Dissociation mechanisms for the doubly-ionized DMDS (CH₃-SS-CH₃) molecule: use of a multivariate normal distribution method.

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Synopsis The use of Multivariate Normal Distribution was used to represent the whole spectra as combination of parameters. Fragmentation and ionic dissociation of dimethyl disulfide (CH₃SSCH₃ or DMDS) at 800 eV is studied for single and multiple coincidence. The proposed methodology allows to obtain dissociation parameters when there is an overlap of the ion-ion data spectrum.

Double ionization of molecules usually leads to highly dissociative states. Time-of-Flight mass spectrometry coupled to ion-ion coincidence techniques allows for the characterization of these unstable ionic states [1]. The principal focus in this work is to represent the correlation between charged ions associated with a given dissociation process using an alternative way, based on a multivariate distribution. We thus, recover some of the initial Frasinsky's covariance approach [2]. Card et al. also used the covariance idea in the description of ammonia clusters subjected to femtosecond lasers pulses [3], but neither Fransinsky nor Card went further in order to represent the whole coincidence spectra as a combination of statistical parameters.

All the bivariate density functions can be expressed as the combination of two matrices, μ and $\sum$:

$$f = \frac{1}{\sqrt{2\pi|\Sigma|}} e^{-\left(\frac{1}{2}(x-\mu)^T \Sigma^{-1}(x-\mu)\right)} \qquad (1)$$

Where μ is the mean vector and $\sum$ is the covariance matrix. As an example, considering the dissociation of DMDS²⁺ into CH₃SS⁺ and CH₃⁺, following electron beam irradiation of the neutral molecule (Fig. 1a), we can show that these matrixes can be defined as:

$$\mu = \begin{pmatrix} 231 \\ 2611 \end{pmatrix}, \ \Sigma = \begin{pmatrix} 206,5 & -107,9 \\ -107,9 & 180,6 \end{pmatrix}$$

Considering also the [SS]⁺ / [CH₃]⁺ ion pair coincidence (Fig.1b), the matrix are represented as:

$$\mu = \begin{pmatrix} 231 \\ 2189 \end{pmatrix}, \qquad \Sigma = \begin{pmatrix} 240,7 & -114,47 \\ -114,47 & 125,2 \end{pmatrix}$$

We can now use the previous information to disentangle the compounded coincidence between an ion and a set of related ionic species, as for instance, [CHnSHn]⁺ / [CH₃]⁺ (Fig.1c)

The latter ion-ion coincidence spectrum shows infinite slope possibilities. Using the presently proposed

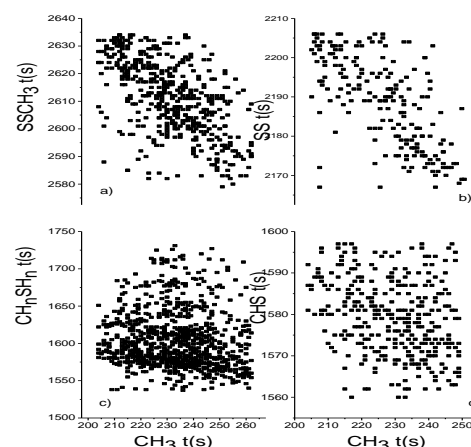methodology we can nonetheless obtain the dissociation parameters for ion pairs such as [CHS]⁺ / [CH₃]⁺ (Fig 1d).

Figure 1. a) [CH₃SS]⁺ / [CH₃]⁺ b) [SS]⁺/ [CH₃]⁺ c) [CHnSHn]⁺ / [CH₃]⁺ d) [CHS]⁺/ [CH3]⁺ coincidence.

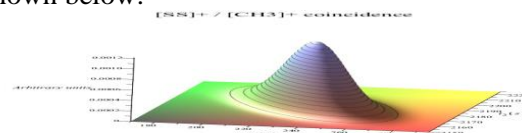Dissociation of the ionic pair [SS]⁺ / [CH₃]⁺ can also be represented in a three-dimensional plot, as shown below:

Figure 2. [SS]⁺/ [CH₃]⁺ coincidence represented.

References

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