The Pursuit of Accurate Measurements: Gas Electron Diffraction from the 1930s to the 1960s

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Introduction

Most scientific instruments and experimental methods have been improved continually since their invention. Such improved methods sometimes change scientific practices and usually enable more accurate measurements that replace existing data with new ones. In his book, *An Introduction to Scientific Research*, the American chemist, E. Bright Wilson wrote the following about measurements at higher accuracy.

> Sometimes measurements at higher accuracy bring to light new and unforeseen discrepancies of fundamental importance. An example of this is the Lamb-Retherford measurements of hyperfine structure of hydrogen spectrum, which showed that the Dirac theory needed modification.[1]

This example showed the interrelationship between the theory and the measurement. The question this raises is: if there are discrepancies between the results of two measurement methods, does this render one of them obsolete or changed? To answer this question, I look to the case of the determination of molecular structures in the gas phase. Gas-phase molecules are less influenced by the environment than in the solid and liquid phase, and gas molecular structural studies have thus provided much fundamental information about molecular structures. In the 1960s, the methods for investigating gas molecules were gas electron diffraction and spectroscopy. In this paper, I trace the history of gas electron diffraction, which was considerably improved in the late 1940s.

The Development and Improvement of the Gas Electron Diffraction

Gas electron diffraction, GED, is a method of determining molecular structures of gases by measuring the internuclear distances and valence angles of molecules by electron diffraction.[2] Herman Mark and Raimund Wierl published a paper on the structure of molecules, such as cyclopentane and tetrachloroethene with GED in 1930.[3] In the same year, Linus Pauling visited Mark and learned about GED, and subsequently wanted to utilize GED for his research. Pauling acquired the design of the apparatus from Mark, who was not going to continue his GED research any longer.[4] After Pauling's return to the US, one of his students, Lawrence

[1] E. Bright Wilson, *An Introduction to Scientific Research*, Dover edition (New York: Dover Publications, 1990, original work published in 1952), p. 59.

[2] In the late 1920s, Peter Debye started to study gas molecules using X-ray diffraction. It took more than ten hours to achieve exposure with X-ray. On the other hand, it took a few seconds with an electron beam because the scattering power of electron is much larger than X-ray's. In the mid-1930s, X-ray diffraction studies on free molecules were abandoned.

[3] Herman Mark and Raimund Wierl, "Die Ermittlung von Molekülstrukturen durch Beugung von Elekronen an einem Dampfstrahl," *Zeitschrift für Electrochemie*, 36 (1930): 675-676.

[4] Linus Pauling, "Fifty Years of Physical Chemistry in the California Institute of Technology," *Annual Review of Physical Chemistry*, 16 (1965): 1-15. Mark invited Odd Hassel to show his GED apparatus in 1930. Hassel started GED in Norway and his group became one of the leading GED research groups before the war.

Brockway constructed an apparatus and this was used to start GED research at Caltech, making Brockway a pioneer in studies of GED. Pauling regarded one of the results of their GED work as empirical evidence of the existence of resonance among several valence-bond structures in 1933.[5]

After the invention of GED, researchers employed what was called the 'visual method', wherein the diffraction intensities on imaging plate were measured using their own eyes. The maximum and minimum intensities were so faint that they could not be measured mechanically, but human eyes were (are) sensitive enough to detect the relative intensity. This procedure is a form of artisanal work wherein trained eyes measure intensity. The GED researchers achieved several successes in structural chemistry by using the visual method.[6] For example, Verner Schomaker and Glauber at Caltech demonstrated the failure of the first Born approximation.[7] As Pauling mentioned in his paper in 1939, Schomaker had an especial skill in measuring electron diffraction photographs.[8]

One of Schomaker's co-workers, however, complained, "But Verner, you can see the rings so much better than I can."[9] Schomaker refuted, "Mostly not so! I just tried harder and got further behind,"[10] This argument demonstrates the subjectivity of GED research. Even if Schomaker worked harder, as did the naturalists in the Enlightenment, with 'meticulous patience and manual delicacy',[11] how could the accuracy of the result be verified or how did the GED researchers decide which molecular structure was the correct one? In reality, the members of Schomaker's group said that the result was always right if it was measured with the well-trained eyes.[12] In most cases, GED results were compared with the results of X-ray diffraction of solid molecular structure because, in general, differences of structure between solid and gas are slight, and were in good agreement. Unfortunately, soon afterward, some of the earlier molecular structures obtained by the visual method proved unreliable or definitely wrong,[13] and this led to a deep-rooted mistrust of GED.

