Birmingham. In the event, he served as Head of the School of Chemistry between 1989 and 1993, and again for a short time in 2001. In his first period as Head of the School, the opportunity arose for some significant new appointments: in 1990 Fraser Stoddart (FRS 1994, Nobel Laureate 2016) came to Birmingham as Professor of Organic Chemistry, and in 1991 Peter Edwards (FRS 1996) joined the School as Professor of Inorganic Chemistry. Ian was elected FRS in 1995 with a citation that is described later. Three Birmingham Chemistry FRSs in as many years. Other key appointments were made during the early 1990s and evidence of the improving status of the Birmingham School of Chemistry came with the rise in its Research Assessment Exercise (RAE) grades from 3 in 1986, to 4 in 1992, to 5 in 1996 and 2001.

Ian had already been awarded the Royal Society of Chemistry (RSC) Special Award for Reaction Kinetics in 1982, and in 1983–84 he was deservedly awarded the prestigious Tilden Prize of the Royal Society of Chemistry. His Tilden Lecture, published in 1985, brought together many of the experimental results of his group and others on the collision dynamics of vibrationally excited molecules (22) and he discussed how the results can be explained by the different forms of the underlying potential energy surfaces.

During his time at Birmingham came the Polanyi Medal of the RSC Gas Kinetics Group, in 1990, his elevation to the Mason Chair of Chemistry, in 1991, and his election to the Fellowship of the Royal Society, in 1995. In 2000, the two low temperature teams in Birmingham and Rennes (with Ian as the overall coordinator) were awarded the European Union’s first Descartes Prize. Ian was in Boulder, Colorado on sabbatical when the prize was awarded, and serious illness prevented his presence at the ceremony, but hopefully the announcement gave a great boost to his recovery. He was the Liversidge Lecturer of the RSC in 2000–01, and President of the Faraday Division of the RSC in 2001–03 (figure 3).

SABBATICALS AND COLLABORATIONS

Ian was a very popular and accomplished lecturer, with many opportunities to travel, and his publication list shows the large number of international collaborators with whom he worked. Many have remarked that collaborating with Ian was delightful because he brought such energy and dedication to the process. He was always willing to take on the lion’s share of the work. Talking to him about science was always fun, and writing a paper together was one of the best ways to do so.

Two sabbatical interludes took him and his family from Cambridge to the Berkeley campus of the University of California in 1972 and 1980, where he worked with the research group of Bradley Moore and forged his lifelong academic friendship with Bill Miller. In 1972, he initiated some experiments on the vibrational relaxation of $\text{HCl}(v=1)$ by Cl atoms, introducing discharge-flow methods to Moore’s group. In 1980, he learnt about the use of tuneable infrared diode laser radiation to monitor concentrations of transient species. He later remarked that there was one unexpected legacy from these trips: his son, Fraser, was clearly so enamoured of the Bay Area that he settled there in the early 90 s. His sabbatical at Boulder, Colorado, in 2000 resulted in collaborations with Steve Leone (who is currently at Berkeley) and A. R. (Ravi) Ravishankara (who is now at Colorado State University) in addition to many others. Ian’s collaboration with Leone on studies using pulsed Laval nozzles (rather



Figure 3. Ian during his time as President of the Faraday Division of the RSC. (Reproduced with kind permission of the Royal Society of Chemistry.)

than the continuous flow nozzles he was using in Birmingham) led to two papers. Leone notes that he greatly benefited from discussions with Ian on the Laval nozzle, and that Ian pulled him into OH kinetics. Ian's collaboration with Ravishankara led to a major paper in the *Journal of Physical Chemistry* on how to recognize and think about reactions of OH radicals with molecules that proceed through the formation of a hydrogen-bonded complex in the entrance channel. This paper (cited more than 150 times to date) has been very influential in atmospheric chemistry where OH reactions with molecules play such an important role (30). In addition, Ian's idea of using vibrational quenching of molecules to estimate the high pressure limit for the addition or complex formation was explored for OH reactions. Altogether, this collaboration led to four papers. In addition to these scientific exploits for a one-year stay, Ian succeeded in getting the gas phase chemists of Boulder into a well-knit community when he was battling an infected appendix. Indeed, the care and love for Ian was evident by the various chemists and their spouses/partners being continuously at the hospital during his recuperation.

