Electrospray Interface

Four Processes:

1. Production of large charged droplets
2. Shrinkage of charged droplets by solvent evaporation
3. Repeated droplet disintegrations
4. Production of very small, charged droplets capable of producing gas phase ions.
Electrospray Process

There are two major theories that explain the final production of gas-phase ions:

The **Ion Evaporation Model** (IEM): suggests that as the droplet reaches a certain radius the field strength at the surface of the droplet becomes large enough to assist the field desorption of solvated ions.

The **Charged Residue Model** (CRM): suggests that electrospray droplets undergo evaporation and fission cycles, eventually leading progeny droplets that contain on average one analyte ion or less. The gas-phase ions form after the remaining solvent molecules evaporate, leaving the analyte with the charges that the droplet carried.

While there is no definite scientific proof, a large body of indirect evidence suggests that small ions are liberated into the gas phase through the ion evaporation mechanism, while larger ions form by charged residue mechanism.
Electrospray Process

The liquid containing the analyte(s) of interest is dispersed by electrospray into a fine aerosol. Because the ion formation involves extensive solvent evaporation, the typical solvents for electrospray ionization are prepared by mixing water with volatile organic compounds (e.g. methanol, acetonitrile). To decrease the initial droplet size, compounds that increase the conductivity (e.g. acetic acid) are customarily added to the solution. Large-flow electrosprays can benefit from additional nebulization by an inert gas such as nitrogen. The aerosol is sampled into the first vacuum stage of a mass spectrometer through a capillary, which can be heated to aid further solvent evaporation from the charged droplets. The solvent evaporates from a charged droplet until it becomes unstable upon reaching its Rayleigh limit. At this point, the droplet deforms and emits charged jets in a process known as Rayleigh fission. During the fission, the droplet loses a small percentage of its mass along with a relatively large percentage of its charge.
Desorption Electrospray Ionization (DESI)


Desorption Electrospray Ionization (DESI) is carried out by directing pneumatically assisted electrosprayed droplets onto a surface to be analyzed at atmospheric conditions. Ions are produced from the sample originally present on the surface. The resulting mass spectra are similar to normal ESI mass spectra. The contents of the solvent spray, the gas flow rate, the amount of applied voltage, the spray angle and the ion uptake angle, as well as the various distances in aligning the spray, sample and mass spectrometer are all variables which can be studied to achieve an optimal mass spectrum for a particular type of sample.

Using DESI, high quality mass spectra have already been obtained for a wide range of molecules by directly interrogating a diverse range of surfaces. For example, explosive agents, chemical warfare simulants, amino acids, peptides, proteins, commercially available drug molecules, alkaloids, terpenoids and steroids have all been successfully ionized using DESI.