

What is a Liquid Beam?

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A liquid beam is a continuous laminar flow of a pure liquid or solution into a high vacuum. The advent of liquid beam technologies has created a frontier field of science that is revolutionizing the study of liquid surfaces and opening up new routes of study in the analytical chemistry of biological molecules. Detection and identification of molecules evaporated from a liquid beam surface, or ions ejected from it, by laser irradiation allows for novel studies of the liquid surface or of the bulk liquid by means of mass spectrometry and laser spectroscopy. The mechanisms of evaporation and laser-induced desorption have been extensively studied, with recent advances quantifying the internal energy content of chemical species liberated from the liquid beam surface.^[1] On the other hand, mass spectrometric analysis of molecules and ions liberated from liquid beams has developed into an analytical tool of great versatility. In particular, specific recent advances in the application of mass spectrometry for the detection and identification of biological molecules (including DNA and

proteins) in aqueous solutions are providing valuable new insight into the native condensed-phase chemistry of these species.^[2,3] In the paragraphs below we describe several of the key studies related to the development of the liquid beam technique.

Mechanistic studies exploring the behaviour of evaporation and laser-induced desorption from liquid beams have begun prior to the development of analytical studies of biological molecules, and are an essential tool in the development of analytical methods. The dynamics of evaporation from solutions were first investigated by measuring the velocity distribution of molecules evaporating from them, and provided tremendous new insight into the nature of evaporation. For example, acetic acid dimers are repelled from the surface of aqueous solutions of acetic acid as a gymnast (the acetic acid dimer) bounces back from a trampoline surface (the liquid surface).^[4] In other studies it has been shown that following the irradiation of a UV laser onto a liquid beam,



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Fumitaka Mafuné was born in Yokohama in Japan in 1966. His initial training took place at the University of Tokyo (B.A. 1989, D.Sci. 1994), where he started a liquid beam experiment with Tamotsu Kondow. He continued his study in the University of Tokyo as a research associate before leaving for the Toyota Technological Institute in 1997. In 2003 he took his current position of Associate Professor of Chemistry at the University of Tokyo.



Jun-ya Kohno, born in Tokyo in 1969, received his degrees (B.S. 1992, M.S. 1994) from the University of Tokyo under the supervision of Tamotsu Kondow. He studied lubricants in the Central Technical Research Laboratory of the Nippon Oil Company (1994–1998) before joining the Genesis Research Institute in 1998. He received his Ph.D. in 2000 from the University of Tokyo under the guidance of Kaoru Yamanouchi. His current research interest is focussed on dynamics of reactions in solutions initiated by laser excitation.

ions are ejected by Coulomb repulsion from a charged liquid surface created by initial rapid electron photo-depletion.^[5,6] On the other hand, the mechanism of desorption by an intense IR laser appears to be more complex than that by a UV laser. In the early stages after an IR laser pulse irradiates the liquid, chemical species are produced nonlinearly by the IR laser and are ejected to the gas phase. These early-liberated species have a high translational energy but a low internal energy. Conversely, species liberated at the later stages are more or less thermalized.^[7] It has been reported that in the excitation of a liquid beam of water by an intense IR laser, an ion pair, $\text{H}^+ - \text{OH}^-$, is formed as an intermediate through the multiphoton excitation of water.^[8,9] Recent experiments measuring the energy partitioning of molecules liberated from a liquid beam surface constitute a seminal contribution to the field. We now know that the rotational temperature of molecules ejected from a liquid surface, for instance, is much lower than the temperature of the liquid beam surface itself.^[1]

The surfaces of liquid beams have been investigated extensively by probing ions and electrons ejected from them. For instance, mass spectroscopic studies of ions ejected from an aqueous solution of phenol by UV laser irradiation have revealed that phenol molecules on the surface of the solution undergo a two-dimensional phase transition in which the phenol molecules become paired when the phenol concentration exceeds a critical value.^[10] More recently, a local structure of water has been detected selectively by measuring the dependence of the intensity of the cluster ions ejected from the liquid beam on the wavelength of the IR laser used. The local water structure contains non-anharmonic OH vibrational modes which allow multiphoton excitation to an intermediate ion pair, $\text{H}^+ - \text{OH}^-$, before forming the resultant cluster ions.^[9] The electronic structures of liquid beams of various liquids and solutions have also been studied by photoelectron spectroscopy.^[11,12] The kinetic energy distribution of photoelectrons from a liquid beam (photoelectron spectrum) contains information describing the electronic structure of the surface as deep as several nanometers because the photoelectrons can escape from it without suffering significant disturbance. Combined with pulsed laser desorption, the liquid beam of a solution behaves as a liquid–vacuum interface for mass spectroscopic measurements of molecules dissolved in the solution. In a practical mass analysis, a sample solution of interest is injected for a short period of time into a continuous solvent flow just before being introduced into a vacuum chamber to form a liquid beam. This approach saves consumption of the sample solution which is often available only in limited quantities.^[2] A liquid-droplet beam (a train of liquid droplets in vacuum) has also recently been developed as an alternative technique for saving the sample consumption.^[3,13] Many biological molecules with high

molecular weight, their non-covalently bonded complexes, decomposition products, and the like, dissolved in aqueous solutions containing various electrolytes and buffers have been identified beautifully by these methods. When it comes to bio-analytical mass spectrometry, liquid beam methods offer several advantages over more established methods such as electrospray ionization (ESI) and matrix-assisted laser desorption/ionization (MALDI) since they (a) enable a target species (molecules, weakly bound complexes and aggregates, etc.) to ionize softly, (b) are tolerant against various buffers and other electrolytes, and (c) sample the target species while maintaining its properties from the original solution.^[2]

The growing versatility of liquid beam injection as a tool for studying a wide variety of physical and chemical phenomena, ranging from characterizing local molecular structures and energy transfer at liquid–vacuum interfaces to bio-analytical mass spectrometry is admirably illustrated in the studies showcased in this issue of the *Australian Journal of Chemistry*. The works described here, including the seminal study quantifying the internal energy content of molecules liberated from liquid beams and the bioanalytical applications of liquid beams, represent significant contributions to the growing international effort focussed on understanding how liquid beams operate and to apply this novel technology to contemporary chemical issues.

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