LIFE AFTER RETIREMENT: 2002–2016

Ian retired from his Chair in Birmingham on 30 September 2002. During that month, a meeting was held in Birmingham to celebrate his career, organized by three younger colleagues in the University. The meeting was attended by many of his scientific friends from around the world, and included many members of his research group, past and present. The scientific programme included 18 lectures, nearly all of them delivered by people that he had published

with during his career, and in that year alone Ian published papers with collaborators from Boulder, Madison, Bordeaux, Perugia, Toronto and London.

Three months before retirement, Ian and Sue moved from Olton, near Birmingham, to a house in the Newnham area of Cambridge. His 'retirement' proved to be as busy as ever, and his publication list shows over 30 more papers published from work in Birmingham, Cambridge and Rennes after 2002. As well as being in demand (as always) as an invited speaker at conferences, he bravely re-entered the undergraduate teaching scene, providing supervision, both for Christ's College and through the Department, to students in a number of other colleges on topics such as spectroscopy, statistical mechanics, atmospheric chemistry and chemical reaction dynamics.

Ian's research continued in two major areas. Following his retirement, Ian Sims, who had co-directed efforts with the Birmingham CRESU apparatus, was offered and accepted an appointment in Rennes. The CRESU apparatus moved with him and was united with its French cousin. Rennes is now the centre for low temperature kinetic research, and Ian (Smith) remained part of the team investigating further the kinetics and dynamics of molecular processes at temperatures down to about 10 K. An example illustrating the power of the method comes in the use of CRESU to determine 'The thermodynamics of the elusive HO₃ radical', a *Science* paper from 2010 (32). Here, a set of temperatures was found such that the kinetic removal of OH radicals in the presence of O₂ led to a non-zero final OH concentration, and from which an equilibrium constant K_c for the OH + O₂ \leftrightarrow HO₃ system could be determined. This was not the first use of kinetics to determine thermodynamic parameters, but illustrates the power of CRESU to 'dial in' temperatures (in this case, 60–110 K) in order to find a region (around 90 K) where values of K_c could be measured. The results showed that, contrary to previous estimations, the binding of OH to O₂ is such that HO₃ is not of importance in atmospheric chemistry. Ian additionally made important contributions as one of the cofounders of KIDA (Kinetic Database for Astrochemistry), using his expertise in measurement and theory to review experimental data and provide realistic estimates of rate coefficients where data are sparse or non-existent for use in models of interstellar chemistry. One of Ian's last publications, establishing the database, has been cited more than 160 times since 2012 (33).

Ian's second project was carried out in the Cambridge Physical Chemistry Laboratory, a return to his experimental roots. The project used a combination of techniques developed in Cambridge and Birmingham, namely the use of tunable infrared laser to pump selected rotational levels N of the CN radical in $v = 2$, followed by state specific measurements of energy transfer and reactive processes (31). This tour de force experiment exemplified Ian's great interest in the kinetics and dynamics of elementary gas reactions (to reprise the title of his book). It required three lasers: one to photolyse the CN precursor: one to pump the ground state radicals to rotationally selected states in $v = 2$; and a third to carry out laser-induced fluorescence on the CN products. For the CN + C₂H₂ reaction, the prominent feature was the increase in rate constant with decreasing N , a result which helps explain the negative temperature coefficient of this and many other rapid low temperature reactions, as demonstrated in the pioneering CRESU experiments carried out by Ian and co-workers.

Ian's mobility started to deteriorate about 10 years after he moved back to Cambridge. After a spell in Addenbrookes, he and Sue eventually moved, in 2016, from their house in Granchester Road to the Woodlands Care Centre in north Cambridge. They continued to receive a stream of visitors from home and abroad, and although Ian was restricted in his



Figure 4. Ian and his family in 2012. (Reproduced with kind permission of the Smith family.)

physical activity, his mind was as fresh as ever. He died peacefully, surrounded by his family, on 8 November 2016. Sue continued to live at Woodlands until her death on 17 May 2017.

