



R. Stephen Berry and the Berry pseudorotation

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Abstract

R. Stephen Berry (1931–2020) was a Harvard-educated American pioneer of molecular structure studies. He is most famous for the phenomenon of Berry pseudorotation and his studies of intramolecular motion and molecular fluxionality. This remembrance focuses on this discovery. He had broad interests in many other aspects of structural chemistry and physical chemistry and also in the economics of energy.

Keywords R. Stephen Berry · William Moffitt · Pseudorotation · Phosphorus pentafluoride · University of Chicago · Time-scales · Cyclopentane

R. Stephen Berry (1931–2020, Fig. 1) was James Franck Distinguished Service Professor, Emeritus, at the University of Chicago at the time of his death. He was a most original and influential physical chemist with major contributions to the science of structures. Obituaries reviewed his accomplishments that concerned a broad spectrum of the physical sciences (see, e.g., [1]). In 1995, one of us recorded a long conversation with him about his career with an emphasis on his discoveries related to intramolecular motion and, in particular, what has become known as Berry pseudorotation [2]. In this remembrance, in addition to a general brief review of his career, we focus on Berry pseudorotation and its implications. We stress that this was only a small fraction of his contribution to the science of structures.

Origin, education, career

Berry was born in Denver, Colorado. His father was in the real estate business and his mother was a teacher. He was 6 years old when he received a chemistry set from his

parents as a Christmas present. Theirs was a Jewish family, but it celebrated both Christmas and Hanukkah. By the time he was at the junior high school, he had built up a chemistry lab in the basement of their house. In ninth grade, he wrote a report about his career choice, and it was about chemistry and physics. It took some courage on his part to go in that direction because at the time anti-Semitic discrimination hindered Jews to get a position as a scientist. The influx of European refugee scientists and their contribution to American defense during World War II helped changing the situation. By the time Berry started his career, he did not experience discrimination to any significant degree. His career choice was strengthened by Paul de Kruif's *Microbe Hunters* and also by Milton Silverman's *Magic in a Bottle* and Bernard Jaffe's *Crucibles: The Story of Chemistry from Ancient Alchemy to Nuclear Fission*. Contrary to general experience, he found chemistry more exciting than physics in high school. This is a good example of how strong influence textbooks and especially teachers may have. According to Berry, as he reminisced decades later, physics as it was being presented in his school was about "ladders leaning against walls," whereas chemistry was about "the structure of the atom and all other interesting stuff, quantum theory, for example" [3].

In his last year of high school, Berry participated in a Westinghouse science competition, and a Westinghouse Talent Fellowship made it possible for him to choose among the best schools for continuing his education. He considered the Massachusetts Institute of Technology, the California Institute of Technology, and Harvard University. His interest in literature and philosophy, beside science, made him opt

"R. Stephen Berry and the Berry pseudorotation" is a contribution to the column "Foundation of structural science."

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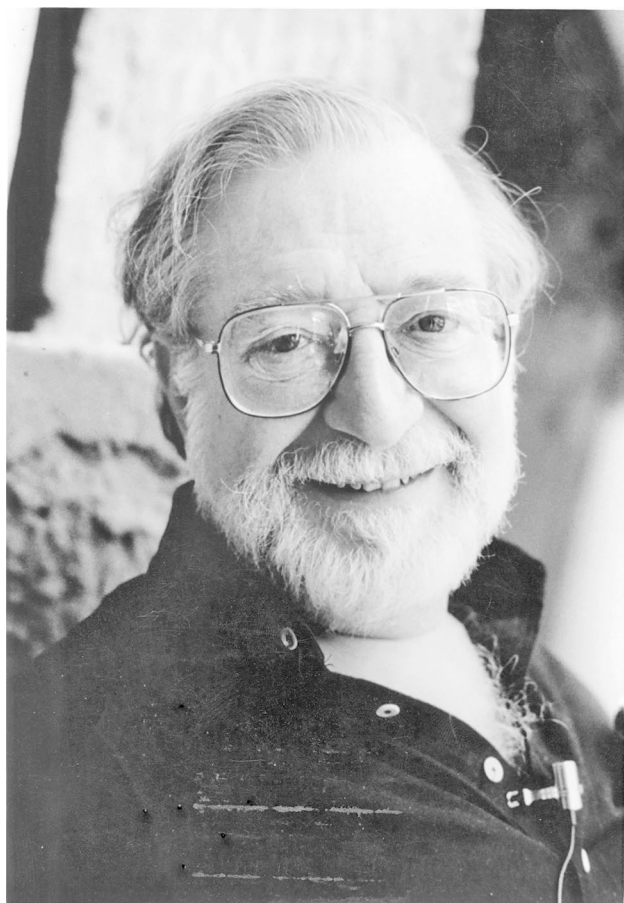


