NATIONAL ACADEMY OF SCIENCES

RICHARD MCLEAN BADGER

1896—1974

A Biographical Memoir by
OLIVER R. WULF

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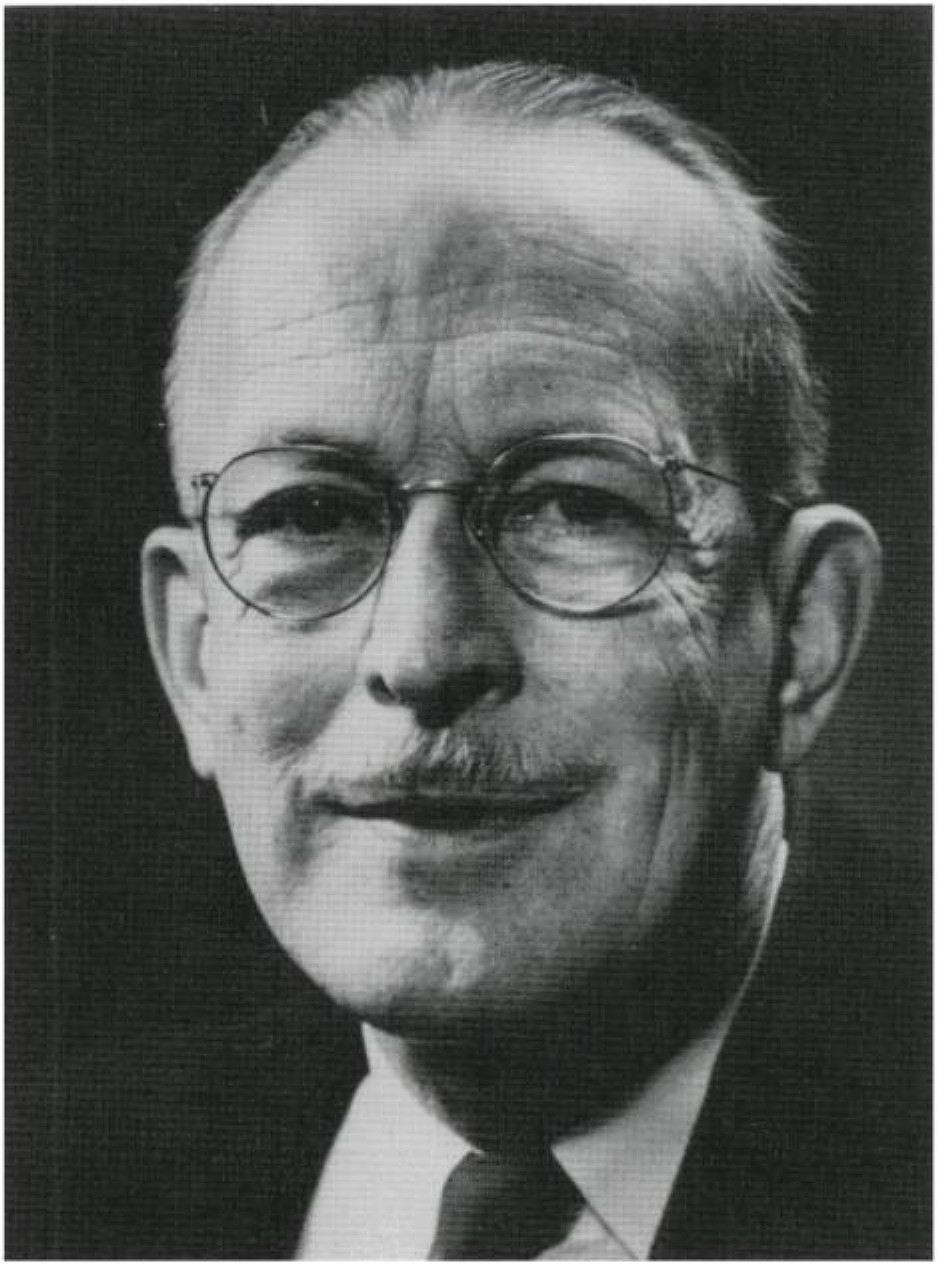
NATIONAL ACADEMY OF SCIENCES
WASHINGTON D.C.



