



# Appropriate choice of event length in sustained off-resonance irradiation collision-induced dissociation (SORI-CID) experiments: Activated ion collision-induced dissociation

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## ARTICLE INFO

### Article history:

Received 27 April 2012

Received in revised form 16 August 2012

Accepted 16 August 2012

Available online 25 August 2012

### Keywords:

SORI

Collision-induced dissociation

FTICR/MS

## ABSTRACT

Sustained off-resonance irradiation collision-induced dissociation (SORI-CID) is used in Fourier transform ion cyclotron resonance mass spectrometry (FTICR/MS) to activate ions through multiple, low-energy collisions. This is done by irradiating the ions with RF energy with a frequency offset,  $\Delta f$ , from their resonant frequency. This causes the orbit radius and kinetic energy of the excited ions to fluctuate with a periodicity of  $1/\Delta f$ . In this paper we demonstrate that the extent of ion activation (and subsequent dissociation) is strongly influenced when SORI-CID event lengths are not integer multiples of  $1/\Delta f$ . This is due to residual kinetic energy in the ions following the SORI event. These effects are seen over a range of  $\Delta f$  values. Small variations in SORI-CID event lengths can therefore be used to enhance or suppress dissociation, and care must be taken to account for these effects when comparing threshold dissociation energies obtained using these methods.

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## 1. Introduction

In Fourier transform ion cyclotron resonance mass spectrometry (FTICR/MS) ions orbit the magnetic field lines at a frequency inversely proportional to the mass-to-charge ratio. This is known as the resonant frequency. All FTICR experiments employ at least one excitation event at or near the resonant frequency to expand the radius of ion motion and impose phase coherence, enabling detection. Many experiments employ additional excitation events to eject ions from the trap or to translationally excite the ions and facilitate subsequent collisional activation. Exciting at the resonant frequency causes the ion orbit radius to expand rapidly and imparts a large amount of kinetic energy. While this allows the kinetic energy to be precisely controlled, on resonance excitation has several drawbacks for tandem mass spectrometry experiments, including short transients [1], often severe space charge effects [2], and other issues [3–7]. In addition, single collisions, even at kinetic energies of hundreds of electron volts, often deposit insufficient internal energy in the ions to induce rapid dissociation. Therefore, a number of other methods have been developed to deposit larger amounts of internal energy and facilitate easier detection

of fragment ions, such as multiple excitation collisional activation [8,9] (MECA), very-low-energy collisional activation [10,11] (VLE-CA), infrared multiphoton dissociation [12–14] (IRMPD), blackbody infrared dissociation [15–18] (BIRD), and sustained off-resonance irradiation collision-induced dissociation [19] (SORI-CID). SORI-CID has been widely used to study fragmentation patterns and relative dissociation energies and was first developed by Gauthier in 1991. The mechanism of energy deposition in SORI-CID has been well characterized by Laskin et al. [20,21]. The SORI-CID excitation event is performed at a frequency offset  $\Delta f$  either above or below the resonant frequency. The SORI-CID event causes the orbit radius of the excited ions to expand and collapse with a beat pattern having a period of  $1/\Delta f$ . It has been noted that to optimize detection of fragment ions in SORI-CID experiments, SORI-CID event lengths should be set to integer values of the beat period [22]. Consideration of ion trajectories under SORI conditions shows that the kinetic energy of the ions varies as the square of the sine of the phase mismatch between the driving RF and the cyclotron frequency of the ions [23]. Thus, one would expect the ions to retain some residual kinetic energy if the SORI excitation waveform does not end in phase with the cyclotron frequency. This paper discusses the effect of setting SORI-CID event lengths to non-integer multiples of  $1/\Delta f$ , and demonstrates experimentally the effects of residual kinetic energy. In particular, we observe enhanced fragmentation for SORI events that use non-integer numbers of cycles.

