Development of Vibrational Spectroscopy of Polyatomic Molecules in the 1930s and Its Implication for the Emergence of “Molecular Science”

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Introduction
When we look back the history of chemistry from 20s to 60s, application of the physical methods have made the most significant impact on the daily activity of chemists. The changes occurred in both of the experimental and theoretical aspects: Various physical instruments commonly equipped in chemical laboratories such as pH meters and chromatographs and more expensive spectrometers and diffractometers installed in department buildings replaced the laborious protocols of qualitative chemical analysis with quantitative data they provide automatically. These data can be now interpreted, thanks to the development of quantum chemistry and its implementation as computer programs, in terms of molecular structure. However, the very nature of chemistry as practice to transform matter into useful products seems to be unchanged, while the forefront of the research has nowadays shifted from homogeneous chemical compounds to heterogeneous nanomaterials.

On the other hand, physics as pursuit to unravel hidden law of nature have been changing in its forefront. In the beginning of the twentieth century atoms and molecules were the hottest target of research, which eventually led to emergence of quantum theory for microscopic entities. Soon it was successfully applied to explain the homopolar bonding of hydrogen molecule and Dirac gave his famous statement in 1929² and forefront of physics has moved to subatomic phenomena or solid-state physics. However, it was in 1930s after his statement that molecular structure of polyatomic molecules has begun to be understood based on quantum chemistry and molecular spectroscopy. This development would not be achieved without persistent contribution of certain number of physicists and chemists and their activity and achievement seems to be “neither physics nor chemistry”.

Such ambivalent situation of this practice already has been recognized by one of the leading scientists. In 1965, at the symposium dedicated to Mulliken, he gave a lecture “Molecular Scientists and Molecular Science: Some Reminiscence”. After describing his experimental study of isotope separation before starting molecular spectroscopy, he said:³

"Since then I have become neither a proper experimentalist nor a proper theorist, but a middleman between experiment and theory --- and between chemistry and physics."

He did not mention the term "molecular science" and simply described his experience through people he met around 1930, as if it is self evident that they were the molecular scientists and their activity was the molecular science.

¹ This work was performed based solely on my personal interest and no relationship with the research activity in my affiliation.
³ R. S. Mulliken, J.Chem. Phys. 43, S2 (1965). It should be noted that the title of his autobiography is “The Life of a Scientist”, neither physicist nor chemist.
Actually the term "Molecular Science" was first widely recognized a few years before his lecture, when it appeared in the title of the book edited by von Hippel. However, it was one of the three volumes on his dielectric materials research and seems different from what Mulliken meant with the same term. Rather it was closely related to the term in 1961 by Japanese scientists for a new research project “molecular science - physicochemical study of molecules” funded by the Grant-in-Aid for Scientific Research, as this project would not be realized without strong promotion by Nagakura who studied in Chicago in 1950s. This activity has materialized Institute for Molecular Science in 1975 and Japan Society for Molecular Science in 2006. Such developments of molecular science in Japan is quite unique and its development would provide a clue to understand Japan’s modern history of chemistry. However, before tackling this issue I would like to go back to 1930s when the studies on the molecular structure came into shape.

Among various branches in experimental studies related to the molecular science, vibrational spectroscopy has been particularly important as the vibrational frequencies and selection rules can be correlated with molecular structure and symmetry through mechanistic molecular models. Although there are several important previous studies on the history of vibrational spectroscopy, they mainly describe the development of the infrared spectra of diatomic molecules until around 1930, or application of the infrared spectroscopy for chemical analysis after 1930. Actually we can learn about the development of vibrational spectroscopy in 1930s from a review article and even from a textbook as the framework of the analysis of the vibrational spectra were established in this period. However, they are mainly the studies of small molecules by the scientists in the United States and it is difficult to know situation of the other countries only from these resources. Of particular important in connection with the emergence of the molecular science is Germany, as young promising Japanese scientists studied there and learned from German textbooks in 1930s. In this presentation I tried to follow the development of vibrational spectroscopy of polyatomic molecules in Germany in 1930s.