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Richard M. Badger

RICHARD McLEAN BADGER

May 4, 1896–November 26, 1974

BY OLIVER R. WULF

THE QUALITIES of a very careful investigator, as well as those of a gifted teacher, combined to make Richard McLean Badger an unusual person. The meticulous care shown in his scientific work and in his teaching was also evident in his artistic activities, for he was an accomplished painter and a craftsman of great ability.

Badger died on November 26, 1974, at the age of seventy-eight. He had been a student, teacher, and researcher at the California Institute of Technology for more than fifty years.

Though born in Elgin, Illinois, several years of his boyhood were spent in Brisbane, Australia, to which city his family had moved. On the return of the family to Elgin, he completed his high school work there, following which he went through the Junior College of the Elgin Academy. After this he enrolled at Northwestern University, but World War I interrupted this portion of his career. He served in France in the 311th Field Signal Battalion of the Army.

Following the war he entered the California Institute of Technology, receiving there his bachelor of science degree in 1921 and his doctor of philosophy in 1924. He was appointed a research fellow at the Institute, a position he occupied from 1924 to 1928. In 1928–29 he was in Germany in postdoctoral work, as a National Research Council Fellow, at the Universities of Göttingen and Bonn. Following this he returned to the California Institute of Technology as assistant professor of chemistry and began, then, his long career of teaching and research.

Badger's many years of teaching undergraduates brought him the award of the Manufacturing Chemists Association for college chemistry teaching. This is presented to teachers of undergraduates who have been "personally responsible over a period of years for awakening in students a genuine interest in chemistry, for inspiring them to serious intellectual effort in studying that field, and for developing that interest into a continuing education."

His love and enthusiasm for the outdoors and the unexplored are well illustrated by the occasion when, in early days, he drove with a close friend to a point in the vicinity of the Big Sur on the coast of California to begin a long backpacking over rough and unmarked terrain to encounter friends who had started from another point on the coast and were moving toward them. He and his companion, after the meeting with the others, continued on to the point at which their friends had left their car, while the friends continued their hike to the point where Badger and his companion had left theirs, the group thus exchanging cars at the ends of the course for the homeward trip.

The writer of this memoir has been much interested in the oft-repeated instances, mentioned when in conversation with others in the course of this work, where Badger took students and colleagues on trips to the California deserts, which he so much loved and which he painted so beautifully.

In his research activities Badger was especially well known for his extensive investigations in the fields of spectroscopy and molecular structure that, with his many students and collaborators, he carried out over a period of four decades.

Though known principally for this work, he did his doctoral thesis in the field of thermodynamics under Professor Arthur A. Noyes. This was an ingenious experimental study of the ammonia, carbon (in the form of charcoal), hydrogen cyanide, hydrogen equilibrium, leading, when combined with heat and heat capacity data, to a value for the free energy of hydrogen cyanide. The investigation was a difficult one because at a temperature high enough for the equilibrium to be measured in a static system, the ammonia would be almost completely dissociated, yielding only a trace of hydrogen cyanide at equilibrium. Using a charcoal that was very active in establishing this equilibrium—and yet that did not decompose ammonia rapidly (this latter being in accord with the knowledge that charcoal is not a good catalyst for the ammonia synthesis)—Badger succeeded, using a flow method, in measuring the equilibrium constant near 800 K, studying, thus, the equilibrium with one of the components in a metastable condition, the ammonia dissociating only slowly in spite of being at a much higher concentration than corresponded to equilibrium with its own dissociation products at this temperature.

During and following graduate work he collaborated with Professor Richard Tolman, on the one hand in a theoretical study of the entropy of diatomic gases and the matter of rotational specific heat, and on the other hand, in an investigation that, it seems, may well have been the cause, or at least the main cause, of his entering the field in which lies the major portion of his life's work.

This latter work with Tolman was a study of the correspondence principle, in which, for the first time, a comparison of experimental data was made of its predictions as to the absolute—rather than merely the relative—strength of spectrum lines. The experimental data on the absolute intensity of spectral lines was, at that time, very limited. Tolman and Badger used Czerny's excellent measurements of the intensities of several lines in the pure rotation spectrum of hydrogen chloride in the far infrared. To carry this study further it was clear that data under higher resolving power would be of much help. The report of this work with Tolman concluded with the remark that "An attempt to obtain further data for this purpose is already under way in this laboratory."

