Nobel Prize for Chemistry: Herzberg and Molecular Spectroscopy

The 1971 Nobel Prize in Chemistry has been awarded to Gerhard Herzberg in recognition of his "contributions to the knowledge of the electronic structure and geometry of molecules, especially free radicals." Scientists throughout the world who have been involved in any way with problems of atomic and molecular structure will be pleased, but not surprised, by this announcement.

Gerhard Herzberg was born in Hamburg, Germany, in 1904, just a few years after the discovery of the electron had given the first clue to the structure of the atom. By the time he was ready to undertake a serious study of physics, the new quantum mechanics had come into being and, by 1928, when he started independent research work at Göttingen, this new mechanics had supplied the key to a full understanding of the electronic structures of atoms. Although quantum mechanics could also be applied to the problems of molecular structure, the much greater difficulties associated with the study of molecular structure caused work on molecules to lag behind work on atoms. It was the study of molecular structure, through a quantum mechanical interpretation of molecular spectra, which first attracted Herzberg's attention and has, in a large measure, retained his attention over the past 40 years. At Göttingen, and in the following 5 years at Bristol and Darmstadt, the results of his numerous experimental studies of molecular spectra established the young Herzberg as one of the leading scientists in the field of molecular structure.

The mid-1930's were the years of the Nazi purges of the German universities, and Gerhard Herzberg was one of the many professors who found it impossible to live under Hitler's regime. Herzberg's reputation was such that, in more normal times, he would have had no difficulty in moving to one of the large universities outside Germany. But these were the years of the great depression when new university appointments were rare indeed, and it was through his acquaintance with one of the then junior staff members (now president) at Saskatoon that Gerhard Herzberg found a place at the University of Saskatchewan—a university which had, at that time, no suitable research equipment, no funds with which to buy such equipment, and no advanced graduate students to use it.

In spite of its unpromising appearance, Herzberg's stay at the University of Saskatchewan was a most fruitful one. Encouraged by a friendly staff and administration if not by the physical resources of the university, he completed the measuring of plates and the calculation of results obtained in Germa y. He devoted a large portion of his time to writing a book on the structure and spectra of diatomic molecules. With the help of a variety of small grants, he slowly secured some equipment for research and, working with candidates for the master's degree, he produced a number of significant papers on molecular spectra before World War II put an end to these research activities.

The war found Herzberg still legally an alien, and he was not allowed to play a major role in wartime research programs. During the war years he devoted a large part of his time to writing his second definitive book, a book on the infrared and Raman spectra of polyatomic molecules.

In 1945, Herzberg, who had always had an interest in astronomy, was offered a post as professor at the Yerkes Observatory of the University of Chicago. This was an invitation to return to a major research institute, with advanced graduate students, with colleagues working in his field, and with vastly increased technical and scientific facilities at his disposal. He reluctantly left Saskatoon and enthusiastically took up his new work at Yerkes, where, within 2 years, he built up a laboratory capable of unique and important experiments involving long absorption paths. This period at Yerkes brought Herzberg in touch with some of the world's leading astronomers and heightened his interest and his knowledge of this subject.

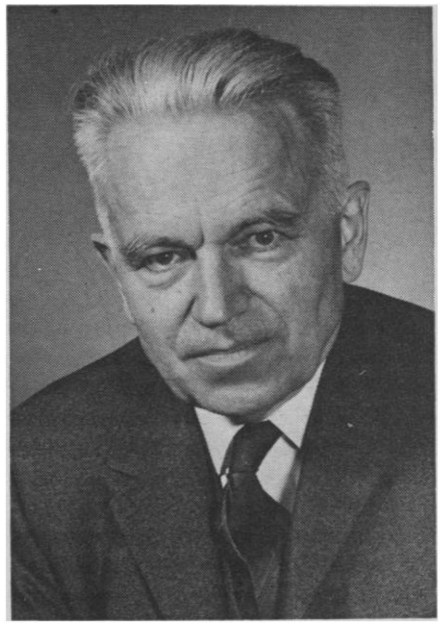
In 1948 Herzberg accepted an invitation to set up a research laboratory in spectroscopy at the National Research Council laboratories in Ottawa. In the following year he was appointed director of the Division of Physics, a post he retained until 1969 when he became the first Distinguished Research Scientist of the National Research Council.

A detailed understanding of Herzberg's work can come only from a study of his papers, about 100 of which represent major contributions to an area of science which bridges physics, chemistry, and astronomy. In order to gain a slight insight into this voluminous work, it is useful to consider four areas: fundamental studies in physics, the study of diatomic molecules, the study of simple polyatomic molecules, and the application of his spectroscopic research to astrophysics.

The physical problems studied by Herzberg have all had either their origins or their solutions in atomic or molecular physics. One of the earliest problems he directed his attention to was the question of the structure of the nucleus. He, together with Heitler, showed that a nitrogen nucleus composed of 14 protons and 7 electrons could not account for the observed intensity alternation in the lines of the spectrum of nitrogen. This work, along with that of other scientists, stimulated the search for a new model of the nucleus—a model that was finally achieved only after the discovery of the neutron. Another of his early papers (1933), with E. Teller, established the rules governing the structures of the absorption bands of polyatomic molecules, and it is interesting to note that this paper was translated into English and widely circulated 30 years after it was published. Another achievement of his early work was his definitive work on predissociation. An understanding of predissociation has made it possible to determine the dissociation energy of many diatomic molecules with an accuracy far beyond that possible with any other method. In more recent years, in a major experimental and theoretical program, he has established the total binding energy and the "Lamb shift" for two of the simplest atoms, hydrogen and helium. A report on his current work, still in press, contains a description of very accurate experimental measurements of the electronic states and the ionization potential of the hydrogen molecule which have been made in order to test the accuracy of recent calculations of these quantities.