Vibrational spectroscopy of polyatomic molecules before 1930

In 1905 Coblenz published a compilation of measured infrared absorption spectra of a large number of organic compounds. He employed a radiometer, a mirror spectrometer and a rock salt or a quartz prism and recorded absorbance point by point and manually plotted the spectra. He found that isomeric compounds show markedly different spectra and certain atomic groups such as the methyl group show their characteristic absorption bands at certain

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10 San-ichiro Mizushima and Juro Horiuti are the most famous cases of the physical chemists studied in Germany in 1930s.
wavelengths. The results indicated that the infrared spectroscopy can provide information on molecular structure and has a potential as a tool for identification of chemical compounds.

At almost the same time Drude attributed dispersion frequencies to intrinsic vibrational frequencies of atoms and molecules, which are proportional to the ratio of the charge and the mass.\textsuperscript{12} Thus the dispersion in the infrared region was due to intrinsic vibration of positively charged atoms in a molecule, whereas electrons are responsible for the dispersion in the ultraviolet region.

The first attempt to assign infrared absorption bands of a polyatomic molecule by calculating its vibrational frequencies was made by Bjerrum in 1914.\textsuperscript{13} He treated carbon dioxide having a bent shape with two equivalent carbon-oxygen bonds and calculated normal vibrations by assuming the system as point masses connected with attractive force between atoms and obtained possible geometries by adjusting the bond angle and force constants to reproduce measured vibrational frequencies. He derived a bent structure by fitting the calculated values to the frequencies of the three absorption bands. Although this was turned to be wrong as one of the absorption bands was actually a combination band, the proposed procedure still works within the framework of the quantum mechanics until today.

In 1925 Dennison applied the same procedure to the analysis of the IR spectra of methane with a tetrahedral model.\textsuperscript{14} By assuming spherical distribution of electrons around the carbon and the four hydrogen atoms, the potential energy of the molecule can be described as a function of the displacements of each of the hydrogen relative to the carbon and the mutual displacements of the hydrogen atoms. The system with nine internal degrees of freedom has only four normal modes, two of them were triply degenerate non-symmetric CH stretching ($\nu_3$) and bending ($\nu_4$) modes. The normal frequencies calculated by adjusting the force constants in the potential energy function were in fairly good agreement with the fundamental vibrational frequencies, although the bands assigned to the totally symmetric modes were later found to be combination bands.

This work was motivated by the infrared spectra of methane measured by Cooley of the same physics laboratory of University of Michigan.\textsuperscript{15} By using a high-resolution grating spectrometer the bands at 7.7 $\mu$ ($\nu_4$) and 3.31$\mu$ ($\nu_3$) were resolved into rotational lines. However, the line spacing of 9.77 cm$^{-1}$ near the center of the $\nu_4$ band was almost twice of that of the $\nu_3$ band (5.41cm$^{-1}$). This seemed puzzling as the line spacing is inversely proportional to the moment of inertia and the three principal values of the spherically symmetric methane molecule should be equal.

The most straightforward solution of this inconsistency is to lower the molecular symmetry to have two different rotational constants. Pyramidal carbon atom has already been proposed from an X-ray crystallographic study of pentaerythritol C(CH$_2$OH)$_4$.\textsuperscript{16} Guillemin calculated pyramidal structure of methane to have two principal values of the moment of inertia derived from the rotational fine structure of the $\nu_3$ and $\nu_4$ bands.\textsuperscript{17} His discussion was based on the ionic molecular model and he noted that the carbon ion should be polarizable to stabilize the pyramidal structure relative to the tetrahedral structure, which minimizes electrostatic repulsion of hydrogen ions. Henri reviewed these papers on the pyramidal structures of the

