Gerhard Herzberg and CH_2: A Personal Tribute to a Great Scientist and a Dear Friend

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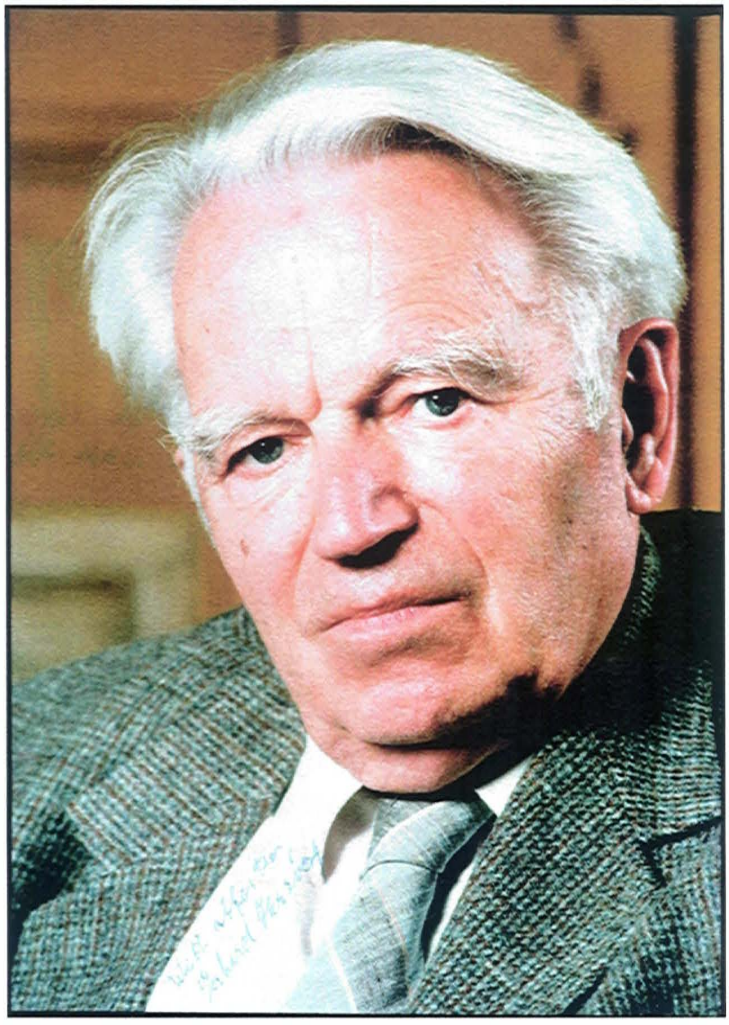
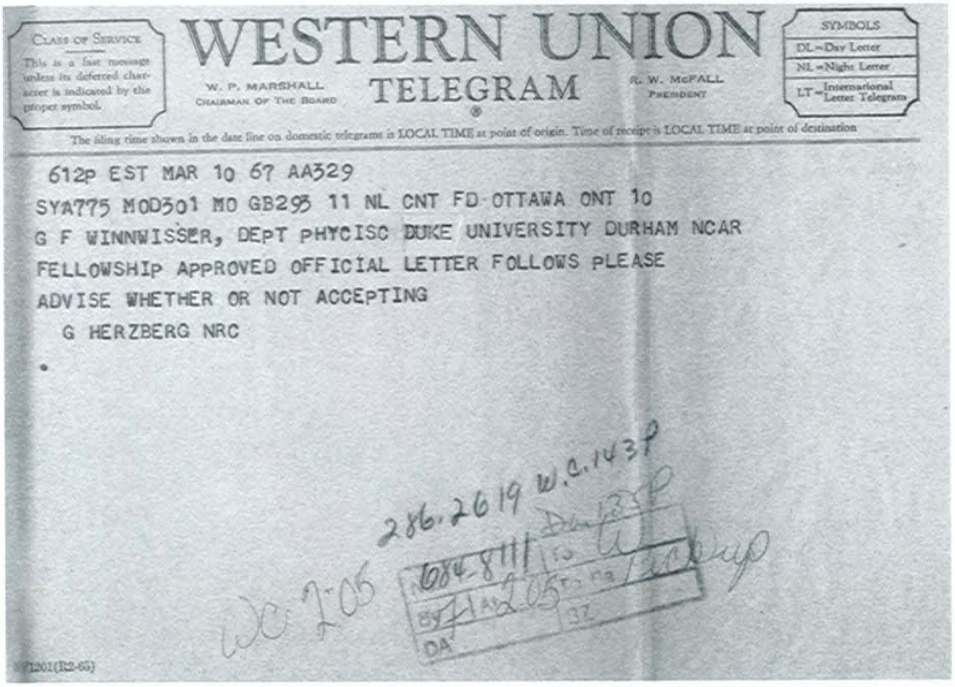


