CHEMILUMINESCENT FINGERPRINTS, CROSSED BEAMS AND THE CHEMICAL LASER

In their early experiments Polanyi and Cashion obtained indications that reactions might give rise to 'population inversion', in which more of the products would be present in high states of excitation than low ones. Light passed through such a medium will be amplified. 'We realised that you could actually get lasing action by extraordinarily simple means: you could just heat a gas and then quickly cool it. The first thing to cool is rotation. You would be left with a gas that was vibrationally hotter than it was rotationally hot. Under these conditions you don't need an overall population inversion to get lasing, you can get inversion relative to a particular emitting transition — "partial population inversion" as we called it'.

This was around 1960, before the first working electronic laser had appeared. 'This sort of lasing is very easy to get. We used to get it accidentally: when we traced our spectra there would be spikes that irritated us — these were lasing action!' It was not until 1965 that George Pimentel and J. V. V. Kasper demonstrated the first chemical laser.

Meanwhile, Polanyi and his collaborators were wrestling with their spectra, trying to make sense of their findings. 'The question was how to communicate them to people. It wasn't much good handing them a table of the vibrational, rotational and translational energy distributions in the products, because they were quite difficult to grasp. So we had to think of some way of exhibiting them'. What emerged were triangle plots with contours of 'equal detailed rate constants' for specified states within the reaction. These give graphic 'fingerprints' of given reactions. In order to interpret these experimental fingerprints the equations of motion for all the particles involved, moving in three dimensions, had to be solved and understood: 'this part was very hard work — nature was very begrudging and seldom offered us anything as a gift. Eventually we groped our way from these plodding descriptions of the physics to a broader degree of understanding of the choreography of chemical reaction'.

In parallel with Polanyi's group using infrared emission spectroscopy, Herschbach and Lee at Berkeley and Harvard were using crossed molecular beams to answer the same sort of questions. While spectroscopy measures vibrational and rotational motion, from which the speed of the particles can be calculated, Herschbach and Lee's method measures the angle and speed of the products directly, from which vibratational motion can be inferred.

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CHANGE OF AUTHORSHIP

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