\begin{thebibliography}{9}
\bibitem{12} P. Drude, \textit{Ann. Physik} \textbf{14}, 677 (1904).
\bibitem{16} H. Mark, K. Weissenberg, \textit{Z. Physik} \textbf{17}, 301 (1923).
\bibitem{17} V. Guillemin, Jr. \textit{Ann. Physik} \textbf{81}, 173 (1926).
\end{thebibliography}
tetravalent carbon compounds and argued that the conformation of the tetravalent carbon atom is dependent on the nature of the atoms or atomic groups connecting to it. However, Richardson mentioned this problem in his introduction in the Faraday Society in 1929 in favor of tetrahedral structure by citing the work by Dennison. In X-ray crystallography Nitta argued for the tetrahedral carbon in pentaerythritol and there seems no strong argument for pyramidal tetravalent carbon after around 1930. These arguments are just before the advent of the quantum chemistry and explanation of the tetrahedral carbon with orbital hybridization. However, they seemed to have certain influence on the chemists' attitude towards application of the physical methods.

The most significant event in the development of the vibrational spectroscopy is definitely the discovery of the Raman effect in 1928. The Raman spectra of any type of substances (liquid, solid, gas) were obtained by use of a very simple setup, which showed bands of the scattered light whose shifts represent natural vibrational frequencies. The effect was discovered almost at the same time by several groups but Pringsheim named it as the Raman effect. Vast number of papers on the Raman effect of various substances appeared and Raman received Nobel Prize in Physics in 1930. Eventually it was recognized that the selection rule of the natural vibrations of the Raman active modes are different from infrared active modes and its explanation based on molecular polarizability and its symmetry was given by Placzek.

Research Activity in Germany in early 1930s

Mulliken's reminiscence is an illustration of not only his close relationship with many friends but at the same time their scientific activities in Germany around 1930. During his visits he also had chances to attend scientific meetings but interestingly he did not attend the meeting of Faraday Society on "Molecular spectra and molecular structure" held in 1929 at Bristol. This meeting is famous in the history of quantum chemistry for discussion on notation of the molecular spectra but the discussion on the electronic spectra and electronic structure was only one part of the meeting and there were other two parts on the Raman effect and the infrared spectra. Scientists from different countries contributed to the discussion.

Next year during his visit to Europe he gave a presentation at the 35th general meeting of the Bunsen Gesellschaft in the next year at Heidelberg. Following lectures were given for the main theme "Spectroscopy and molecular structure".

- J. Franck, "Determination of thermochemical quantities from spectroscopic data"
- R. Mecke, "Experimental results and goals of the band research"
- F. Hund, "Methods of interpretation and prediction of molecular spectra"
- W. Weizel, "Structure and spectra of molecules H₂ and He₂"
- R. S. Mulliken, "Electronic state und chemical bond in diatomic molecules"
- O. Stelling, "Correlation between chemical constitution and K X-ray absorption spectra"
- P. Debye, "Interferometric determination of structure of single molecule"

23 G. Placzek, Z. Physik 70, 84 (1931).
26 Titles of the session and presentations were tentatively translated into English by the present author.
M. Czerny, "Infrared spectroscopy"
A. Smekal, "The Raman effect and its interpretation for the spectroscopy of molecular structure"
R. Ladenburg, "Allowed and forbidden quantum transitions"
C. Ramsauer, "Cross section and molecular structure"
W. Heitler, "On quantum theory of homopolar bonding"
E. Hückel, "On quantum theory of the double bond and their stereochemical behavior"

In contrast to the Faraday Society meeting there were few foreign scientists. However, the list of the lectures clearly shows activity of German scientists on experimental and theoretical issues on molecular spectra and molecular structure. Mulliken was the only scientist from the United States in the list, and his friendship with Hund is well known as two founders of molecular orbital theory and they met in Leipzig where Hund was full professor of theoretical physics from 1929. Heisenberg already became full professor of theoretical physics in 1927 and in the same year Debye moved from Zurich as full professor of experimental physics. They attracted young scientists from all over the world and Leipzig was emerging as a new center of quantum physics. Heisenberg himself had once worked on problems on polyatomic molecules when he was in Göttingen but he seemed to have lost interest on molecular problem. However, his students and visiting scientists like Teller, Placzek, Tisza, Fujioka worked on molecular spectra.