G.H. (December, 25th, 1904 - March, 3rd, 1999)
Nobelprize in Chemistry 1971

Gerhard Herzberg was an incredibly well-organized man who spent every hour - from early morning to late evening - on his beloved subject: Molecular Spectroscopy. Dr. Herzberg was affectionately known amongst the inner circle at the National Research Council (NRC, in Ottawa, Ontario, Canada)

as "G.H." This polite, generous, affectionate, and always modest researcher was born on December 25th, 1904, so the coming year will bring the 100th anniversary of his birthday. G.H. led a rich scientific life during which he freely shared his deep understanding of spectroscopy and set global standards in his field. We will always remember him for his three superbly written textbooks on molecular spectroscopy; this was a tremendously arduous and creative undertaking that still serves to shape and lead our current understanding. These texts, along with his many other scientific and technical contributions, have become an important part of the basic knowledge of mankind [2]. This truly great scientist passed away in Ottawa on March 3, 1999, in his 95th year.



WESTERN UNION

TELEGRAM

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G F WINNWISSER, DEPT PHYCISC DUKE UNIVERSITY DURHAM NCAR
FELLOWSHIP APPROVED OFFICIAL LETTER FOLLOWS PLEASE
ADVISE WHETHER OR NOT ACCEPTING
G HERZBERG NRC

Fig. 1. Telegram from G.H.

We at the University of Cologne were, needless to say, quite proud to welcome G.H. as our very first visitor on the Gornergrat; he was the first to inspect our newly installed 3-meter submillimeter-wave telescope. The Gornergrat is located in the central Swiss Alps, a mere 7 kilometers from the world's most famous alpine peak - the Matterhorn, at 4478 meters - and snuggled against the second highest mountain in the Alps - Monte Rosa, at 4634 meters. In honour of G.H.'s 100th birthday, we have dedicated the Astrochemistry Session of the 4th Cologne-Bonn-Zermatt Symposium to him. This short, personal contribution on G.H. resulted from suggestions made to me by the chairman, Prof. P. Thaddeus, and also by Prof. W. Klemperer. It is most fitting to commemorate G.H.'s birthday here, and it is also fitting that Volume IV of the Symposium Proceedings will appear in 2004, just in time for the 100th anniversary of his birth.

My connection with Prof. Herzberg began with my receipt, on March 10th, 1967, of a telegram (shown in Fig. 1) that read something like this: "Fellowship approved. Official letter follows. Please advise whether or not accepting. G. Herzberg, NRC." This was somewhat of a surprise for me, since I had not applied for any positions at the NRC! However, shortly before receiving the telegram, I had met Takeshi Oka during his visit with Prof. Walter Gordy at Duke University (Durham, NC, USA), and it was through this brief encounter that I received my opportunity to work with one of the world's greatest scientists and his team. [1]

Shortly after arriving in Ottawa and taking up my fellowship, I participated in my first weekly meeting of the NRC spectroscopy group. In these meetings, experimental and theoretical results were reported and scrutinized. That first group meeting ended in another surprise for me - a surprise I will never forget. Gerhard Herzberg spoke that day, as well, and presented some portions of the texts he was at that time preparing for publication. Imagine my shock when Dr. Alex Douglas suggested that the great man make several

