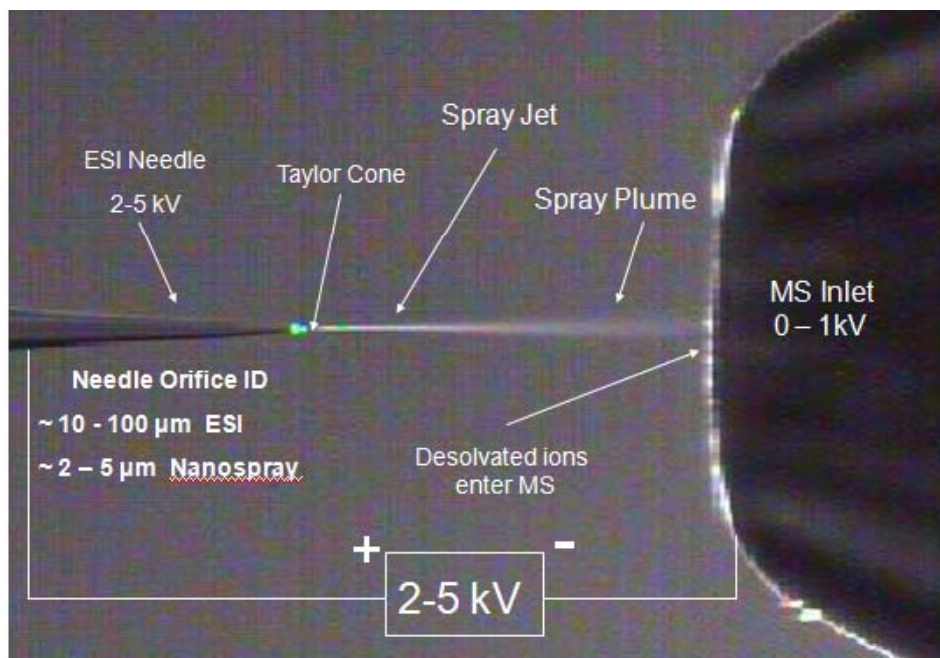
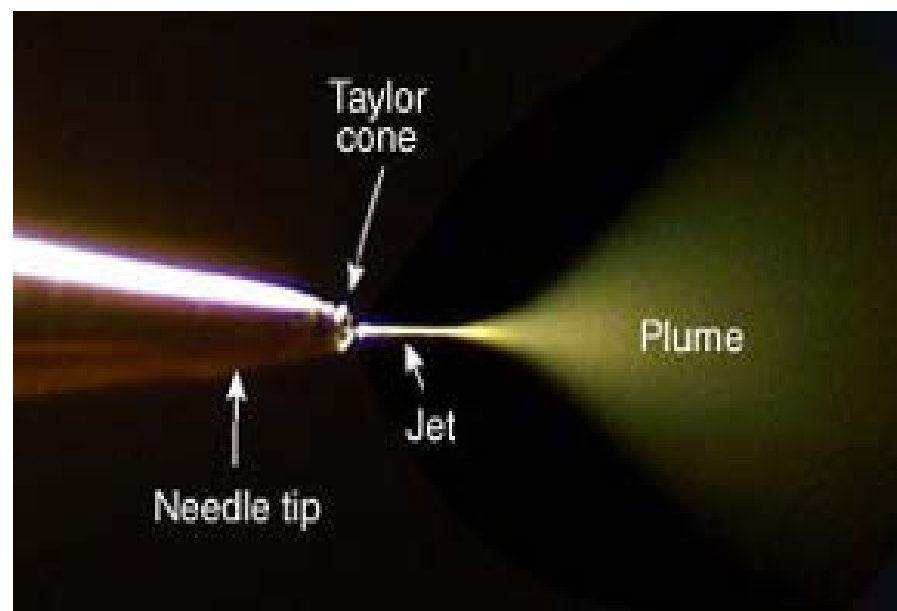


Electrospray ionization. An analyte solution is sprayed through a charged capillary towards the sampling orifice of the mass spectrometer; individual ions are sampled by the mass spectrometer in the gas-phase.