Debye was already an eminent professor in experimental physics when he moved to Leipzig and many young scientists came to his laboratory including Hückel and Mizushima. He organized a series of "Leipzig lecture" from 1928 and they were soon published as monographs. The lecture in 1931 published as an English translation "The Structure of Molecules" included following contributions.

K. L. Wolf, "Problems of free rotation about single and double carbon bonds"
R. Mecke, "Experimental results obtained from band spectroscopy of polyatomic molecules"
F. Rasetti, "The Raman effect and the structure of molecules and crystals"
G. Placzek, "The Raman effect and molecular structure"
H. Sponer, "Band spectra and dissociation"
V. Henri, "The experimental basis of the theory of predissociation of molecules"
R. de L. Kronig, "On predissociation"
G. Herzberg, "Valency and the electronic structure of molecules"

After 1933 many scientists had to leave Germany, including Franck, Sponer and Herzberg among the above-mentioned Bunsen society and the Leipzig lecture on molecular structure. However, many other contributors remained in Germany and continued working on the molecular spectra and structure. In 1934, following lectures were given at the 39th general meeting of the Bunsen Gesellschaft on the theme "Mission of the physico-chemical research in organic chemistry."

E. Hertel, "Physico-chemical problems in organic chemistry"
H. Mark, "About the spatial image of organic molecules and molecular aggregates"
K. F. Bonhoeffer, "Photochemistry of simple organic compounds"
K. W. F. Kohlrausch, "Raman spectrum and organic chemistry"

27 Titles of the lecture series were Quantentheorie und chemie (1928), Dipolmoment und chemische Struktur (1929), Elektroninterferenzen (1930), Molekülstruktur (1931) and Magnetismus (1933).
29 Z. Elektrochem. 40, 405 (1934).
R. Mecke, "Spectroscopic structure determination of simple hydrocarbons and their derivatives"

Although the number of the lectures decreased from four years ago, and Hückel did not accept invitation, their contents indicate significant development of the methods and accumulation of the quantitative data on molecular structure. Mark summarized methods for determination of the molecular structure (X-ray and electron diffraction, permanent electric moment, polarization, vibrational spectra (infrared and Raman), specific heat) with their objects and available data in one table and compared their relative merits in another table. Long lists of typical bond lengths and valence bond angles followed in the paper, which included large number of data obtained by electron diffraction. The paper by Kohlrausch summarized his long series of papers on the Raman effect since 1929 showing alteration of the Raman spectra along homologous substitution in certain types of molecules. He wrote, although it is the first step of the detailed analysis, "The molecular spectrum is additively assembled from the spectra of the individual groups belonged to the molecule." As described also in the approach by Mecke on the infrared spectra, studies on the molecular structure by German scientists in this period made progress towards understanding of more complex molecules, rather than more detailed and complete analysis of simple molecules.

**Teller and Placzek**

Contributions of Teller and Placzek are particularly important for theoretical development of vibrational spectroscopy. Teller was born in Budapest and came to Germany to study chemistry in Karlsruhe. During this period he had chances to attend lectures on quantum theory by Mark from I. G. Farben and he determined to change his subject to physics. He first moved to Munich in 1928 but soon moved again to Leipzig. Heisenberg told him to study application of group theory on quantum mechanics by Wigner. Teller calculated excited states of hydrogen molecule ion for his dissertation and after completing this work he became an assistant of Heisenberg. In autumn of 1930 he studied the problem of the rotational constants of methane and methyl halides with his Hungarian friend Tisza. He knew about this problem while he was in Karlsruhe from Mecke's work. Teller believed that the tetrahedral carbon should be retained in the solution of this problem. They found that an angular momentum arising from superposition of two degenerate vibrations perpendicular to the symmetry axis couples with molecular rotation to alter the moment of inertia. Thus the riddle of the two different rotational constants of methane was solved and the tetrahedral carbon model was credited with another experimental evidence.

Placzek was born in Brno and studied physics in Wien. Then he moved to Utrecht as a postdoc of Kramers who was famous for his dispersion theory and began to study the Raman effect. He derived the selection rule of the Raman lines and pointed out that molecular vibrations which affect polarizability are Raman active. This selection rule is different from the infrared spectra and in highly symmetric molecules they are mutually exclusive.

