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Determination of kinetic energy release from metastable peak widths: An investigation of the instrument-dependence☆

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ABSTRACT

The kinetic energy that is released upon bond rupture is often represented as $T_{1/2}$. A value that is derived from the FWHM of a fragment peak by the use of two different conversion formulas. The choice of formula depends on whether the peak is recorded by scanning a magnetic sector or an electrostatic analyzer. We have conducted a systematic variation of the possible scan configurations of two different double focusing instruments in two countries. We have found that a double focusing mass spectrometer in normal geometry gives rise to $T_{1/2}$ values that are 1.4 times larger when analyzing peaks that are obtained from magnet scans compared to the peaks that are obtained by scanning an electrostatic analyzer. The E scans (MIKE experiments) give rise to the same values for both of the employed mass spectrometers. The results are explained in terms of energy defocusing when the reactions take place too far away from the focal points and show that only the E scans $T_{1/2}$ values can be compared from instrument to instrument.

1. Introduction

Kinetic energy release (KER) data obtained from the metastable signals observed within a sector mass spectrometer have provided a valuable window of insight into the reaction dynamics of metastable ions in the gas phase [1,2]. The extraction of these data from the broadening of the metastable signals was made easily comprehensible by the textbook of Cooks et al. [3] of 1973, and measuring the signal width at half height was common, converting this signal width into a single-valued KER often referred to as $T_{1/2}$ [4]. This quantification has been applied both to the broad flat-topped and dished signals as well as the more slim signals which are commonly of Gaussian shape.

However, a KER is seldom monoenergetic. To address this concern, there is a general consensus that the theoretical peak-shape of a single valued KER is approximately rectangular [5–7] although this was not clearly demonstrated until 1992 [8], and that a metastable signal could then – in principle – be described by the stacking of boxes as illustrated by Laskin and Lifshitz [9]. Kinetic energy release distributions (KERD's) were thereby introduced [4,7,10–15].

Unfortunately, the 'rectangular box' picture does not take the instrumental discrimination into account, which at large KER's have the effect of 'carving out' the center of the rectangular flat-top to become dished or to an extend where only the sides remain fairly untouched [3]. To address this instrument-depending effect, the so-called basis functions [4–8,11,14,15] are established, which are the single-KER 'box' functions convoluted by the discriminating influence of one specific instrument with specified slit settings. The KERD is then established by fitting a linear combination of the basisfunctions to the metastable signal. The derivation of the basisfunctions is quite complex and involves trajectory calculations on the ions decomposing on various locations in the field-free region. In particular the Z-axial discrimination of the collector slit having a finite height can be severe.

In a review Uggerud [4] suggests, that the $T_{1/2}$ value is 'rather arbitrary, and gives instrument geometry dependent – but often comparable – values'. We wish to report a systematic study of the apparent contradiction within arbitrary/comparable, focusing on the signal width dependency on instrument geometry as described by $T_{1/2}$-values. This study, and a discussion of the consequences of the findings, is the scope of this paper.

2. Experimental

A JEOL four-sector double-focusing JMSHX110/HX110A mass spectrometer (E1B1E2B2 geometry) was used in two-sector mode with 70 eV electron impact ionization, *ca.* 200 °C ion source temperature and 10 kV acceleration potential to record mass spectra (reactions in the ion

☆ Dedicated in admiration to Terry McMahon on the occasion of his 70th year birthday. The data that is the foundation of the present work was obtained during a stay at École Polytechnique in Palaiseau where Terry also was present. Thanks Terry for the long runs around campus and for the marathon coaching.

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source) by employing the first two sectors (E1B1). In these mass spectra metastable peaks are observed at non-integer masses as consequence of metastable reactions that have taken place between E1 and B1. Mass-analyzed ion kinetic energy (MIKE) spectra (reactions of metastable radical cations) were recorded in three-sector mode by selecting a precursor ion with a fixed setting on E1B1 and then scanning the E2 sector of the instrument. Reactions between E2 and B2 were investigated by holding E1B1E2 steady while scanning B2. Under the same conditions a VG ZAB-2F instrument located at École Polytechnique in Palaiseau was employed to investigate the reverse geometry constellation of BE. In this case the reactions in the field free regions that can be investigated are those that take place between the acceleration region and the magnet – observed as metastable peaks at non-integer masses in the regular mass spectrum – and those that take place between the magnet (at a fixed value) and the E sector. The latter are giving rise to MIKE spectra just as those from the JEOL instrument.