[1] There, at the Physics Department of Duke University, Durham, NC, USA, Takeshi and myself met. I was just engaged in trying to find a simple way to display the impressive ${}^{r}Q_0$ and the ${}^{r}Q_1$ branch of HSSH, located at 139.9 GHz and 420 GHz, respectively. I was duely impressed, how fast Takeshi understood the issue and problematic of this particular molecule. That afternoon he asked me whether I would be interested to join the spectroscopy group at NRC and I agreed. Prof. Walter Gordy supported that idea whole-heartedly by telling me that I am now on the "professional lane" of spectroscopy. - Late that year, I arrived in Ottawa and I became an accepted member of the world-famous spectroscopy group of G.H. in the Division of Pure Physics of NRC. The Herzberg spectroscopy group was subdivided into various smaller units and I worked with Dr. Cec Costain and Dr. Takeshi Oka. I shared the"smallest office" in town - without a window or fresh air intake - with a Japanese couple from Tokio, Tadao and Fumiko Shimizu. In fact, the office was so small, that always one of us had to get up, so the door could be opened and the exchange of one person at a time could take place, ... but we had tremendous fun with each other ... up to the present day.

Prof. Dr. Takeshi Oka on the other hand recollects that visit in Dr. Gordy's laboratory: "It was in March 1966 when I saw you for the first time. There was an American Physical Society meetig in Durham from March 28-31, 1966 and I was an invited speaker to a symposium titled "New Techniques in Spectroscopy". Other speakers were Bill Dalby (UBC), Egerhardt (Georgia Tech); Peter Franken, Bill Klemperer, Madden (NBS), George Pimentel, David Rank, Harold Welsh, and Bill Weltner. I talked with a title "Microwave-Optical Double Resonance". That was my first invited talk in a major conference and I have a printed manuscript of my talk. I visited Gordy's lab after the symposium, very likely on the 31st. I saw you there and was fascinated by the beautiful H_2S_2 spectrum.

And he adds to it concerning the famous Herzberg telegram: "Curiously there is no exchange of letter about your application to NRC. So your recollection of "not applied for any position at the NRC" may be correct. I accepted the fellowship and it was very good, even so we can not trace, who initiated the invitation! It just happened.

revisions to them! However, I soon learned that G.H. insisted on this sort of honest scientific exchange, and expected everyone in the group - himself included- to accept, apply, and appreciate others' opinions. This experience also brought home the fact that I would have to use all my energy, experience, and intuition to compete at this high intellectual level. And there were more surprises to come.....

The NRC is a government agency, so all of us were required to sign in when working over the weekend. The second Saturday after my arrival in Ottawa I went to the lab, at 100 Sussex Drive, at about 9 AM. There I found, to my great surprise, that one "Dr. G. Herzberg" had been the first to sign in that day, at 7.57 AM. My curiosity was aroused, so on the next Saturday I went again to 100 Sussex Drive, at nearly the same time, only to find the G.H. had signed in 8.01 AM. At this point I suspected what became very clear to me over the next few months: G.H. was always in his office at 100 Sussex Drive at 8.00 AM, the only exceptions being those days when he was out of town. Even the harsh Canadian winters failed to alter his schedule and keep him from arriving punctually at the laboratory.

It came as no surprise, then, when sometime later Gerhard said about his texts that

"...it really took a long long time. I have estimated that per printed page, I spent a full working day, at a time when I was still working hard. I mean, now I can't say if I have a full working day because of interruptions. I am too old for working hard. But I worked really hard, and if you think of the number of pages that there are, some 2000 pages, 2000 full working days, that's a lot of time of one's life. ...but I am not a person who writes easily!"

(The above is an excerpt from an interview [3] conducted by my sister-in-law, Dr. Brenda P. Winnewisser, as part of a program conducted by the Center for the History of Physics, American Institute of Physics, in Washington, DC, USA.)

