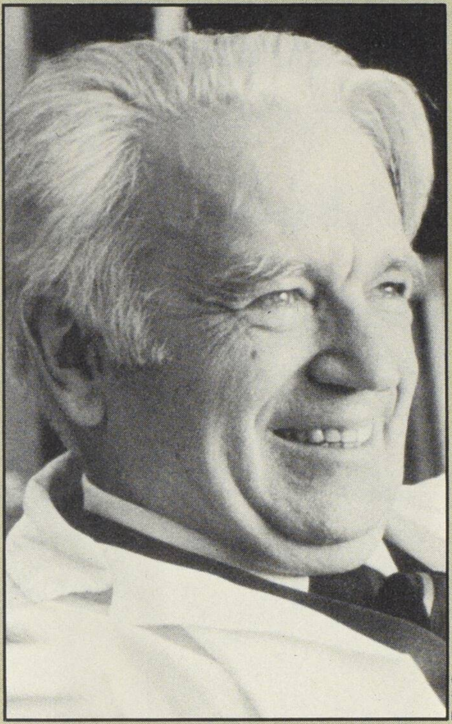
Gerhard Herzberg-Work In Progress

Spectroscopists — scientists who study photons emitted and absorbed by matter — have a special kind of patience. Working in darkened laboratories, they shine light through samples of matter to derive absorption spectra, and subject other samples to high-voltage electrical discharges to produce spectra of emission.

Gerhard Herzberg (b.1904) was already a distinguished spectroscopist when he left Nazi Germany in 1935 and came to Canada. In the half-century since then, he has fulfilled a brilliant promise with a career that includes the Nobel Prize in Chemistry.

What won Herzberg the Nobel? "For a chemical reaction to occur," reads his 1971 Prize citation, "molecules must break up into fragments which rearrange to form new molecules. These fragments, called 'free radicals,' are very difficult to study, as their lifetimes are measured in millionths of a second." Despite these difficulties, Herzberg devised a series of classic experiments which opened up free radicals to scrutiny for the first time.

Even for a spectroscopist, Gerhard Herzberg has patience — his successful search for the free radical methylene, for instance, took fourteen years. But Canada's only living Nobel laureate still does not consider his work complete: Herzberg keeps regular hours at his Ottawa laboratories in the NRC Institute now named for him. Last October, Science Dimension *interviewed him there.*



Ted Grant

Science Dimension: Rather than review your previous work, let's discuss what you've done since 1971, and what you still hope to do.

Herzberg: Well, since I won the Prize my time has been somewhat limited because of interviews like these! But in 1979, I did discover a spectrum of triatomic hydrogen. It was pure serendipity; anyone could have seen it fifty years ago.

Our group had been looking for the emission spectrum of *ionized* triatomic hydrogen, H_3+, a system comprising two electrons and three protons. We never found H_3+, but we did discover instead H_3 *neutral* — *three* electrons and three protons. That one extra electron doesn't sound like a great change, but it produces a markedly different series of emission lines.

Science Dimension: If the neutral H_3 spectrum could have been seen fifty years ago, why wasn't it found until 1979?

Herzberg: Nobody looked for it. Workers in this field, myself included, were convinced that H_3 neutral could not exist. I myself thought a lot about the ion, H_3+, but I never considered the system with an additional electron, because everyone working with hydrogen knew that system was unstable! And so it is, in the 'ground state' — when it's unexcited. Then it's just a hydrogen atom, H, and a hydrogen molecule, H_2, which have no attraction for one another. What wasn't apparent until 1979, when we obtained this new spectrum, was that under certain conditions, you *can* have H_3 neutral. The trick is to add energy to either the H or the H_2 before you bring them together. Then they attract one another very well.

But we didn't know this at first: all we had was an emission spectrum that we knew wasn't H_3+, or anything else we were familiar with for that matter. It was a typical scientific detective story. I kept the spectrum here on my desk, on a viewer, and now and then I looked at it and said, "Well, is it an artifact?" In other words, is it a real spectrum, or merely an illusion produced by our experimental technique? Then, one morning in January 1979, it suddenly occurred to me what it was.

Science Dimension: Just like that?

Herzberg: It's very difficult to describe this sort of thing: after months of puzzlement, it took me only a few minutes to realize what was going on. First I recalled certain predictions that had been made in the literature about H_3+, the ion. It was supposed to be an equilateral triangle with a side length of about 0.87 angstroms; this, in turn, predicts a definite value for a molecular rotation constant known as the B-value. I remembered, that morning, that I could read the B-value of my mystery molecule right off its spectrum by using an ordinary ruler, and I did so. It proved to be in exactly the location predicted for H_3+, even though we knew for certain that this was not H_3+ we were looking at. So I thought: "What if the structure of this unknown molecule is very similar to the triangular structure of H_3+? That would explain the identical B-value."

Now, we had produced this unexplained spectrum under conditions where you can see the spectrum of ordinary hydrogen. What, then, if you might also get *neutral* triatomic hydrogen under these conditions? What, in other words, if H and H_2 could attain states in which they did *not* repel? To accomplish this, the extra electron that converts H_3+ to a neutral molecule would have to be sufficiently far from the three central protons of the molecule so as not to disturb their spatial relationship. It would have to be, in other words, what is called a Rydberg electron: occupying an excited state, an outer orbital.

At this point, everything just dropped into place. It all fitted that H_3 is stable in 'Rydberg states', where one electron is removed from the core of the molecule. And so I con-

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