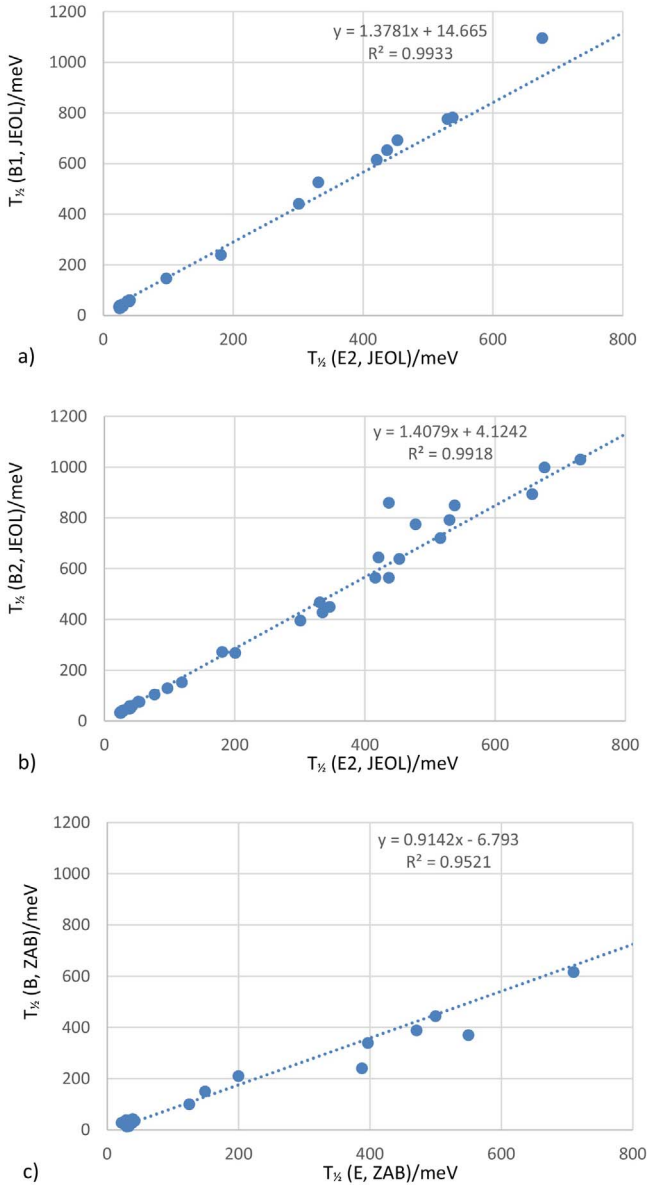

Fig. 1. $T_{1/2}$ from a magnet scan plotted against $T_{1/2}$ from the scanning of an electrostatic analyzer. The two top panels are results from the Copenhagen 4-sector (EBEB) JEOL instrument a) from reactions in the second field free region whereas b) are from the fourth field free region, both plotted against the results from the third field free region. The bottom panel is from reactions in the first field free regions the ZAB-2F (BE) instrument at École Polytechnique.

To derive single valued representations of the kinetic energy releases we employed Eqs. (1) and (2) with correction for the main beam signal width as prescribed by Cooks et al. [3]:

$$T_{1/2} = \frac{eV_{acc}m_2}{16m_3}\left(\frac{\Delta E}{E_2}\right)^2 \quad (1)$$

$$T_{1/2} = \frac{eV_{acc}m_2}{16m_3}\left(\frac{\Delta m}{m^*}\right)^2 \quad (2)$$

In Eq. (1) m_2 is the mass of the fragment ion, m_3 is the mass of the lost neutral, ΔE is the full width at half maximum of the metastable peak measured in Volts, E_2 is the center potential of the E sector at which the fragment ion beam is transmitted and V_{acc} is the acceleration voltage. In Eq. (2) the values are the same except m^* which is the non-integer position of the metastable peak and Δm is its width.

Most compounds were purchased from Aldrich and used without further purification. Some were synthesized by standard procedures and their purity were verified by NMR and GCMS.

3. Results

We have conducted a systematic variation of the possible scan configurations of two different double focusing instruments. The $T_{1/2}$ results from the peaks obtained in a series of magnet scans have been compared with the results from a series of E sector scans (MIKE experiments). Moreover we have compared the B scan results internally both from one instrument and in between instruments. Finally we have compared the E scan results obtained in between the two instruments. The comparisons are shown as plots in Figs. 1–3 .

The results presented in Fig. 1 show how the scanning of the magnets on the JEOL instrument gives single-valued representations of

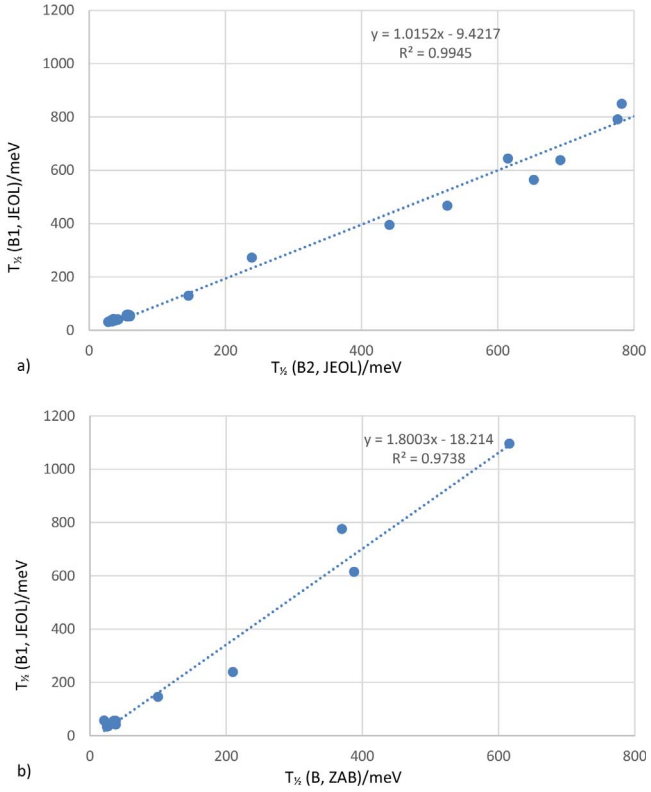

Fig. 2. Magnet scan *vs.* magnet scan. Panel a) shows the results from reactions in the second FFR of the JEOL instrument (B1 scan) plotted against the results from the fourth FFR (B2 scan) of the JEOL instrument. The bottom panel b) is from reactions in the second FFR of the JEOL instrument (B1 scan) plotted against the results from the first field free region (B scan) in the ZAB-2F instrument at École Polytechnique.