G.H. was always very modest, even when he was awarded the Nobel Prize in Chemistry in 1971 "for his contributions to the knowledge of electronic structure and geometry of molecules, particularly free radicals." The Nobel jury must have had CH_2 in mind. According to G.H.'s Nobel lecture, he had spent more than 20 years determining the nature of the electronic states of this difficult radical; he was finally able to show, beyond a shadow of a doubt [4, 5], that its lowest electronic configuration is a ^3B state, and that this configuration is followed closely above by a ^1A state (Figure 2).

Upon his return from Stockholm, as we picked him up at the Ottawa airport, I asked G.H. how he felt about receiving the Nobel Prize. After a short pause he answered, "I feel that my scientific life has been rewarding beyond anything that I deserve." The award did not change him at all; he remained, in his modest way, the world's foremost molecular spectroscopist and the leader in a research field of fundamental importance. His attitude to scientific work is best summarized by the following verse; it is written in

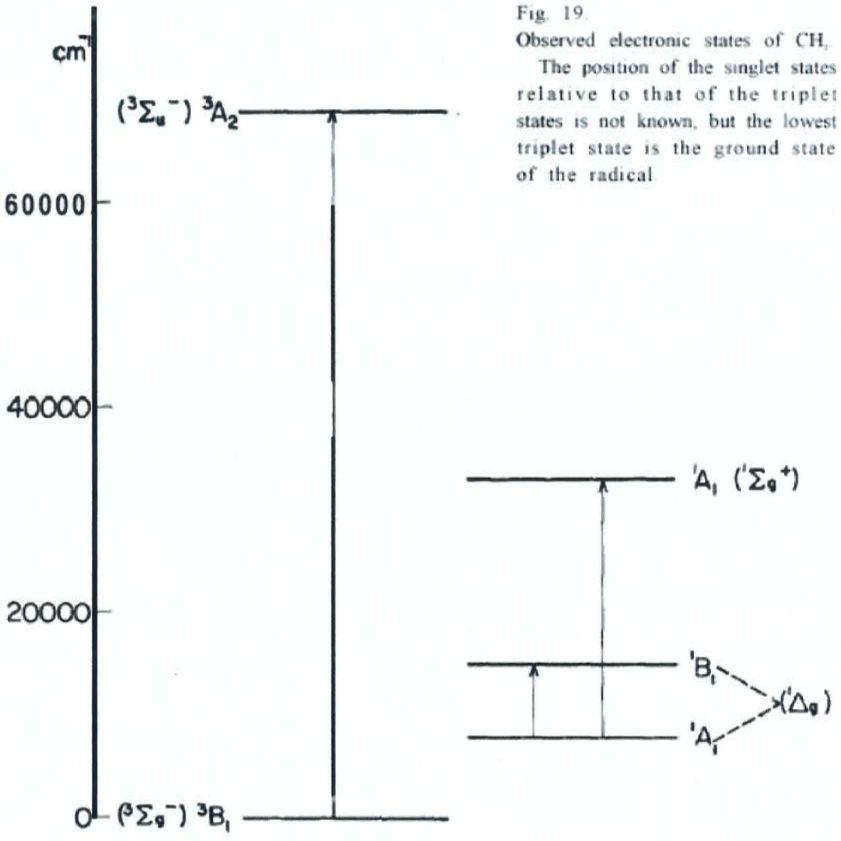

Fig. 19
Observed electronic states of CH_2. The position of the singlet states relative to that of the triplet states is not known, but the lowest triplet state is the ground state of the radical

Fig. 2. Observed electronic states of CH_2. The electronic ground state is labeled $^3B_1$ (G.H., Nobel Lecture, 1971).

stone over an archway at Cambridge University, and which I copied down as a young student:

Use every hour for time goes fast,
And what is now may soon be past,
A future time may never be,
The present is the time for thee!

