COMMENTS

Comment on "Energy-Resolved Collision-Induced Dissociation of $Fe_2(CO)_y^+$ ($y = 1-9$)"

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In their work, Markin and Sugawara provide threshold data from energy-resolved FT-ICR collision-induced dissociation experiments of diiron carbonyl cluster cations, $Fe_2(CO)_y^+$ ($y = 1-9$).[1] For the data analysis, they followed a procedure applied in a number of previous FT-ICR studies,[2,3] fitting the obtained threshold curves to a model fit function,[4,5]

$$\sigma(E) = A(E - E_t)^n/E \tag{1}$$

where E is the center of mass energy, E_t is the threshold energy, A is a scaling factor, and n is an adjustable exponent. E_t, A, and n are treated as fit parameters.

In the theoretical model, $\sigma(E)$ is the cross section associated with the endothermic process, the threshold of which is to be fitted. Markin and Sugawara, like the groups before, apply eq 1 to fit ion intensities instead of cross sections, implying that $\sigma(E)$ is a linear function of the ion intensity. We would like to point out that this is, in general, not the case. The cross section is defined via the exponent in Beer's law of absorption:

$$I_r = (I_r + \sum I_p) \exp(-\sigma_{tot} nl) \tag{2}$$

or

$$\sigma_{tot} = (1/nl) \ln((I_r + \sum I_p)/I_r) \tag{3}$$

where I_r is the reactant ion intensity measured at the end of the experiment, I_p is the individual product intensities, n is the number density of the collision gas, and l is the interaction path length. Individual product cross sections σ_p are calculated as fractions of the total cross section σ_{tot}:

$$\sigma_p = (I_p/\sum I_p)\sigma_{tot} \tag{4}$$

As shown previously,[6,7] eqs 3 and 4 are easily evaluated for FT-ICR experiments. The number density n is easily calculated from the collision gas pressure, and the interaction path length l is given by the laboratory frame kinetic energy E_{lab} of the reactant ion and the collision time t_{CID}:

$$l = t_{CID}\sqrt{2E_{lab}/m_r} \tag{5}$$

Figure 1 illustrates that the shape of the theoretical threshold curve differs considerably when plotted as cross section or as intensity for a typical FT-ICR experiment where t_{CID} is held constant. For simplicity, fragmentation to a single product ion is assumed. The cross section curve $\sigma(E)$ was calculated according to eq 1 with $E_t = 1$ eV, $n = 2$, and $A = 2.0 \times 10^{-16}$ cm^{-2}. The weighted product ion intensity $I_p(E)/(I_r(E) + I_p(E))$, which is usually taken as ion intensity, is derived from eq 2 as

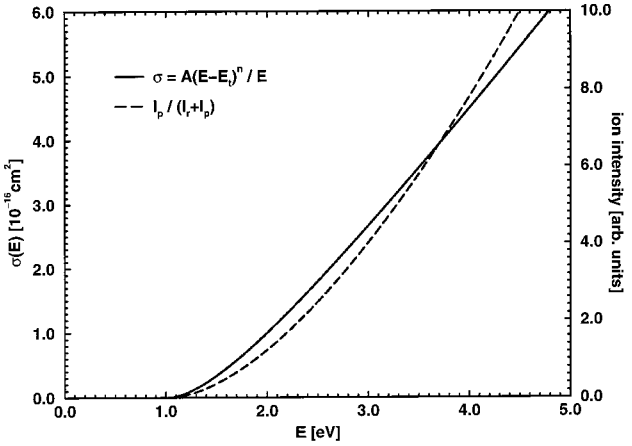

Figure 1. Comparison of a theoretical cross section curve, calculated from eq 1, with the corresponding ideal ion intensity threshold curve of a typical FT-ICR experiment with constant t_{CID}. The two curves differ significantly in their curvature, and cannot be superimposed with an arbitrary scaling factor.

$$I_p(E)/(I_r(E) + I_p(E)) = 1 - \exp(-\sigma(E)nl) \tag{6}$$

The difference in the curvature of the two curves is apparent, as they cannot be superimposed by an arbitrary scaling factor. In the experiment, the actual onset is hidden under the noise level and blurred by the distributions of ion and collision gas energies. The threshold region, however, is crucial for accurate fits.[8] The difference in curvature leads to a different exponential fit parameter n. This, together with the convolutions over the ion and collision gas energy distributions, which are again derived for cross sections and not intensities, is almost certainly leading to a change in the fitted threshold energy E_t.

As the number of FT-ICR instruments is rapidly growing, more research groups[9] are performing energy-resolved threshold experiments such as those of Markin and Sugawara. With this comment, we want to bring the cross section problem to the attention of the community and encourage researchers to calculate cross sections from their intensity data as outlined above. While the error in the threshold energy E_t may be small, the additional effort is negligible, and the benefit is apparent. The data become independent from randomly chosen experimental parameters and can be directly compared with data from other techniques. Above all, it is the only rigorous way of evaluating energy-resolved threshold experiments in FT-ICR mass spectrometry.

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