To aid in accomplishing such measurements, Badger devised two experimental improvements, which illustrate well, at an early date, his scientific craftsmanship and ability as an instrument maker: a balanced thermocouple and a special type of echlette grating, both of much help in spectrometric investigations in the region of very long waves where the energy available is small.

With apparatus incorporating these new helpful features Badger proceeded to measure the absolute intensity of the absorption of hydrogen chloride in the vicinity of 80 μ. Thus the extensive investigations throughout his life in the field of molecular rotation-vibration spectra had begun.

Foreseeing the importance of such spectra in the study of the structures of *polyatomic* molecules, where, of course, the main chemical interest lay, Badger chose ammonia as a first polyatomic molecule to investigate. This had a symmetrical pyramidal structure that could lead to some simplification in the increasing complexity of the spectra of polyatomic molecules. He early reported, in a brief note in *Nature*, the finding of an unexpectedly simple spectrum of six lines in the far infrared lying between 55 μ and 130 μ. This early note opens with an acknowledgment of the assistance received in the work from Mr. C. H. Cartwright, and it is followed directly by a paper in the *Physical Review* by Badger and Cartwright, "The Pure Rotation Spectrum of Ammonia." Thus began Badger's long series of investigations with a large number of graduate students and associates in the field of molecular spectra and molecular structure.

An intermission in the work at Caltech occurred at this time, when he spent the year (mentioned above) in Germany on a National Research Council Fellowship. For the first part of the year he was at Professor Franck's Institute in Göttingen. There he carried out an interesting research on the fluorescence from open (ambient-pressure) flames. Under such conditions of high pressure, one might have expected that deactivation by collisions would lead to quenching of the fluorescence. Nevertheless, this research showed clearly that pressure broadening offset the effect of deactivation and by increasing the absorption of the broad lines from the source exciting the fluorescence.

A return to the work on the spectra of polyatomic molecules was evident in the second part of the year, which he spent at Professor Mecke's Institute in Bonn. Badger and Mecke, recognizing the inherent difficulties in obtaining sensitivity and high resolution in the middle and far infrared, turned to the measurement of the spectra of polyatomic molecules in their overtones and combination tones, which lie in the near infrared and visible region of the spectrum. Here there were two important advantages: the use of photographic plates (which now could be sensitized for this region) permitting extended exposure times, and the high resolution obtainable with long-focus gratings.

Upon going to the use of a long-focus grating and high resolution, they encountered the interesting circumstance that with this considerable laboratory air path, there always appeared in absorption on their plates the lines of an oxygen molecule band at 7600 Å, well-known in the solar spectrum, Fraunhofer's A. This band had been measured earlier several times, but always in the solar spectrum where the lines were strongly broadened by the long atmospheric path and difficult to measure, and it had never been observed in absorption in the laboratory. This latter they now had under favorable circumstances for measurement. Since this transition in the oxygen molecule was of some theoretical interest, they proceeded to measure the many lines of the band and to study the combination relations of this electronic transition. The work verified Mulliken's term assignment of $^1\Sigma$—$^3\Sigma$ to it.

There followed with Mecke an extensive investigation and analysis of rotation-vibration bands of ammonia in the near infrared and visible. This established several features of the molecule—the frequencies of the three fundamental vibrations of the symmetrical NH_3 pyramid, the two moments of inertia, and the N–H bond length.

On return to Pasadena, and utilizing the high resolution obtainable with long-focus gratings and photography, Badger instituted a program for the investigation of the rotation-vibration spectra of a number of the simpler polyatomic molecules. This developed into a long series of studies with graduate students and associates, continuing into the spectra of molecules of increasingly complicated structure, and becoming the main portion of his life's scientific work.

An experimental observation by R. W. Wood and F. W. Loomis concerning the fluorescence of the iodine molecule indicated that there were two forms of the molecule, presumably ortho and para forms analogous to ortho and para hydrogen. This led Badger and Urmston at this early date to an interesting photochemical experiment involving separation of two forms of the same molecule.

Wood and Loomis had found that the iodine bands in fluorescence stimulated by white light differed from those in the fluorescence excited by the green mercury line λ5461 in that half of the lines were missing in the bands observed in the latter case. Badger and Urmston saw that it should be possible to remove from the gas the form of the molecule that absorbed the green mercury line if some molecule could be found that reacted preferentially with this optically excited species. This they found in the molecule of hexene, and they were able to show a small depletion of the number of molecules in the ortho form of the iodine molecule by this photochemical reaction.