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5 Lawrence O. Brockway and Linus Pauling, "The electron-diffraction investigation of the structure of molecules of methylazide and carbonsuboxide," *Proceedings of the National Academy of Sciences*, 19 (1933): 860-867.

6 Kozo Kuchitsu, "Gas Electron Diffraction," in ed. Peter Goodman, *Fifty Years of Electron Diffraction*, (Dordrecht, Holland; Boston: D. Reidel, 1981), pp. 356-377, p. 359.

7 Verner Schomaker and Roy Glauber, "The Born Approximation in Electron Diffraction," *Nature*, 170 (1952): 290-291.; Roy Glauber and Verner Schomaker, "The Theory of Electron Diffraction," *Physical Review*, 89 (1953): 667-671.

8 Linus Pauling, H.D. Springall, and K.J. Palmer, "The Electron Diffraction Investigation of Methylacetylene, Dimethylacetylene, Dimethyldiacetylene, Methyl Cynaide, Diacetylene, and Cyanogen," *Journal of American Chemical Society*, 61 (1939): 927-937.

9 Verner Schomaker and Kenneth Hedberg, "Gas Electron Diffraction: Continuation at Cal Tech and Oregon State," in ed. Peter Goodman, *Fifty Years of Electron Diffraction*, (Dordrecht, Holland; Boston: D. Reidel, 1981), pp. 208-221.

10 Schomaker & Hedberg (note 9), 211.

11 Lorraine Daston, "Attention and the Values of Nature in the Enlightenment," in eds. Lorraine Daston and Fernando Vidal, *The Moral Authority of Nature* (Chicago and London: The University of Chicago Press, 2003), pp. 100-126, p. 115. I thank Dr. Buhm Soon Park for this information.

12 Masao Kimura, "Kitai Denshisen Kaisetsu to Karuforunia Kodai (The Gas Electron Diffraction and Caltech)," *Kagaku to Kogyo*, 12 (1959): 628-633. (in Japanese), p. 630. (the author's translation) Kimura's report of this visit to the GED group at Caltech describes how Schomaker conducted GED experiment. When Schomaker left Caltech in 1958 the GED research at Caltech was terminated.

13 Wheatley pointed out that there were two main reasons for the errors. The first was the ignorance of hydrogen atoms for determining molecular structures because the scattering from them was small, and the effect could be submerged in the scattering due to heavier atoms. The second was that the number of diffraction rings were insufficient to investigate structures of gas molecules and it sometimes led to completely incorrect models of molecular structures. (Peter J. Wheatley, *The Determination of Molecular Structure*, 2nd ed. (New York: Dover Publications, 1981, original work published 1968), p. 86.

In the late 1940s, several GED researchers in Norway and the US developed the sector method independently. By using a rotation sector above the imaging plate during recording the diffraction pattern, the sector method made it possible to mechanically measure the intensity on the imaging plate with a micro-photometer. The sector method became widely used from around 1950, and it gave credibility to GED as this mechanical method was more objective and accurate than the artisanal visual method.[14]

Above all, the importance of the improved measurement method was brought to light by Isabella Karle and Jerome Karle at the Naval Research Institute in the US. In 1949 they demonstrated the ability of GED measurement to evaluate vibrations between pairs of atoms in a molecule by the sector method.[15] It broadened the range of application for GED in structural chemistry.