A very substantial portion of Herzberg's research over the past 40 years has been devoted to the study of the spectra of diatomic molecules. Much of this work has concerned the most abundant and important molecules such as N_2, O_2, H_2, CO, C_2, and CH. In these studies he often devised methods of investigation that were new and superior to any which previously existed. In his various investigations of molecular hydrogen, for example, he made the first observation of the infrared quadrupole spectrum by using an absorption path of more than 5 kilometers (1948), he observed pressure-induced absorption bands in the photographic infrared with a path length of 80 meters at a pressure of 100 atmospheres and a temperature of 78°K (1952), he observed almost all the vibration-rotation levels of the ground electronic state by observing the absorption spectrum a few microseconds after the gas had been excited by the discharge of a condenser (1968), and he analyzed the complex Rydberg series in the 800-angstrom region by obtaining high-resolution spectra of para-hydrogen at a temperature of 78°K. This work on diatomic molecules, which he began in 1927, still goes on with astonishing success, and within the past few years Herzberg has discovered the only known discrete spectrum of a negative diatomic ion (C_2^-) and, in still unpublished work, has collaborated in establishing the energy of the lowest Rydberg state of N_2.

Although the basic theory of the electronic spectra of polyatomic molecules was developed about 40 years ago, when Herzberg started to set up the Ottawa laboratory in 1949 the fine structure of not one electronic transition had been analyzed correctly and only for CO_2^+ and H_2CO did a partial analysis exist. The analysis of the electronic spectra of polyatomic molecules has been one of Herzberg's major accomplishments in Ottawa. Although, starting with C_2H_2 and HCN, he analyzed the spectra of a number of stable molecules, his most fruitful study has been the production and analysis of the spectra of unstable species (free radicals). These radicals, which had long been postulated as the intermediates in many chemical reactions, had proved particularly difficult to characterize by any of the usual chemical means. Herzberg and his research group in Ottawa were able to obtain high-resolution spectra of a large number of radicals by flash photolysis and other methods. The analysis of these spectra not only gave unambiguous information on the electronic and geometric structure of the radicals but also provided excellent examples of various types of spectra of polyatomic molecules. These spectra stimulated further theoretical work which, in turn, made possible a complete analysis of the spectra and a better understanding of molecular structure. Significant papers have appeared describing the spectra and structure of HCO, NH_2, HNO, NCO, NCN, CNC, HNF, HCF, BO_2, CH_2, CH_3, N_3, C_3, CF_2, and other radicals. Microwave spectroscopy, spin resonance, and laser methods, in addition to optical methods, are now being used to establish the spectra and structure of radicals, but it is clear that Herzberg will always be remembered as the founding father of this field.



Gerhard Herzberg

Perhaps none of the spectra Herzberg discovered gave him greater pleasure than those of CH_2 and CH_3. The CH_2 and CH_3 radicals had been postulated as intermediates in many chemical reactions, they are the building blocks for many larger molecules, and their electronic and geometric structures are of great theoretical interest. Herzberg's search for these spectra spanned 15 years. His early attempts to obtain these spectra by a variety of discharge and photolysis methods were, we now know, frustrated by a variety of problems arising out of the size and power of his apparatus. Persistence and determination were rewarded, first in 1956 when the spectrum of CH_3 was found and then, shortly thereafter, when the triplet and the singlet spectra of CH_2 were found. Herzberg was indeed happy to be able to give a description of these spectra in his Bakerian lecture to the Royal Society in 1960.

Throughout his career Herzberg had had a continuing interest in astronomy. He identified the interstellar CH^+ lines and assisted in the identification of other lines. He was the first to produce the long unidentified 4050-angstrom (C_3) cometary bands in the laboratory and later gave a substantially complete analysis of this spectrum. He has contributed to the understanding of the spectrum of the atmospheres of the outer planets and of stars, and he has interpreted the spectrum of the night sky. It is understandable that, in certain parts of the scientific world, Herzberg is regarded as an astrophysicist.

In the available space it is not possible to discuss the many other aspects of Herzberg's work. His contributions as a teacher, his forceful and lucid lectures before many scientific organizations, his three major books which have done so much to clarify and unify the whole field of spectroscopy and molecular structure, his infrared work, and his review articles must all be glossed over here. Nor is it possible in this short space to describe Herzberg's dedication to the freedom of choice in science and his insistence on high quality. But a generation of students and colleagues know him as a dynamic scientist who generated enthusiasm both within and beyond his laboratory. His friends know him as an unassuming and generous man who loves music and the outdoors. All will be pleased that the many honors he has received in the past have now been augmented by the highest award in science.

A. E. Douglas
Division of Physics,
National Research Council of
Canada, Ottawa, Ontario