Recognizing the importance of regularities in behavior from molecule to molecule in understanding the nature of the chemical bond, and giving consideration to the earlier attempts to express these analytically, Badger carried out an extensive survey of the information available on the force constant and internuclear distance in a considerable number of diatomic molecules.

The result of this survey led him to the expression for diatomic molecules $k_o(r_e - d_{ij})^3 = 1.86 \times 10^5$, where k_o is in 10^5 dynes/cm, and r_e and d_{ij} are in Ångströms, a relation widely spoken of as "Badger's rule." This is probably the best known of this type of relation, and what is particularly important, it can be extended in a rather simple manner, as Badger further showed, to polyatomic molecules.

To do this, however, was not entirely devoid of difficulties. There were but few cases available where one knew internuclear distances and at the same time had adequate vibrational data. Also it was difficult to know the best form of potential function to apply for polyatomic molecules. Since, in the study of molecular properties, it had been found that they may be expressed to a good approximation as sums of several individual parts, Badger found it convenient to express the potential energy as made up of three parts. The first and most important part was taken to be dependent only on the distances between atoms that are directly bonded to each other. The second part was dependent on the angles between the chemical bonds, and finally, the third part contained terms arising from interactions between atoms not directly bonded to each other. These last terms are usually small.

Foreseeing the help that spectroscopic studies in the photographic infrared could contribute to an understanding of the special type of chemical linkage known as the hydrogen bond, Badger initiated in 1937 a series of researches that contributed greatly to the elucidation of this phenomenon, as it appears in both inter- and intramolecular bonding by hydrogen atoms.

Utilizing the excellent spectroscopic facilities that he had developed, he, with a considerable number of graduate students and postdoctoral fellows, studied, over the ensuing years, the spectra of a series of compounds in which this type of linkage occurred, each of these studies helping to clarify the manner in which hydrogen atoms act in forming such a bond.

Somewhat early in these researches and in a manner reminiscent of his previous study on the relation of force constant and internuclear distance in diatomic and simple polyatomic molecules (the study that yielded "Badger's Rule"), he investigated the relation between the energy of a hydrogen bond and the frequencies of the bands of an OH group involved in the formation of an intramolecular bond. He was able to throw interesting light on the character of the vibrations of the OH group in their dependence on the unusual potential function of such bonds.

During World War II Badger remained at Caltech working on fundamental physical problems for the Manhattan District and investigating the properties of smokeless powder for the Navy Bureau of Ordnance. He also was engaged in projects for the Office of Scientific Research and Development and the Army Air Corps. Important advances in technology and instrumentation during these years facilitated his distinguished work in infrared spectroscopy.

Following World War II, Badger, with his students and postdoctoral fellows, studied organic molecules of increasing complexity and of greater interest to chemists, introducing new experimental techniques in the course of the work. The spectra of urea and thiourea were among the early studies of this kind, which continued into the spectra of polypeptides and proteins.

A further excellent illustration of his unusual ability in designing and constructing apparatus is contained in instances that permitted extending these researches not only to organic molecules of greatly increasing complexity, but also to the optical investigation of these substances in the solid state. The work required the use of polarized infrared radiation and measurements of circular dichroism, working with minute crystalline specimens. It involved the construction of a "microilluminator" with a polarizer of silver chloride plates, suitable for measuring the absorption in the infrared of tiny crystals at low temperatures.

A still further illustration of his craftsmanship is contained in a mechanical model that he constructed to aid in the study of the vibrations of the peptide group, a model in which unusual attention was given to the character of the springs, helical springs being avoided because of the likelihood of their having vibrational modes of their own that would interfere. The type of spring used consisted of a single circular loop of spring-steel wire provided with diametrical projections for attachment to the atoms. The model gave automatically about the correct ratio of the force constants for stretching and bending of the peptide group.

Treating the increasingly complex spectra of ever more complex molecules presented new difficulties. This was both because of their not being resolvable into lines, even with perfect resolution, and because many or most of these molecules were unsymmetrical rotators. Under these conditions the features of their spectra that were of importance and actual help to the chemist were the envelopes of the bands. Badger gave special effort to the calculation of the theoretical envelopes of the bands of such molecules.