What Kinds of Problems Were Caused by the Different Method? - The Discrepancies and the Mistrust

After World War II, a promising method achieved status as one of the most powerful techniques with high accuracy to investigate molecular structures. It was microwave spectroscopy. The GED researchers compared the results provided by spectroscopy and GED of molecular structures at 0.001Å-digit accuracy. However, they found that there were the discrepancies between them.[16]

There were two different reactions from GED people to the discrepancies. One was negative, the other positive. Brockway, the pioneer of GED, was typical of those who reacted negatively. The discrepancies made him pessimistic about the future of this method. For example, at an international conference in 1961, he expressed concern that "[n]o standard procedure can be applied in an automatic fashion with a guaranteed precision."[17] On the other hand, Yonezo Morino's attitude was positive. He believed that the discrepancies could be explained by taking into account the fact that a molecule is a dynamical system and also pointed out, especially, that the GED researchers believed that all researchers who engaged the molecular structure determination investigated the same dimension of a molecule.[18]

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[14] Even after the sector method became available, Schomaker clung to the visual method. Pauling suggested that they should introduce the sector method and Schomaker finally agreed and introduced it. (Schomaker (note 9))

[15] Isabella Lugoski Karle and Jerome Karle, "Internal Motion and Molecular Structure Studies by Electron Diffraction," *Journal of Chemical Physics*, 17 (1949): 1052-1058. Concerning this paper, Yonezo Morino pointed out that the formula by Peter Debye which Karle and Karle introduced for the discussion on the thermal motion, should be corrected. (Yonezo Morino, "On the Mean Amplitudes of Thermal Vibrations in CO_2 Molecule," *Journal of Chemical Physics*, 18 (1950): 395.) This case shows that the measurement at higher accuracy revealed the discrepancy between theory and experiments.

[16] James has pointed out that comparisons of results from different techniques could provide a basis for extrapolation. (Jeremiah James, "Modelling the Scale of Atoms and Bonds: The Origins of Space-filling Parameters," in eds., Ursala Klein and Carsten Reinhardt, *Objects of Chemical Inquiry*, (USA: Science History Publications, 2014), pp. 281-320.)

[17] Lawrence O. Brockway, "Recent Problems in Diffraction by Gases," in *Proceedings of the International Conference on Magnetism and Crystallography, Kyoto, 25-30 September, 1961*, pp. 1-3.

[18] Yonezo Morino, "Jitsurei wo Toshite 'Seimitsu Sokutei wo Kangaeru (Examining the Precise Measurement through the Examples), *Kagaku Sosetsu* 10 (1976): 40-48. (in Japanese) I think that there were the directional differences between the GED researchers, Brockway and Morino. Brockway often asserted the precision of GED measurement. On the other hand, Morino wanted accurate measurement. In 1963, Churchill Eisenhart defined the difference between precision and accuracy: precision has to do with closeness of results to each other and accuracy has to with closeness to the truth. (Churchill Eisenhardt, "Realistic Evaluation of the Precision and Accuracy of Instrument Calibration Systems," *Journal of Research of the National Bureau of*

Practically, GED involves looking at the thermal distribution of vibrational states, whereas microwave spectroscopy looks at a molecule in a specific vibrational state. In other words, the gas electron diffractionists and the microwave spectroscopists were looking at different states. The words 'molecular structure' meant different things to different people.[19] Some diffractionists and spectroscopists mentioned this difference in their papers by the middle of the 1960s.[20]

Morino was one of the researchers who noticed the difference. Moreover, Morino had introduced microwave spectroscopy for investigating molecular structures along with GED in the late 1950s. He had a background in spectroscopy for determining molecular structures. He had started Raman spectroscopy with San-ichiro Mizushima when he was a graduate student, although he had been attracted to GED at the time.[21] It seems natural that he took such an interdisciplinary approach because of his background. He thought, "if the two methods were properly combined, we might gain more advanced knowledge of molecular structure."[22] Pursuing accurate measurement with not only on measuring technique was one of his strategies to better understand the true nature of molecules.[23] In Morino's phrase, he aimed at "unified molecular structure."[24] This was a scientific approach to the problem of the discrepancies, which would be later tackled by James Boggs and his colleague with the social and organizational method of using symposia, which Peter Galison has called a 'Trading Zone'.[25]

Morino and his students at the University of Tokyo performed GED research and utilized the spectroscopic method, combining the results from different techniques for determining the accurate molecular structure. When they proposed an internuclear distance parameter in 1962, Morino and his students noted:

Standards- c. Engineering and Instrumentation, 670 (1963): 161-187.) This definition is important when thinking about the difference between Brockway's and Morino's research-programs.