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31 H. Mark, Z. Elektrochem. 40, 413 (1934).
In 1930 Teller moved Göttingen as an assistant of Eucken and collaborated with Franck and Herzberg on electronic spectra of polyatomic molecules.\textsuperscript{36} Placzek also moved from Leipzig to Göttingen and they worked together on the theory of rotational line intensity of the Raman spectra. While this collaboration yielded a beautiful result, Teller recalls their relationship:\textsuperscript{37}

"I began my collaboration with Placzek with enthusiasm, but as it turned out, our joint effort was one of the few times I did not enjoy a friendship with a collaborator. Placzek treated me to a large dose of derision, most of it trivial; for instance, he called me "Herr Molekular-Inspektor". The inference was that such a pursuit was a lower-class activity. As far as I was concerned, what happened in physics between 1920 and 1933 was so magnificent that it was a privilege to work even on minor details, and I thought it perfectly grand to be recognized even in an unglamorous field. I had made that decision in all consciousness, and I was content to remain Herr Molekular Inspektor."

Before completion of their collaborative work Placzek left to Fermi's group in Rome and worked on the Raman spectra of gases.\textsuperscript{38} He wrote a monograph on the Raman effect in \textit{Handbuch der Radiologie} which was published after he moved to Copenhagen and this became a standard textbook.\textsuperscript{39} Teller also moved to Copenhagen when he had to leave Germany. Both of them finally settled in the United States and their wartime efforts are already well known. While after publishing the monograph Placzek changed subject to other scattering phenomena such as neutron, Teller continued working for a while on molecular spectra as still well known by the effects with his name (Herzberg-, Renner-, Jahn-Teller) and the review article on electronic spectra with Sponer as a good collaborator.\textsuperscript{40}

\textbf{Mecke}

The most active scientist in vibrational spectroscopy during this period in Germany was definitely Mecke.\textsuperscript{41} After having studied the band spectra of diatomic molecules he started to measure electronic spectra of polyatomic molecules in late 1920s, which were found to be too complicated for detailed analysis. Then he shifted the target to measure overtone and combination vibrational bands of simple polyatomic molecules by using the newly developed plates for infrared photography. Although absorption coefficients of the overtone and combination bands were much weaker than those of the fundamental bands, photographic detection was more sensitive than the bolometers for infrared detection and it could deserve the merit of the larger spectrograph for higher resolution.

The first report appeared in the general discussion of The Faraday Society in 1929.\textsuperscript{42} He showed the spectrum of ammonia which corresponds to the third overtone of the NH stretching mode observed at 3 micron. Due to higher resolution he could determine the moment of inertia of ammonia as a symmetric top and consequently determined its pyramidal equilibrium geometry. Combination bands were assigned based on their position and the shape. Comparison was made for vibrational frequencies and bond lengths of a series of simple hydrides (CH\textsubscript{4}, NH\textsubscript{3}, H\textsubscript{2}O, HF) with their corresponding diatomic hydrides (CH, NH,

\begin{thebibliography}{99}
\bibitem{37} Teller and Shooolery (note 33).
\bibitem{39} G. Placzek, \textit{Rayleigh-Streuung und Raman-Effekt (Handbuch der Radiologie; Bd. 6, T. 2 (2. Aufl.))}, Akademische Verlagsgesellschaft (1934).
\bibitem{40} H. Sponer, E. Teller, \textit{Rev. Mod. Phys.} \textbf{13}, 75 (1941).
\end{thebibliography}
OH, HF). This indicates that he already tried to interpret natural frequencies of polyatomic molecules from experimental data of diatomic molecules which he was very familiar.

The most successful results were obtained for acetylene as three papers in 1930.\textsuperscript{43} Although acetylene contains four atoms it is a highly symmetric rod like molecule and it was possible to determine its moment of inertia. By assuming the same CH bond length as that of CH, the length of the CC triple bond was determined. Rotational lines showed intensity alteration of approximately 3:1 and this was due to nuclear spin states of two hydrogen having S=1/2. After consolidating a linear symmetric structure of acetylene, he showed in the third paper that the natural frequencies of linear tri- and tetraatomic molecules could be interpreted as n-1 stretching modes and n-2 doubly degenerate deformation modes. This distinction of the valence and the deformation vibrations was extended to the case of ethylene to successfully assign its natural frequencies.