The initial sample used for this study is decamethylcucurbit[5]uril (hereafter mc5) complexed with one  $\text{Cs}^+$  and one  $\text{Li}^+$ .

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**Table 1**  
Experimental parameters for off-resonance excitation.

Parent ion	<i>m/z</i>	$\Delta f$ (kHz) <sup>b</sup>	$V_{pp}$ <sup>c</sup>	$E_{cm}$ (eV) <sup>a</sup>		Cyclotron radius (mm)	
				Average	Maximum	Average	Maximum
[mc5 + LiCs] <sup>2+</sup>	555.2	1.00	11.0	1.6	9.9	1.2	3.1
[mc5 + LiCs] <sup>2+</sup>	555.2	1.00	12.6	2.1	13.0	1.4	3.6
18c6-Cs <sup>+</sup>	397.1	0.95	8.2	0.8	5.2	1.3	3.3
18c6-Cs <sup>+</sup>	397.1	1.81	15.6	3.0	19.0	2.5	6.2
18c6-Cs <sup>+</sup>	397.1	2.73	24.0	7.1	44.9	3.8	9.6

<sup>a</sup> Kinetic energy in the center-of-mass reference frame.<sup>b</sup> Frequency offset above the resonant frequency.<sup>c</sup> Excitation voltage measured across the excite plates at the vacuum feedthrough to the trapping cell.

A member of the cucurbit[n]uril family [24] of molecular cages, mc5 [25] consists of five modified glycoluril monomers connected in a cyclic fashion to form a cage with two carbonyl-lined portals. When Li<sup>+</sup> and Cs<sup>+</sup> are added to the electrospray solution, they spontaneously complex on the mc5 portals. We selected the doubly charged mixed-metal complex for this study. Under SORI conditions, this complex dissociates exclusively via loss of the less-strongly bound cation, Cs<sup>+</sup>. Further experiments were performed using Cs<sup>+</sup> complexed with 18-crown-6 (hereafter 18c6), which dissociates by loss of Cs<sup>+</sup>.

## 2. Experimental

### 2.1. Mass spectrometer and materials

All experiments were done using a Fourier transform ion-cyclotron resonance mass spectrometer (Bruker model Apex 47e FT-ICR MS) equipped with a MIDAS PREDATOR [26,27] data system (National High Magnetic Field Ion Cyclotron Resonance Facility, Tallahassee, FL). Samples of mc5 were provided by IBC Advanced Technologies (American Fork, UT) and used without further purification. Alkali metal salts (LiCl: Fisher Scientific, Fair Lawn, NJ; CsCl: Mallinckrodt, Paris, KY) and samples of 18-crown-6 (Sigma–Aldrich Corp., St. Louis, MO) were also used without further purification. Aqueous solutions containing either LiCl, CsCl, and mc5; or CsCl and 18c6 each at 100  $\mu$ M, were electrosprayed with a typical flow rate of 30  $\mu$ L/h using a microelectrospray source [28] modified from an Analytica (Analytica of Branford, Branford, MA) design and a heated metal capillary tube [29] based on an Eyler design. The peak of interest was isolated using stored waveform inverse Fourier transform (SWIFT) [30] techniques.

### 2.2. SORI-CID

SORI-CID on mc5 was carried out by irradiating 1 kHz below resonance at constant amplitude (either 12.6 or 11.0  $V_{pp}$ ). The 18c6 complexes were studied at 1 kHz off-resonance as well as at frequency offsets of 0.5%, 1.0%, and 1.5% of the molecule's resonant frequency (181.573 kHz) at amplitudes of 8.2, 15.6, and 24.0  $V_{pp}$ , respectively. The experimental conditions for the 18c6 complex were chosen to investigate the effects that off-resonant frequency choice has on the dissociation patterns. The literature-suggested offset is 1.5% of the molecule's resonant frequency [31]. The kinetic energies in the center-of-mass reference frame [23], as well as the cyclotron radii for ions at these energies [32], are reported in Table 1.