Fig. 1 R. Stephen Berry, 1995, in Erice, Sicily, during an international school of crystallography on clusters (photograph by Istvan Hargittai)

for Harvard in 1948. He got his bachelor's degree in 1952, Master's in 1954, and PhD in 1956, all from Harvard.

He had a remarkable scientist to mentor his doctoral work, the British (Scottish) William (Bill) Moffitt (1925–1958). Moffitt was educated at Oxford University and did his doctorate under the famous theoretical chemist and applied mathematician Charles A. Coulson (1910–1974) who was a pioneer in applying quantum mechanics to valency and other aspects of molecular structure. Moffitt solved a series of problems in the electronic structure of molecules and developed a new concept known as “atoms-in-molecule.” He joined Harvard University in 1953 as an assistant professor of chemistry, soon to be promoted to associate professor. Several of the rising stars of the field, such as Roald Hoffmann, wanted to have him as their mentor. Alas, Moffitt's untimely death denied the world of chemistry of a most talented and charismatic leader. He lived his short life to the fullest, and he died on the squash court stressing himself to the limit in spite of previously diagnosed heart problems.

After his PhD, Berry stayed at Harvard as a temporary instructor for a year and a half. Then, he worked, as instructor, at the University of Michigan in Ann Arbor, 1957–1960. This was followed by a tenure-track assistant professorship at Yale University, 1960–1964. There was no offer yet for a tenured position at Yale when the University of Chicago offered him one, so he moved there in 1964 and stayed at Chicago for the rest of his life. By the time Berry started his Chicago career, the great science at its James Franck Institute of the post-World War II period had become memory, yet its aura stayed on. Berry had a considerable share in maintaining the high level of science at the University of Chicago.

He attacked fundamental questions, such as how a system decides to become a glass or a crystal, or how does a protein fold to the right structure. One of the major areas of his research at the University of Chicago was the formation and behavior of atomic and molecular clusters and especially their dynamics. Our recording took place during a NATO workshop on clusters. Berry was interested in a variety of issues concerning science and public policy and, beside at Chemistry, held an appointment in the School of Public Policy Studies at the University of Chicago. He was a Fellow of the American Academy of Arts and Sciences (1978) and a member of the National Academy of Sciences (NAS, 1980), serving as the Home Secretary of NAS between 1999 and 2003. He was a Foreign Member of the Royal Danish Academy of Sciences (1980). He held a great number of distinguished lectureships, including the Hinshelwood lectureship at Oxford University, the Löwdin lectureship at Uppsala University, and the Sackler lectureship at Tel Aviv University. He was the Centennial Speaker of the American Physical Society (1999). Among his other recognition, he was recipient of the Alexander von Humboldt-Stiftung Senior Scientist Award (Germany) and the Heyrovsky Medal of Merit (the Czech Republic).

Many of the scientific problems that occupied him during the later period of his career could be traced back to his early discoveries in the 1960s regarding intramolecular motion, especially those involving large-amplitude deformation motion, and fluxionality—essentially to what has become known as Berry pseudorotation.