In his presentation in the Leipzig Lecture in 1931 he calculated binding constants of polyatomic molecules by assigning the observed vibrational frequency to a certain bond of the molecule.\textsuperscript{44} In this treatment he assumed that the potential function is quadratic to the bond displacement and angle deformation with force constants $k$ and $b$, respectively, and the vibrational frequencies are expressed as functions of these force constants as well as bond lengths. Actually $k$ was estimated to be ten times larger than $b$ and by expanding the vibrational frequency as a power series of $b/k$ the frequencies of the stretching and the bending modes can be approximately obtained with $k$ and $b$ only, respectively. Calculated binding constants along a series of molecules were surprisingly constant, indicating that they may be retained even in more complicated compounds. Then he derived figures of atomic displacements in vibrational modes of polyatomic molecules up to five atoms (tetrahedron) and assigned measured natural frequencies of some representative molecules of each type.

In 1932 he further extended the concept of the separation of valence and deformation vibrations in a series of papers.\textsuperscript{45} He added the Coulombic interaction terms between bond dipoles to the potential function of the elastic terms and estimated their constants from measured vibrational frequencies of simple polyatomic molecules up to six atoms. For example, in the case of triatomic molecules such interaction was found to be much smaller than the elastic term in the case of linear molecules like CO$_2$, whereas the dipolar interaction had stabilization effect in the case of hydrides like H$_2$O and their magnitude was fairly large.

Although he made great success in the detailed analysis of rovibrational spectra of simple polyatomic molecules in the gas phase, the method is limited to small molecules as the rotational lines are not resolved even in the overtone and combination bands for larger molecules and completely absent in the liquid phase. However it was possible to discuss the position and shape of these near-infrared bands and he focused on the overtone bands of the CH stretching modes to study the effect of the neighboring group or resonance effect on their position and intensity, which are expected to be enhanced in the overtone compared to the fundamental bands.\textsuperscript{46} The overtone bands of CH stretching mode were largely altered by the bond order (single, double or triple) of the carbon atom on which the CH unit is attached. Intensity of the CH overtone band of halogen-substituted alkanes was approximately proportional to the number of hydrogen atoms but the changes in the band position and their shape were did not allow simple interpretation. He developed his theory of interacting local valence vibrations for perturbative calculation of anharmonic vibrational frequencies and

\textsuperscript{43} K. Hedfed, R. Mecke, Z. Physik 64, 151; W. H. J. Childs, R. Mecke, 64, 162; R. Mecke, 64, 173 (1930).
\textsuperscript{44} Mecke (note 28).
\textsuperscript{45} R. Mecke, Z. Phys. Chem. B16, 409; 421; B17, 1 (1932).
\textsuperscript{46} R. Mecke, Angew. Chem. 48, 320 (1935).
absorption intensity of the overtone bands and estimated bond dipole from the observed band intensity.\textsuperscript{47} He also developed a general scheme for polyatomic molecules containing the same atomic groups such as hydrocarbons by second order perturbation theory and derived equations of coupling constants.\textsuperscript{48} However, its practical application seems to be unpublished. Anyway, they were developed mostly within the harmonic approximation and did not go into treatment of vibration-rotation interaction or other higher order interactions as developed by theorists in the United States.

\textbf{Conclusion}

In this study I tried to describe the development of vibrational spectroscopy in Germany in 1930s. Although it is less known than the development in the United States, German scientists were active in this field in early 30s and their achievements were characterised by their efforts towards systematic understanding of the more complex organic molecules. Following studies are expected to clarify the relevance of these characteristics to the emergence of molecular science in Japan in 1930s as represented by the research by Mizushima and his coworkers on the rotational isomerism.

\textsuperscript{48} R. Mecke, Z. Physik \textbf{104}, 291 (1936).