As the reader might imagine, I was both flattered and nervous when this great man - the recipient of so many accolades and even a Nobel Prize! - asked me to try to measure one or two rotational transitions of CH_2. I had recently constructed a submillimeter-wave spectrometer for the NRC, and its sensitivity was comparable to other spectrometers of its day. With hindsight, and particularly in light of some recent measurements made with the terahertz spectrometer in Cologne with magnetic modulation. From this it is clear that we had no chance to detect the weak transitions of CH_2 in those early days. I regretfully declined then to make the attempt; his requests for CH_2 microwave data were, like the man himself, simply 25 years ahead of their time. Gerhard,

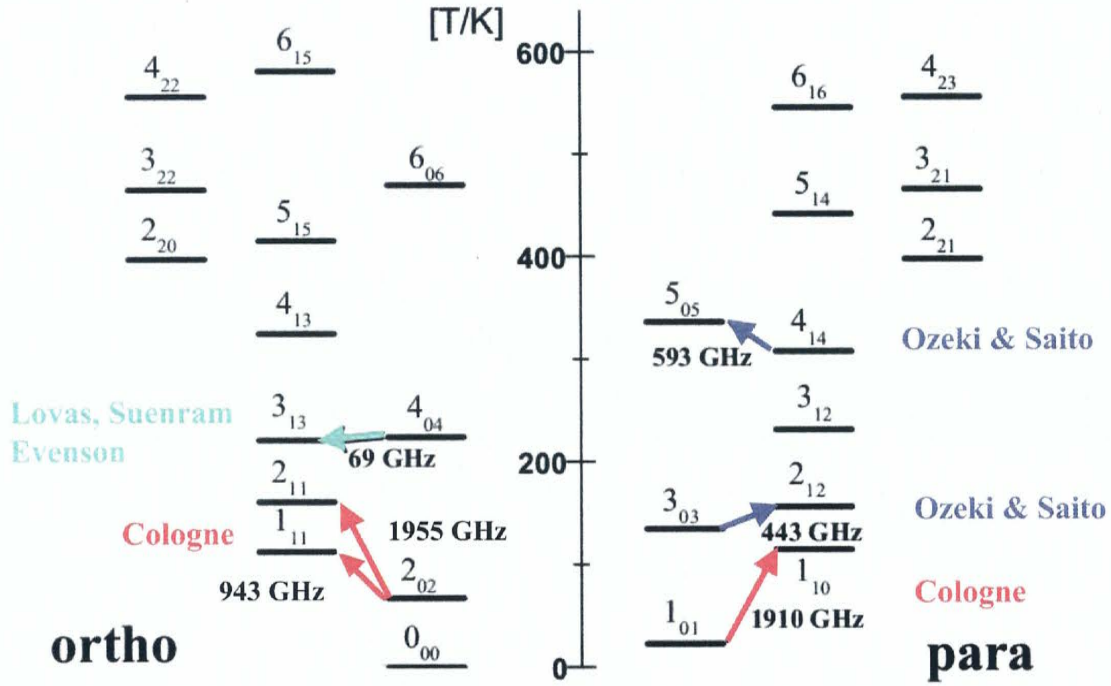

Fig. 3. Part of the pure rotational energy levels divided into ortho- and para-form and sorted for the $^3B_1$ electronic ground state of CH_2. All observed rotational transitions are indicated. The transition at 69 GHz has been seen in the interstellar medium, in Orion [6]. The fine and hyperfine structure of the pure rotational levels is not indicated.

we are sorry for being so late in recording the first high-resolution transitions-but we had to build the Terahertz apparatus first!

Gerhard said in his Nobel lecture "... of course the spectrum of CH_2 has given me a great deal of pleasure ...". His first attempts to savour it date back to 1942, and the story of its discovery is long and difficult. The methylene radical was first observed in electronic spectra covering the UV and the visible region [4, 5]. In the early eighties there was strong push within the spectroscopy group at the NRC (led by P.R. Bunker and A.R.W. McKellar and with a strong involvement of T.J. Sears and P. Jensen, see e.g. [7]) to detect the infrared spectrum of CH_2. These are the vibration-rotation transitions of the radical in its $^3B_1$ electronic ground state. After much hard work, the ν_2 bending vibration was finally detected using laser magnetic resonance in the range 880 to 940 cm^{-1}. The presently best numerical value for the ν_2 of CH_2 is 963 cm^{-1}.