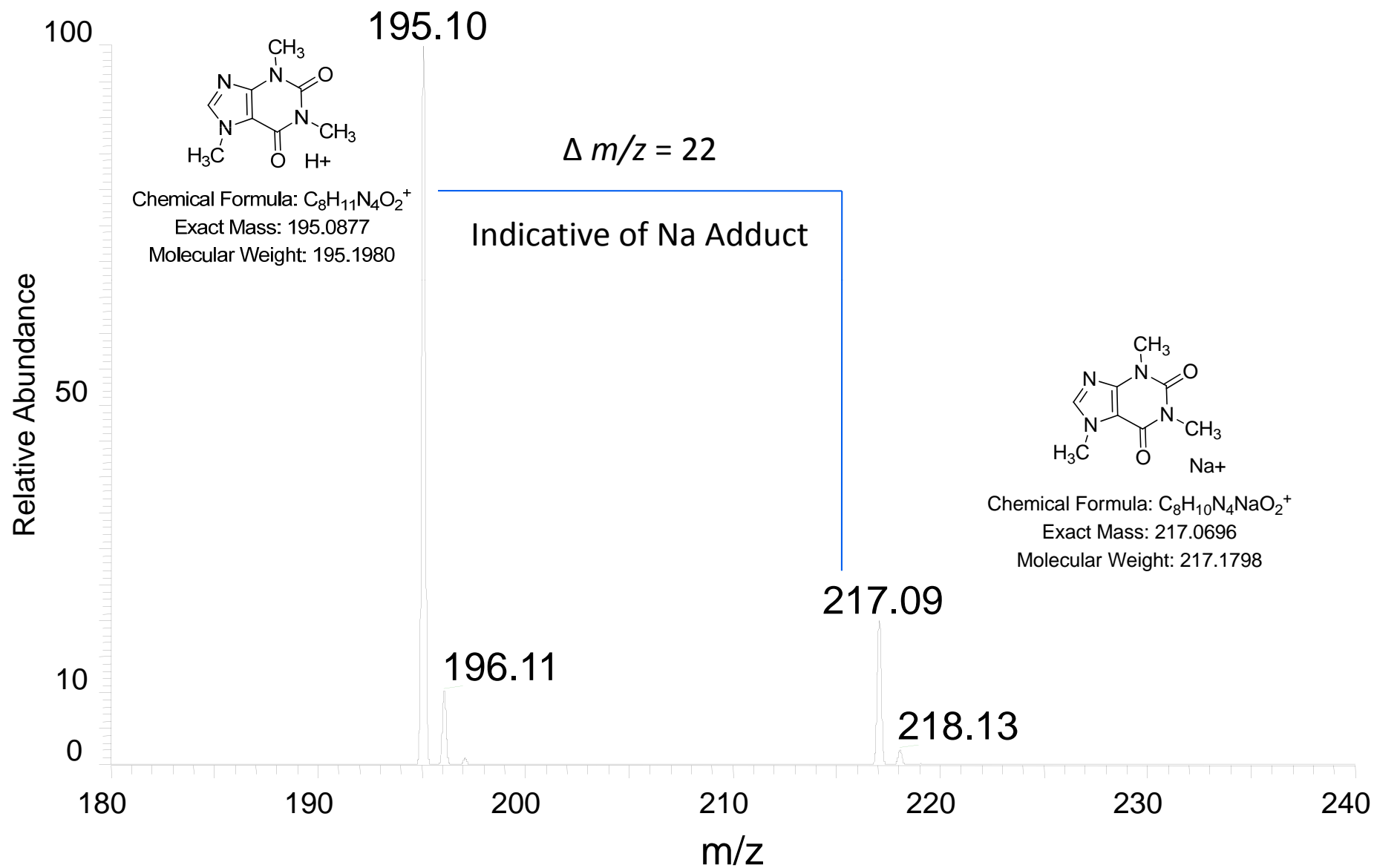


- The ESI process can produce multiply charged ions, $[M+nH]^{n+}$ or $[M-nH]^{n-}$
- Advantage: multiple charging decreases the m/z of larger molecules and enables them to be analyzed on mass analyzers with limited upper mass ranges (quadrupoles, ion traps, Orbi Trap, FTICR).
- Disadvantage: multiple charging splits an ion's signal into multiple m/z values which can decrease sensitivity.

- The ESI process produces molecular ion adducts
 - ESI (+): $[M+H]^+$, $[M+Na]^+$, $[M+K]^+$, $[M+NH_4]^+$
 - ESI (-): $[M-H]^-$
- To promote ionization solutions may be doped with a volatile acid (formic or acetic acid) or volatile base (most typically ammonium salts: acetate, formate, bicarbonate, or ammonium hydroxide).
- Volatile solvents and buffers should be used (Water, ACN, MeOH, IPA, ect).
- Allows LC to be coupled with mass spectrometry



- Applies a strong electric field at atmospheric pressure to liquid passing through an ESI spray capillary
- Charge accumulates on the surface of the droplets at the end of the capillary causing them to be dispersed into a “mist” of highly surface charged droplets
- As droplets move away from the capillary towards the inlet of the mass spectrometer they interact with atmospheric gas as well as sheath gas that may be applied along the outside of the ESI capillary.
 - ESI typical liquid flow rates: 1 $\mu\text{L}/\text{min}$ – 500 $\mu\text{L}/\text{min}$
 - nanoESI typical liquid flow rates: 10 nL/min - 1 $\mu\text{L}/\text{min}$
- Heat may also be applied to the source to promote desolvation
- There are two primary models that describe the production of gas phase ions in ESI: the ion evaporation model & the columbic explosion model
 - Droplets moving toward the inlet of the MS shrink to the point that the charge-to-surface area ratio becomes so high that desolvated gas phase ion are ejected directly from the ever shrinking droplet (**Ion Evaporation Model**).
 - Droplets moving toward the inlet of the MS shrink to the point that the charge-to-surface area ratio becomes so high that “columbic explosion” occurs producing smaller highly charge droplets. Eventually, a series of columbic explosion events produces desolvated gas phase ions, which enter the MS (**Columbic Explosion Model**).
- The point at which the surface charge of the droplet overcomes the surface tension of the droplet leading to ion evaporation or columbic explosion is referred to as the **Rayleigh Limit**



$$z = 1/(\Delta m/z)$$

