Thermalisation in CID MS/MS on a QqQ: towards ion trap CID excitation conditions ?

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Collision Induced Dissociation is one of the most used excitation technique to fragment ions on mass spectrometric instruments. It is mainly used for analytical purposes to obtain structural and quantitative information but also for gas-phase thermochemical studies. From the analytical point of view, an important issue is the lack of strong similarity of MS/MS spectra obtained on different MS plateforms, which is desirable to generate robust MS spectral libraries. Energy-Resolved tandem MS analysis is a technique that consists in performing CID MS/MS experiments at different excitation voltages applied to the precursor ions, which provides access to the energetics of the fragmentation processes observed and may also give relevant complementary analytical information (e.g. in the case of iso-meric/baric mixtures[1,2]).

We have used the protonated leucine enkephalin pentapeptide as a reference molecule[3] to compare the energetics of its fragmentation as a function of CID collision gas pressure on an ion trap[4,5] and on a QqQ[6]. We want to evaluate how this parameter (often neglected in routine analysis) can affect the energetics of fragmentation and if it can become a relevant parameter to consider in order to achieve comparable fragmentation conditions and similar MS/MS spectra. If it was intially observed on a QqQ a negative linear dependence of the necessary voltage to achieve fragmentation as a function of collision gas pressure[6], this trend is opposite (positive dependence) when it is performed on an ion trap[4,5].

Recently, it was shown that such analysis at very low pressures on a QqQ lead to the determination of the number of collisions experienced by the precurosr ions[7]. In this study, we extend this analysis on a wider pressure range to show that several distinct pressure regimes with different energetic behaviors are emerging. In particular, it appears a positive dependence at large pressures that is similar to ion traps. Considering this trend on ion traps can partly be explained by the thermalization of ions, we hypothesize thermalization to occur on QqQ on such pressure range. According to our results, this pressure range can also be determined quite accurately using such a pressure-dependence analysis, Energy-resolved tandem mass spectrometry experiments and the Survival Yield technique.

References

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