Berry pseudorotation

Pseudorotation (Fig. 2) appears when identical atoms, with no distinguishing labels on the atoms, permute among non-equivalent sites, and the process looks like a rotation of the molecule. If the atoms are labeled, it is seen that there is permutation as well as rotation. What Berry discovered was the first real example of a large-amplitude pseudorotation that scrambles bonds. The specific discovery happened for the

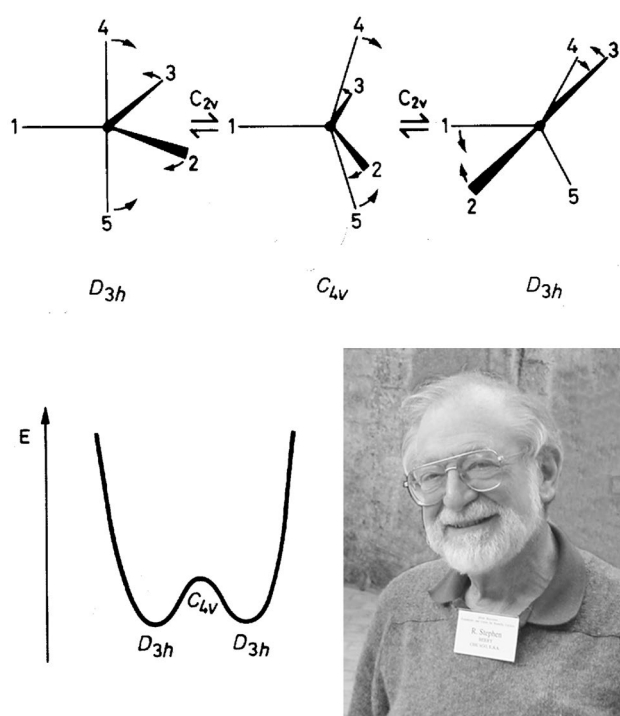


Fig. 2 Berry pseudorotation of PF_5 -type molecules with a potential energy profile and R. Stephen Berry's portrait (by the authors). Reproduced from Ref. [4]

motions of the fluorine ligands in phosphorus pentafluoride. It was in the early days of nuclear magnetic resonance when it was observed that identical atoms in chemically inequivalent sites had different magnetic resonance frequencies. These differences were called chemical shifts. It was shown first by Herbert S. Gutowsky, David W. McCall, and Charles P. Slichter at the University of Illinois [5] that if there was rapid exchange of inequivalent protons, one would see an average signal and the chemically non-equivalent sites could not be distinguished from one another.

Further, Gutowsky and Andy Liehr (then, an undergraduate) [6] found a single fluorine frequency for PF_5 . In contrast, PF_5 had been determined by electron diffraction to have a trigonal bipyramid geometry with axial and equatorial P–F bonds whose lengths differed significantly [7]. Berry proposed a mechanism [8] in which the longer axial pair of fluorines bent away from the linear F–P–F line and moved over to form a triangle with one of the equatorial fluorines. Simultaneously, two of the three fluorines in the equatorial plane moved out to become new axial atoms. The net result is as if the PF_5 molecule is rotated by 90° with the polar axis moving from vertical to horizontal. Berry also explained why the NMR spectra showed equivalence of the fluorines. He proposed that the process was fast compared with the observation time of the nuclear magnetic resonance experiment. This was a seminal discovery, but it is possible that

Berry himself did not recognize its significance at the time. He described it in a brief section of a longer paper, titled “Correlation of rates of intramolecular tunneling processes, with application to some group V compounds.” The thrust of the paper was a discussion of systematic relations for large-amplitude motions, especially *tunneling* motions [8].

