Richard P. Van Duyne (1945–2019)

Professor Richard P. Van Duyne was the discoverer of surface-enhanced Raman spectroscopy (SERS), a widely used experimental method for detecting and sensing molecules. The technique was the first of the many surface-enhanced spectroscopies that are now routinely used in physics, chemistry and biology. Van Duyne's research and leadership also provided an early focal point for the transition of new technologies and methodologies in nanoscience — such as scanning probe microscopy, electron microscopy, chemical functionalization of nanoparticles, ultrafast optical spectroscopy, computational electromagnetics and electronic structure calculations — into practical applications. His impact in science greatly transcends the content of his papers.

Van Duyne was an inspiration to a generation of scientists who are now active in the field of surface-enhanced spectroscopy, and especially to many female former students and postdocs. I remember conversations with Van Duyne about his strategies for female postdocs to accommodate child rearing and laboratory research responsibilities such that they could remain productive; his ideas have been helpful to a number of colleagues.

Van Duyne was born on 28 October 1945 in Orange, NJ and died on 28 July 2019 in Wilmette, IL. His father was an engineer, and his grandfather was a chemist, so Rick (as he was known to his friends) was attracted to these fields. He went to Rensselaer Polytechnic Institute for his undergraduate degree in Chemistry, doing research with David Aikens in electrochemistry. Subsequently he did his PhD work at the University of North Carolina, where he studied electrode reaction kinetics with Charles N. Reilly. Van Duyne arrived at Northwestern University in 1971, where he quickly got involved in a combination of electrochemistry experiments and optical spectroscopy measurements using Raman spectroscopy.

Raman spectroscopy is an inelastic light scattering technique that provides a vibrational fingerprint of molecules. While the technique was studied since its original discovery in the 1920s, the intensities associated with this effect are so low that detecting monolayers of molecules on electrode surfaces was not considered feasible when Van Duyne started his work in the mid 1970s. It was therefore of great interest to Rick that he was able to generate high quality spectra of many molecules that were adsorbed onto roughened silver electrodes. There had been earlier related work by others who attributed the high intensities to the high surface area of these electrodes, but Van Duyne's careful work demonstrated the existence of an enhancement factor of 10^6 above the effect of increased surface area. On my first day at Northwestern University in 1976, Rick confessed to me that he was concerned with his discovery of SERS. He asked me to verify his enhancement calculations, which I did, and in the process I realized that there were significant opportunities for me to collaborate with him on SERS theory. It took many rejections before Van Duyne's first SERS paper was published in the Journal of Electroanalytical Chemistry in 1977. Fortunately, quick confirmation by other groups generated significant interest in the research community. Although the term SERS was not used in Van Duyne's first paper, he used it subsequently and this became the standard terminology for enhanced Raman scattering associated with plasmon excitation.

Credit: Image courtesy of Northwestern University

Despite this promising beginning, the SERS field progressed slowly for Van Duyne in the 1980s and 1990s, in part because the basic tools of nanoscience for preparing and characterizing nanoparticles that were SERS active were not available at the time. This suppressed Van Duyne's productivity, especially in the 1980s.

In the 1990s, Van Duyne's research moved away from SERS measurements, and instead focused on the extinction (scattering and absorption) of light by silver and gold particles that were made using a cheap vapour deposition method known as nanosphere lithography. This era produced particles whose shape and size could be controlled, and where computational electrodynamics methods could be used to understand spectra. This led to the index of refraction-based methods for sensing the presence of proteins and other molecules. A related technique known as surface plasmon resonance is commercially used today.

Now armed with nanoparticles whose properties he understood, Van Duyne returned his attention to SERS in the 2000s. One of the important results from this work was a quantitative determination of the SERS enhancement factor, where he showed that enhancements of 10^9 and even higher can be achieved with optimized substrates. This also led to an explanation of single-molecule SERS (which had been discovered by other groups in the 1990s), where he found that a single molecule with big Raman cross-section trapped in the crevices of metallic nanoparticle aggregates can scatter light with enough intensity to be detected.

In the past ten years, Van Duyne turned his attention to three topics that reveal new strengths of the SERS technique: ultrafast SERS, high-resolution scanning probe SERS known as TERS (tip-enhanced Raman spectroscopy), and the combination of TERS with electrochemistry. These investigations led to important discoveries, including the first observation of surface-enhanced femtosecond stimulated Raman spectra, the realization that sub-nanometre imaging is possible using TERS and the first single-molecule electrochemistry experiments. Van Duyne was a brilliant experimentalist and could often come up with truly ingenious set-ups. Besides fundamental discoveries, he pursued SERS for practical applications, including devices for hand-held glucose detection and art-conservation projects. This incredible depth and breadth leaves a significant legacy that will influence science for a long time. ❐

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