

The Secret Lives of Gas-Phase Radical Cations

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It was not too long ago that the ionization of a stable neutral molecule was thought to be a trivial process generating the resulting molecular radical cation. It still remains a fairly common practice, when faced with an ion having a particular elemental composition, to assign the structure of the ion to that of the "most reasonable" corresponding neutral molecule. For example, when an observation leads to an ion with m/z 32 having the composition $\text{CH}_4\text{O}^{+\bullet}$, one's first thoughts lead to ionized methanol, $\text{CH}_3\text{OH}^{+\bullet}$. However, we now know this to be naive, and that there is a much more thermodynamically stable isomer, $\text{CH}_2\text{OH}_2^{+\bullet}$ that is usually present. In my talk I will highlight several investigations from our group into the unimolecular and bimolecular chemistry of "small" gas-phase radical cations, studies that showcase their (often) unexpected behaviour. Along the way I will discuss the use of experimental techniques (tandem mass spectrometry, threshold photoelectron photoion coincidence spectroscopy and collision spectroscopy) in probing radical cation chemistry and the critical contributions of computational chemistry. Hopefully, this talk will change the way you look gas-phase ions.