Dynamic processes like the Berry pseudorotation had been proposed for other phenomena before and Berry himself stressed this [9]. Thus, what may have been the first such proposal had been by John Wheeler and Edward Teller in the late 1930s when they attempted to interpret the behavior of the neon-20 nucleus. They described it by an alpha-particle-model of five alphas. In this model, the five alphas take a trigonal bipyramidal configuration, which demonstrates pseudorotation. This explanation eventually proved wrong, but the idea was original and valuable. Berry did not refer to Wheeler and Teller because at the time, he was not aware of their work. He made reference to another, unpublished, proposal concerning the CH_5^+ molecular ion. The pseudorotation model did not prove correct for CH_5^+ either, because its geometry is not trigonal bipyramidal in the first place. Rather, CH_3^+ and H_2 are held together by a weak interaction in it. This was reinforced by recent computational work: The carbocation CH_5^+ has a structure of C_s symmetry with three 2-center-2-electron bonds and one 3-center-2-electron bond [10].

Another forerunner of the discovery of Berry pseudorotation was Kenneth S. Pitzer's observation of the pseudorotation of cyclopentane [11]. There, small-amplitude motions lead to pseudorotation. There is a near-symmetry-axis for the non-planar pentagonal molecule, and rotation appears conspicuously. Pitzer called it cyclopentane pseudorotation. In a simplified way the pseudorotation of cyclopentane may be described as follows [12]: imagine one of the five carbons out of the plane of the other four carbons. Then, the out-of-plane carbon exchanges roles with one of its two neighbors (and their hydrogen ligands that always move along with their carbon). This exchange is equivalent to a rotation of this motion by $2\pi/5$ about the near-symmetry-axis perpendicular to the ring (see, e.g., Ref. [13]). This description brings up a favorite topic for Matisse's art of five dancers forming a ring. Now, imagine one of the dancers jump while the other four stay on ground. Then, the next dancer jumps, and so on. The motion rotates, not the dancers. If taking a quick snapshot, it catches one of the dancers in the air and the ensemble has a symmetry plane. If, however, the exposure time is sufficiently long, there will be a blurred image with all the dancers slightly about ground and there will be fivefold symmetry.

Berry pseudorotation has become well known, but it has remained unclear when and by whom Berry's name was attached to it, no doubt, deservedly. Berry himself thought of several possibilities [9]. He corresponded with F. Albert

Cotton about the possibility of pseudorotation for Cotton's transition metal carbonyls, so Cotton might have also coined this name. Berry also corresponded with Earl Muetterties about it, and Muetterties was especially interested in the relationship between the lifetime of structures and the reaction times of physical measurements. There was then the possibility that Frank Westheimer may have added Berry's name to pseudorotation. Westheimer found the most far-reaching implications of the process in studying RNA chemistry. He and his students showed that pseudorotation accompanies the hydrolysis of some cyclic phosphate esters [14]. Four-coordinate phosphorus goes into a transition state, then, goes through the pseudorotation as five-coordinate, and finally goes back to four-coordinate. There is analogy here with the PF_5 structure in that the axial positions have weaker bonds than the equatorial positions. Something would come in to form an axial bond and rearrange to form a stronger equatorial bond, and something else would then become axial and break off.

The time-scale relationships are important in interpreting the data that different experimental measurements may yield on various structures. There is an apparent paradox that non-identical nuclei could occupy observably equivalent sites and vice versa, and identical nuclei might occupy non-equivalent sites. According to quantum mechanics, identical electrons or other identical particles have to be indistinguishable and the wave function for identical particles has to reflect this indistinguishability. In contrast, chemistry is based on the distinguishability of different sites in molecules. The answer to this apparent paradox is in time-scale differences in the variability of the relationship between the lifetime of a structure and the observation time of the physical phenomenon being used for its determination. For the cyclopentane molecule, it will be definitely non-symmetrical if being observed with a very quick physical phenomenon, and possessing fivefold symmetry if the measurement is sufficiently slow.

Decades after his original discovery, Berry returned to more studies of pseudorotation and its implications. He was increasingly interested also in clusters. Eventually, however, his thinking turned toward the more general question of the intricacies of complex potential surfaces. He was trying to resolve the problem of getting out more information about such systems from computations than could be reasonably digested. He was formulating puzzles that to us resembled those faced by developmental biologists: why do some things form well-defined structures, while others form glasses?

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