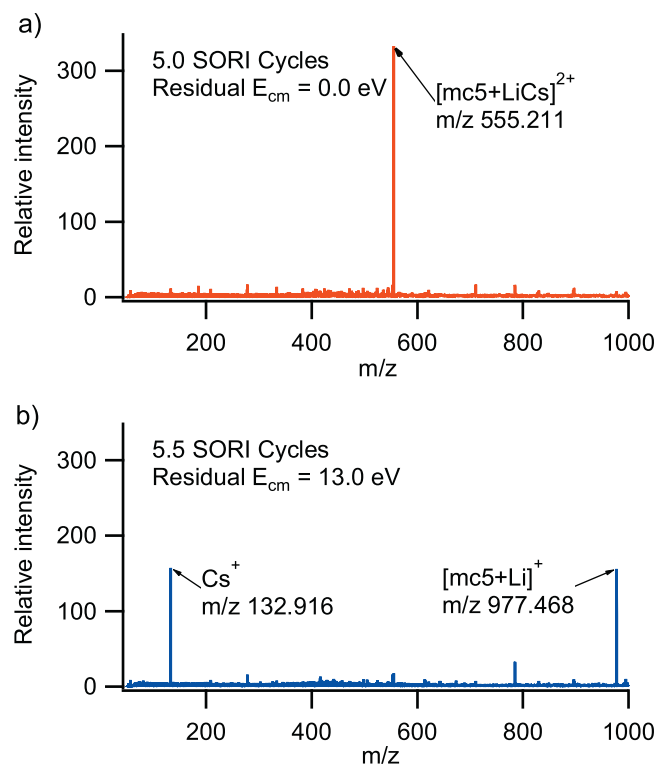
Argon collision gas was introduced using a Freiser-type [33] pulsed leak valve. This enabled the cell pressure to be reproducibly held constant at around  $10^{-5}$  mbar for the duration of SORI-CID events, and then pumped down to around  $10^{-9}$  mbar immediately after to facilitate detection. The duration of the SORI-CID activation event, and hence the total SORI energy deposited, was varied

programmatically from 1 to 20 ms using tcl scripts. A 3 s delay followed the SORI event in each experiment, allowing the SORI collision gas to be pumped away prior to detection. Each spectrum consisted of three co-added scans. The spectra were peak picked and relative ion abundances were determined from peak amplitudes. The reported values are averages, and error bars in the resulting graphs represent  $\pm 1$  standard deviation.