19 Wheatley (note 13), i.

20 The spectroscopists, Herschbach and Laurie, noted that most of the discrepancy arises from the inherent difference in the nature of the experimentally determined quantities. Dudley R. Herschbach and Victor W. Laurie, "Influence of Vibrations on Molecular Structure Determinations. I. General Formulation of Vibration—Rotation Interactions," *Journal of Chemical Physics*, 37 (1962): 1668-1686. The comparison between the results from spectroscopy and diffraction also fascinated the theoretical chemists. Charles Coulson expressed an interest in why spectroscopy and diffraction provided different value of the bond lengths. And, he believed that it would be very useful to obtain electron diffraction data on diatomic molecules for comparison with existing spectroscopic data. (Charles A. Coulson, "Comments on paper by B.P. Stoicheff," in the Epistelogue (Paper Symposium) on the Effect of Environment on the Properties of Carbon Bonds, *Tetrahedron*, 17 (1962): 254-255.) Understanding the origin of the discrepancies was not an experimental interest but also a theoretical one. In the early 1960s, there were several theories explaining the variation in C-C bond lengths, such as resonance, conjugation, hybridization, and non-bonded interaction.

21 Mizushima's group, including Morino, performed GED work before World War II with the surface scientist Shigeto Yamaguchi at the Institute of Physical and Chemical Research, who had an electron-diffraction camera. Morino started his own GED work with help from the electron diffractionist, Ryoji Uyeda at Nagoya University after he left Mizushima group. Since Seishi Kikuchi observed the electron diffraction pattern from a thin crystal of mica in 1928, electron diffraction research became one of the strongest research areas before the war in Japan. I thank Dr. Jeremiah James for his question on this point.

22 Yonezo Morino, "Fifty years in Tokyo, Nagoya, and Tokyo," in ed. Peter Goodman, *Fifty Years of Electron Diffraction*, (Dordrecht, Holland; Boston: D. Reidel, 1981), pp. 136-143, p. 141.

23 One of his achievements was the Bastiansen-Morino shrinkage effect in 1960, where the vibrational motion of the atoms in a molecule have an effect on the structure. Morino explained the molecular structure, which Otto Bastiansen in Norway measured with GED, by means of calculation based on the spectroscopic data.

24 Morino (note 22), 141.

25 Peter Galison, *Image and Logic: A Material Culture of Microphysics* (Chicago and London: The University of Chicago Press, 1997)

> it is not our intention to cause a confusion by introducing new distance parameters, but it seems to be of practical importance to get a reasonable way of correlating diffraction and spectroscopic parameters with each other of reading the equilibrium distance r_e based on these experimental quantities.[26]

This statement is a sort of defense against the criticism from other researchers. Indeed, most of those in the GED community had reacted unfavorably. For example, at an international conference in 1961, Brockway said that electron diffractioners would not conform to other disciplines.[27] And at the Congress of the International Union of Crystallography in 1963, Jerome Karle criticized Morino's idea saying that the result of spectroscopy should not be used if one wanted to determine molecular parameters from the GED experiment.[28] Morino needed more time and a change in situation to achieve acceptance of his idea in the field.[29]

The discrepancies threw into sharp relief the mistrust between the practitioners of the two methods. There had been mistrust between the two tribes, although both were struggling to give detailed and accurate information on molecular structures. Of this situation, James Boggs, the American chemist, wrote, "we were very concerned…to be frank, [about] the scorn with which each regards the other."[30]

What brought such distrust between them? A GED researcher said, for example, that spectroscopists showed no clear understanding of the extent to which that accuracy disappears by the time it is related to a molecular geometry parameter.[31]Also, Boggs said that he was told that [a diffractionist] "should never trust a microwave spectroscopist."[32] In return, Wilson, a microwaver, was "very skeptical at the time about the reliability of electron diffraction as a structural research tool,"[33] even after the development of the sector method.