Ian's citation for his election to the Royal Society reads:

Ian Smith made outstanding contributions to the understanding of molecular processes by his wide-ranging studies of gas-phase chemical kinetics, molecular reaction dynamics and energy transfer. He has been among the first to exploit and develop new spectroscopic techniques and combinations of techniques to measure rate and state-to-state data for elementary processes. Not only could he claim a number of valuable theoretical contributions himself, but his choice of systems for experimental study and the interpretation of the results display insight into the fundamental nature of molecular processes and what determines their dynamics.

He clearly was a remarkable scientist, but so much more than that—a devoted husband, father of four and grandfather of 11 (figure 4), and a man of true integrity, an inspiring teacher and a dear friend to many. Ian supervised 48 graduate students, hosted 33 post-doctoral workers and research fellows and 12 sabbatical visitors. Their names are recorded in the supplementary electronic material.

AWARDS AND HONOURS

- | | |
|---------|--|
| 1960 | BA in Natural Sciences (First Class), University of Cambridge |
| 1960–64 | PhD in Chemistry, University of Cambridge (supervisor: Dr A. B. Callear) |

- 1963–66 College Research Fellow, Christ’s College Cambridge
- 1964–65 Post-doctoral Fellow, Department of Chemistry, University of Toronto, Canada (research group of Professor J. C. Polanyi, Nobel Laureate 1986)
- 1965–66 ICI Research Fellow, Department of Physical Chemistry, University of Cambridge
- 1966–71 University Demonstrator in Physical Chemistry, University of Cambridge
- 1966–85 Staff Fellow and College lecturer, Christ’s College Cambridge
- 1971–85 Lecturer in Physical Chemistry, University of Cambridge
- 1972–85 Director of Studies, Christ’s College Cambridge
- 1972 Visiting Scientist, Department of Chemistry, University of California, Berkeley (with Professor C. B. Moore)
- 1980 NATO Senior Scientists Visiting Fellow, Department of Chemistry, University of California, Berkeley (with Professor C. B. Moore)
- 1982 Royal Society of Chemistry: Special Award for Reaction Kinetics
- 1983–84 Royal Society of Chemistry: Tilden Medal and Lectureship
- 1985–91 Professor of Chemistry, The University of Birmingham
- 1989–93 Head of the School of Chemistry, The University of Birmingham
- 1990 Royal Society of Chemistry, Gas Kinetics Group: Polanyi Medal and Lectureship
- 1991–2002 Mason Chair of Chemistry, The University of Birmingham
- 1995 Elected Fellow of the Royal Society
- 1996 Miller Visiting Research Professor, University of California, Berkeley
- 1999 Visiting Professor, Université de Rennes I
- 2000 Fellow at the Joint Institute for Laboratory Astrophysics (JILA), University of Colorado, Boulder
- 2000 Stauffer Lectureship in Science, University of Southern California
- 2000 Royal Society of Chemistry, Liversidge Lecturer
- 2000 First Descartes Prize of the European Union
- 2001 Head of the School of Chemistry, The University of Birmingham
- 2001–03 President of the Faraday Division of the Royal Society of Chemistry
- 2002–16 Emeritus Mason Professor of Chemistry, The University of Birmingham
- 2002–16 Fellow-Commoner, Christ’s College Cambridge
- 2003 Wilhelm Jost Memorial Lectures (Germany: lectures delivered in Marburg, Hannover, Berlin, Heidelberg, Göttingen, Leipzig, Halle and Essen)

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AUTHOR PROFILE

Gus Hancock



Gus Hancock is Emeritus Professor of Chemistry at the University of Oxford and Emeritus Fellow of Trinity College, Oxford. He did his first degree at Trinity College, University of Dublin, and his PhD at the University of Cambridge, where he was Ian Smith's first graduate student. Following a post-doctoral position at the University of California, San Diego, he moved to the University of Bielefeld as Wissenschaftlicher Angestellter, before being appointed as Lecturer in Physical Chemistry at the University of Oxford in 1976, and Professor of Chemistry in 1996. He is the recipient of the Corday Morgan Medal, the Reaction Kinetics award, the Polanyi Medal and the Reaction Dynamics Award from the Royal Society of Chemistry, and the fourteenth Italgas Prize for Science and Technology of the Environment.

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