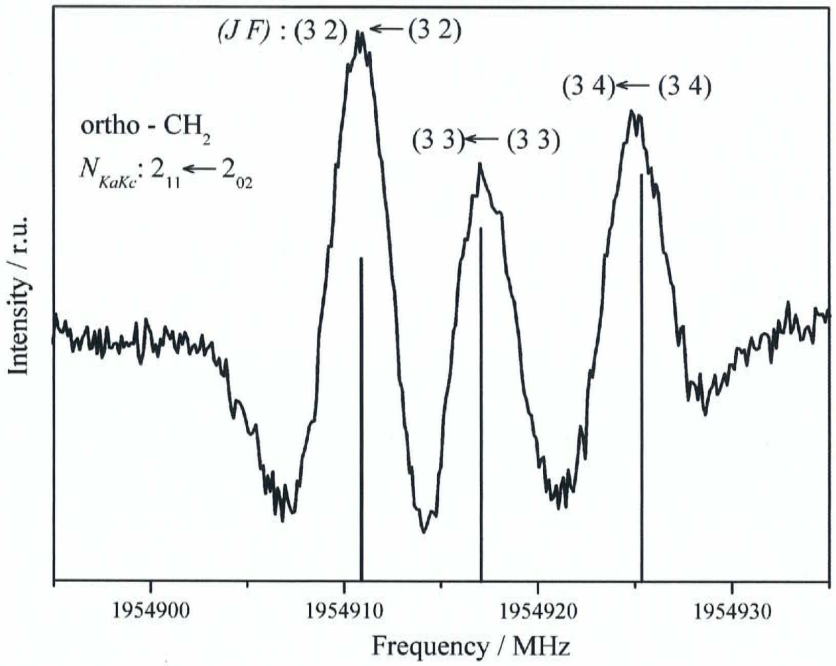

Fig. 4. The $2_{11} - 2_{02}$ rotational transition of ortho-CH_2 at 1.9 THz obtained with the Cologne Terahertz spectrometer. The observed splitting of the pure rotational transition into many components (about 30) the strongest triplet of which is shown. The splitting is caused by fine- and hyperfine interaction.

However, little information regarding the pure rotational spectrum had been gleaned in the laboratory; in fact, only three transitions [6, 8] below 450 GHz have ever been measured. We have recently measured three additional transitions in Cologne with our Terahertz - and Laser Sideband-Spectrometers, and plan to extend these measurements in the near future, perhaps to frequencies as high as 5 THz.

In the electronic energy level scheme of CH_2 established by G.H., the X^3B_1 electronic ground state rotational energy levels are sorted into ortho- and para- forms of CH_2 (Figure 3). We have indicated in Figure 3 the six pure rotational transitions that are presently known [6, 8, 9, 10]; the transitions falling between 1 and 2 THz are those recently measured in Cologne, i.e. the ortho transition $2_{11} - 2_{01}$ and the para transition $1_{10} - 1_{01}$. One of these is shown in detail in Figure 4, which reveals, for the first time, the beautiful, fully resolved fine and hyperfine structures. The entire Cologne Spectroscopy Group presents this bouquet of transitions as a belated 100th birthday present to Gerhard Herzberg.

Improvements in sensitivity gained in the performance of these measurements have put us in a position to search for many more transitions of CH_2 and other light radicals. These laboratory results will be useful in attempts to

measure interstellar CH_2, though its astronomical detection clearly calls for space-borne observations with instrumentation such as that aboard SOFIA or Herschel. These prospects offer further, even greater, challenges for our young astronomers and spectroscopists.

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