Moreover, there was little social interaction between the two tribes. By the middle of 1960s, GED researchers usually attended chemistry meetings and were interested in structural information and theory. On the other hand, microwavers mostly attended physics meetings and were interested in the absolute values of molecular structure.[34] It should be mentioned that the GED community was very small and there were ten or fewer GED groups in the world in the late 1950s.[35] Spectroscopists had been having large meetings on spectroscopy,

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[26] Yonezo Morino, Kozo Kuchitsu, and Takeshi Oka, "Internuclear Distance Parameters," *Journal of Chemical Physics*, 36 (1962): 1108-1109, p. 1109.

[27] Brockway (note 17), 2.

[28] Yonezo Morino, "Roma Kaigi ni Okeru Kitai Denshisen Kaisetsu ni Kansuru Hokoku (The report of the Conference on Gas Electron Diffraction at the Rome Conference), *Nihon Kessyo Gakkaishi*, 6 (1964): 31-33. (in Japanese)

[29] One of Morino's students, Kozo Kuchitsu pursued the idea of combining the analysis of GED and spectroscopic data and established the methods. The history of the process is also interesting, but needs more investigation.

[30] James E. Boggs, "History of the Austin Symposium," https://sites.smu.edu/dedman/austinsymposium/history.html, accessed June 30, 2014.

[31] James E. Boggs, "The integration of structure determination by computation, electron diffraction and microwave spectroscopy," *Journal of Molecular Structure*, 97 (1983): 1-16, pp. 1-2.

[32] Boggs (note 31), 2. Following this description, he continues, "[m]y own observation told me that you should never trust a result coming from electron diffraction either."

[33] Roberts L. Kuczkowski, "Lawrence S. Bartell: biographical notes," *Journal of Molecular Structure*, 485-486 (1999): xi-xxvii.

[34] Boggs (note 31), 3.; Leslie E. Sutton (ed.), *Tables of Interatomic Distances and Configuration in Molecules and Ions (Supplement 1956-1959)* Special Publication No.18 (London: The Chemical Society 1965), p. 6.

[35] Kozo Kuchitsu, "Kitai Denshisen Kaisetsu (Gas Electron Diffraction)", *Kagaku no Ryouiki*, 11 (1957): 52-76, p. 53. (in Japanese)

but the GED people had been having symposia and usually attended crystallography meetings or electron diffraction meetings.[36]

The GED researchers attended several meetings that were related to their interest, molecular structures. Occasionally, there were some cases where GED and microwave researchers met – or rather, attacked – each other. One of these few occasions was the Ohio State University International Symposium on Molecular Structure and Spectroscopy.[37] At the meeting in 1963, the participants witnessed a heated argument between Larry Bartell, a diffractionist, and Bright Wilson, a microwaver.[38] Around that time there were people who were very concerned about the situation.

Mediating a Settlement- A Symposium for Two Tribes

Boggs and his colleague, Harold Hanson, a GED researcher, at Texas University were the people concerned about the situation. Boggs was one of Brockway's students, but, interestingly, he did not earn his PhD degree for GED research. The two researchers thought that the lack of communication between the practitioners of the two methods caused difficulties for molecular structure studies.[39] They devised a social and organizational method to "force them to listen to each other"[40] and invited leading researchers from the two areas, who were mainly in the US.

The confrontation site was the 1966 Austin Symposium on Gas Molecular Structure, which was a session of the American Crystallographic Association Annual Meeting.[41] This was expected a one-off highly focused meeting. The topic of the symposium was accurate measurement of the molecular structures.