At the same time investigations were being carried out on a number of simpler molecules of special interest. Spectra in the visible and ultraviolet, as well as in the infrared, contributed to an understanding of their structures and of their photochemical behavior.

Uncertainties regarding the structure of the isothiocyanic acid molecule led Badger, with one of his students, to record a portion of the infrared spectrum of isothiocyanic acid vapor, an analysis of which contributed importantly to an understanding of the structure of this molecule.

The infrared spectrum and molecular configuration of hydrogen persulfide, the sulfur analog of hydrogen peroxide, were studied, the results strongly supporting a chain structure for the molecule.

The infrared absorption of the urea molecule in the crystalline state was recorded, working with single micro-crystals of urea and with polarized radiation. This was done using the microilluminator with polarizing attachment, mentioned above. The results of this study established reasonably well the complete planarity of the urea molecule in the crystal.

The structure of the ozone molecule had remained uncertain for a number of years during which Badger, with his students and postdoctoral associates, made several contributions to knowledge of the spectrum of this substance in the infrared, visible, and ultraviolet. Especially important in one of these was the finding of a new fundamental vibration, ν_1. This permitted a revised vibrational analysis that left little doubt that the molecule was in the form of an isosceles triangle with an *obtuse* apical angle, in accord with the structure indicated by electron diffraction studies.

The infrared spectra of hydrogen hypochlorite and of deuterium hypochlorite were studies in the 1–15 μ region. These seem to have been the first infrared spectral observations of these substances. The O–Cl and the O–H fundamentals were measured as well as the bending frequency, and the first overtone of the O–H stretching mode of HOCl was studied under high dispersion. This band was a good example of a hybrid band, a type of band named and first correctly interpreted by Badger and his associates. In this case the band was a band from a nearly symmetrical-top molecule with the top axis the axis of least moment of inertia.

Several studies of the spectra and structure of oxides of nitrogen and related compounds by Badger and his coworkers yielded important results. Thus, one of these having to do with the molecule NO_2, led to the observation in the infrared of two of the fundamental vibrational frequencies of the molecule and to a structure in accord with that indicated by electron diffraction observations.

Also, an extensive spectroscopic study of the infrared spectrum and the structure of gaseous nitrous acid, using both the molecules HONO and DONO, showed that this substance exists in two tautomeric forms, apparently trans and cis, the cis-form being the form of higher energy. A complete vibrational analysis was given, yielding the OH (and OD) frequencies (both in-plane and out-of-plane) for both the trans- and cis-forms. An estimate was given of the ONO angle in both the trans- and cis-forms, from which some conclusions were drawn regarding the electronic structure of the molecule. From the frequencies and the moments of inertia, estimates were made of certain thermodynamic properties of nitrous acid.

There followed later a further study of the infrared spectrum of NO_2, resulting in a remarkably complete description of the vibrational and rotational constants of the molecule.

Spectroscopic observations on the ultraviolet absorption of the NO molecule removed an uncertainty that had existed for some time concerning a possible pressure broadening in the gamma bands of NO, thought to have been observed by others. It was shown that such does not exist.

Professor Badger was famed for his teaching, especially in his undergraduate course in physical chemistry. His informal notes, prepared for the students, on his lectures and on the laboratory work were well known for their excellence and for having been carefully revised every year.

Badger's last scientific publication illustrates particularly well his concern for helping undergraduate students. In this research he had two collaborators. The work concerned the very weak transition in the oxygen molecule involving the low-lying $^1\Delta$ level. The writer of this biography, in referring back to that research, had occasion to look for the doctoral theses of the two collaborators, assuming that they had been graduate students. To his surprise no theses were catalogued under these two names, and on further inquiry he discovered that they were both undergraduates. This was very much in the tradition of Professor A. A. Noyes, who showed constant concern for undergraduate education, and under whom Badger himself carried out the research leading to his doctorate many years before.

THE WRITER of this biographical memoir sincerely acknowledges his great indebtedness to Professor William H. Eberhardt, Dr. Edward W. Hughes, Professor John D. Roberts, Professor and Mrs. Verner Schomaker, and to the editor of the journal *Engineering and Science* of the California Institute of Technology for permission to use material from that journal. He feels strongly his gratitude for all of this help.

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