

Solitons, From Below

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It was 3:15 A.M. on a cold night in Urbana, Illinois about 25 years ago. I had been on my feet since the previous morning, preparing the experiment. Professor Enrico Gratton had instructed me to machine a brass piece to replace a window in the cryostat. I finished the piece on a lathe, drilled a hole in the center, soldered a 1/4-in. copper tube and sealed the end outside the cryostat with a copper cap. I bent the open end so that it was a couple of millimeters from a calcium fluoride window, taking care not to obstruct the infrared beam from the interferometer. I loaded some acetanilide powder in the copper tube—it would serve as a crude but effective oven. The first nervous test passed when my clumsy solder job actually held vacuum. The whole procedure had taken a long time because of my inexperience. When the cryostat was finally cold, I took a heat gun and gently warmed the tube on the outside. A few micrograms of the material sublimated and got deposited into an amorphous film on the cold window. Prof Gratton was looking at the emerging infrared spectrum as the film developed. There was the amide I band, near $1,667\text{ cm}^{-1}$, familiar from many past experiments on crystals. *But the soliton band at $1,650\text{ cm}^{-1}$ was missing.* That was it! We had confirmed Al Scott's interpretation of the anomalous infrared band in acetanilide. But even as we celebrated, I knew in my heart that we had just had doomed prospects for Scott–Davydov solitons in proteins. As a biological physicist in training, I would never really work on this wonderful problem again.

It was then, and still remains, beautiful physics. Years later, when my colleague Bob Austin attempted to lure me back to do some more experiments, I resisted. Along the way, I had the privilege of meeting brilliant physicists like Al Scott and mavericks like Giorgio Careri. My admiration remains for superb theorists like Denise Alexander, who deserves to be remembered for her memorable paper in a tragically short career. Peter Hamm's beautiful experiments provided not only confirmation but also greatly expanded on the original idea. For all that, the lesson learned on a cold Midwestern night was permanently

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etched in my heart: beautiful physics is sometimes irrelevant to biology. My advisor, Prof Hans Frauenfelder, had taught me that.

My interaction with Al Scott and his ideas on the Davydov soliton started with Enrico Gratton, who was a superbly gifted mentor to me. I was a beginning graduate student, struggling with all aspects of physics. Prof Gratton came to my desk and showed me some papers with complicated mathematics—papers from Al Scott and Davydov among others. *You are Indian, you must be good at mathematics*. Clearly, Professor Gratton had forgotten the oral examination in which he asked me to derive Ohm's law from first principles. I had struggled mightily, butchering the expression for the drift velocity. And that was a *linear* problem! He had nevertheless passed me in an act of grace and kindness. But he needed an assistant in infrared spectroscopy. I had just learned how to take an infrared spectrum without breaking too many expensive CaF₂ windows. So, Ohm's law or not, I got the job. A clumsy experimentalist with indifferent mathematical skills—that was my rather unpromising entry into the heady world of self-trapped states. I began to learn about the great problem in energy transfer that Davydov had set out to solve. I read Scott's infrared-active extension of the audacious proposal for a particular type of a soliton. And Enrico taught me about Giorgio Careri's ideas on acetanilide as a model system. We started a systematic series of experiments to test whether Careri's work could be married to Scott's innovation. First, we repeated earlier cryogenic studies on acetanilide in pressed KBr pellets. The temperature data could be reasonably well fit with Scott's model. But the amide peaks were evidently being distorted in the KBr pellets. So I learned from Professor Dana Dlott how to zone refine the material, how to grow crystals large enough to study high harmonics, and how to deuterate the samples. I learned how to grow extremely large crystals for high harmonic studies and how to grow extremely thin single crystals for polarization studies. One particular experiment stands out in my mind. I had mounted a thin $\sim 1 \mu\text{m}$ ACN crystal on a cryostat using an Al foil as holder. As I cooled the sample below 77 K, the all important soliton band grew as predicted by Scott. But when I cooled to 10 K, all of a sudden, the peak disappeared and I got a 300 K spectrum. It took a few anxious moments to realize what had happened: the crystal had separated slightly from the Al foil, which was in fact at 10 K. The infrared beam from spectrometer had then heated the thermally insulated thin crystal all the way to near room temperature. More careful mounting of the crystal solved this problem. Single crystal studies allowed us to make polarization measurements, providing further support to Scott's interpretation. Eventually, the studies led up to one final prediction of the Scott model: the soliton band should disappear in the amorphous phase. That led to the memorable later night experiment on amorphous ACN. We published a number of papers on our results. I am proud to say that our experimental results have held up robustly. Over the years, the model has been criticized on theoretical grounds and alternative interpretations proposed. Scientists far more qualified than I will talk about this work elsewhere in this issue. For me, the most appealing interpretation came from a brilliant young theory graduate student at Cornell, Denise Alexander. She had been working with Jim Krumhansl's group and had learnt from that great master to be as comfortable with nonlinear phenomena as I had been intimidated by them. She proposed a remarkable model that was inspired by the Holstein small polaron, but with the role of the electrons played by the optical phonon coupled to a bath of acoustic phonons. It fit our data well. Denise was sufficiently enthused by her success that she decided to switch to biological physics. Tragically, she was killed in a car accident in New York City where she had moved for post-doctoral research—a huge loss to the field. Someone at the time remarked that singularly bad luck seemed to pursue all the great theorists working in the field. I think she would

have been very happy with Peter Hamm's ultrafast studies, and her insights would have been invaluable.

How can I best explain my mixed emotions on that Illinois night? Our experiments showed me that solitons as proposed were simply too delicate to survive in biology. Prof Frauenfelder taught us that proteins in fact existed in a great number of conformational substates. Even proteins with apparently well-defined crystal structures were in fact dynamic entities, with fluctuations that revealed themselves in the Debye–Waller factor and in non-exponential binding kinetics. A universal scheme for transferring energy in biological processes needs to be robust because of the messy and arbitrary nature of fluctuations and mutations. A delicate phenomenon that needed a precise and subtle crystal structure simply could not survive the rigors of evolution. That was what our experiment on a cold night in Illinois showed. I believe that the concept of self-trapped states in proteins is strong and has plenty of experimental and theoretical support. But the self-trapped states are not the solitons as envisioned in acetanilide. Bob Austin's article in this volume makes the case rather convincing. Over the years, I have admired Al Scott and his brilliant insights. He was remarkably generous with his time and continued to maintain his amazingly positive outlook even after his debilitating accident. He will remain a bright light in my memory, and a model scientist. I am grateful for the opportunity of having met him and of doing experiments inspired by him.