At the meeting, the participants shared problems and ideas about the determination of gas-phase molecules. For example, 'accurate bond length' was one of the topics at the meeting. Cecil C. Costain, who was a spectroscopist, started his talk by saying, "Those who were at the banquet last night will appreciate the fact that one can no longer discuss the accuracy of bond length without putting his money on the table."[42] This witty remark depicted the situation well.

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[36] The GED researchers tried to create an opportunity in the early 1960s to have a meeting with spectroscopists in order to discuss molecular structures. In 1963 during the Congress of the International Union of Crystallography in Rome, the GED people discussed the possibility of a joint symposium with spectroscopists, especially microwavers, on the determination of accurate molecular structure (Morino (note 28). It was supposed to be held at the European Congress on Molecular Spectroscopy in Copenhagen in 1963, but I have not yet been able to find any evidence that this symposium was actually held.

[37] By the 1970s, the organizers of the Ohio State University meeting decided not to include crystallography and gas electron diffraction because the symposium became larger and crystallographers and diffractionists began to attend other meetings. (Brenda P. Winnewisser, "An Array of Scarlet and Grey Booklets: 65 Years of the Symposium on Molecular Spectroscopy," *Journal of Molecular Spectroscopy*, 269 (2011): 2-11, p. 3.)

[38] These witness reports came from Kuczkowski's article (Kuczkowski (note 33)) and personal correspondence with John Muenter, dated August 28, 2014.

[39] Boggs (note 30)

[40] Boggs (note 30)

[41] The organizers arranged the symposium at the crystallography meeting because Hanson was a diffractionist and Boggs was a theoretical chemist, and the crystallography meetings might be one of their sphere of activities. I thank Dr. Mary Jo Nye for her question on this point.

[42] Cecil C. Costain, "Further Comments on the Accuracy of r_s substitution structures," in Proceedings of the Symposium on Machine Interpretations of Patterson Functions and Alternative Direct Approaches and the Austin Symposium on Gas Phase Molecular Structure at Austin, Texas, Feb. 28-March 2, 1966. *Transactions of the American Crystallographic Association*, 2 (1966): 157-164, p. 157.

Costain thereafter expressed his belief in the necessity of the collaboration between two areas, saying "I think ethyl fluoride is one example of a molecule for which we should ask for help and collaboration from the electron diffraction people."[43] In the discussion part of his presentation, several researchers from the both camps suggested that they should cooperate to determine accurate bond length.[44]

The meeting was a great success and Boggs and Hanson decided to continue the symposium biennially. The second symposium was held in 1968. The speakers at the symposium came from the US, Europe and Japan. Six invited speakers, including Morino, were from each tribe and there were two group discussions between both sides to discuss unsolved problems and think about the future of structural chemistry. They admitted the limitations of their own methods and the complementary relationship between the results from the two measurement methods for studies on gas molecule structure.

Conclusion

I have traced the history of gas electron diffraction to answer the question, if there are discrepancies between the results of two measurement methods, does this render one of them obsolete or changed? Improved GED with higher accuracy revealed the discrepancies in the results of GED and microwave spectroscopy. For example, Morino explained the origin of the discrepancies and combined the results from the two methods to pursue accurate molecular structure. However, his approach seemed a long shot at the time, and exposed the mistrust between two instrumental communities. Meanwhile Boggs and his colleague offered the binding site, or 'Trading Zone', of the Austin Symposium. In that zone, the researchers from the two disciplines exchanged ideas and shared information about their research on gas molecular structure. As a first step, the participants admitted that the information provided by both methods was a mutually complementary and that they shared a common goal – that of understanding molecular structure.

This case shows that, although the discrepancies in the results of the two different measurement methods revealed the biased attitudes on the both sides, neither method needed to be modified or corrected because of the discrepancies. Rather, the discrepancies triggered the collaboration between the two method people, and such collaboration eventually resulted in advancing knowledge about the target.

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[43] Costain (note 42), 160.
[44] Costain (note 42), 161-164.