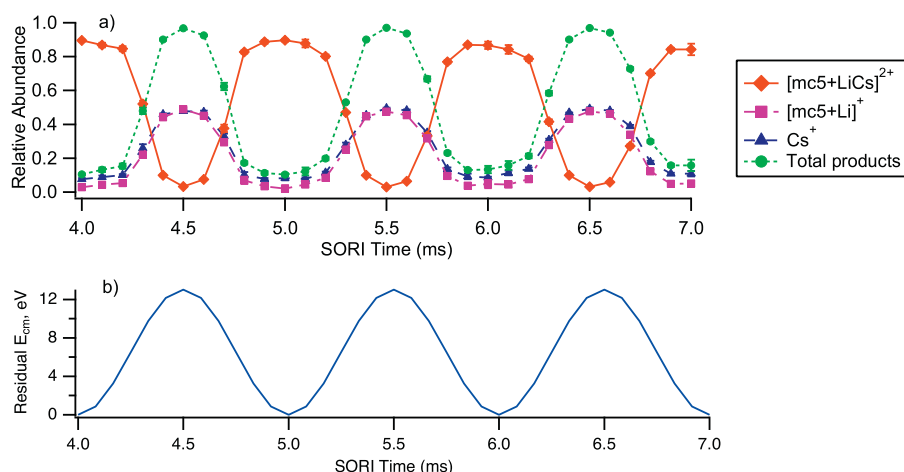
## 3. Results and discussion

For the mc5 complexes,  $\Delta f$  is 1.00 kHz and a complete SORI-CID cycle occurs every 1.00 ms. As seen in the mass spectra of Fig. 1, the extent of dissociation of the complex ion strongly depends on the length of the SORI-CID event. Fig. 2a shows how parent and product ion intensities vary with the length of the SORI event. At integer multiples of the 1 ms SORI cycle, little or no dissociation occurs. However, when the SORI-CID activation duration is at half-integer values, dissociation of the complex is complete. Overall, the pattern is sinusoidal.

These results can be explained by considering the mechanism of SORI-CID activation in the absence of collisions. As ions are excited



**Fig. 1.** Mass spectra recorded at the end of (a) an integer number of SORI cycles, showing the isolated parent ion with no dissociation and (b) after a half-integer number of cycles, showing nearly complete dissociation of the parent ion.



**Fig. 2.** (a) Dissociation curve of  $[mc5 + LiCs]^{2+}$  when excited 1 kHz below resonance at 12.6 V (peak-to-peak, measured at the input to the trapping cell). SORI-CID event length was varied with 0.1 ms intervals from 4 to 7 ms. (b) Computed residual kinetic energy in the center-of-mass frame at the end of the SORI event for the same range of SORI durations.

off resonance, after a few SORI cycles they are in phase with the driving RF at the beginning of each cycle. The ions are excited to higher kinetic energies by the driving field, but as the cycle proceeds the phase mismatch between the ion orbits and the driving RF increases. Halfway through the cycle the ions have been accelerated to maximum kinetic energy but are  $180^\circ$  out of phase with the driving RF, so no further kinetic energy is added. In fact, during the second half of the SORI cycle, the out-of-phase driving RF slows the ions and correspondingly their kinetic energy decreases, until at the end of the cycle the kinetic energy is again at minimum. Of course, in real SORI experiments the ions undergo collisions randomly during the cycle, but the average behavior of the ions should be quite similar to what we have described. Trajectory modeling of this process [23] shows that the residual kinetic energy has a  $\sin^2$  dependence on the phase mismatch between the reduced cyclotron and driving frequencies [31], and the residual kinetic energy in the center-of-mass reference frame for the conditions of Fig. 2 is shown in Fig. 2b. The total product ion curve of the mc5 complex shown in Fig. 2a is seen to closely mirror the residual kinetic energy in the center-of-mass reference frame, shown in Fig. 2b. This is not surprising, as the computed value of the binding energy for this complex,  $D[Cs^+ - mc5Li^+]$ , is only 1.1 eV [34] (weak binding energies are not unusual in supramolecular systems).

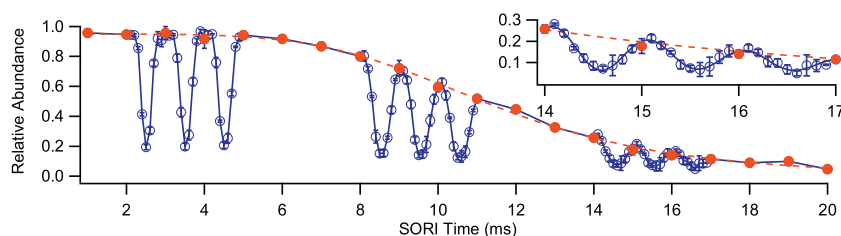
The experimental data nicely reflect the phase relationship between the driving field and the ion motion. If the SORI activation does not last for an integer number of SORI cycles, the ions are left translationally excited, just as if they had been excited by a short on-resonant excitation; subsequent collisions convert translational energy to internal energy, and the ions then dissociate. Hence, the process observed here might better be termed “activated ion CID:” the ions are slowly activated via SORI, then may

undergo harder collision-induced dissociation due to the residual kinetic energy, with all of this occurring in a single event in the experimental sequence.

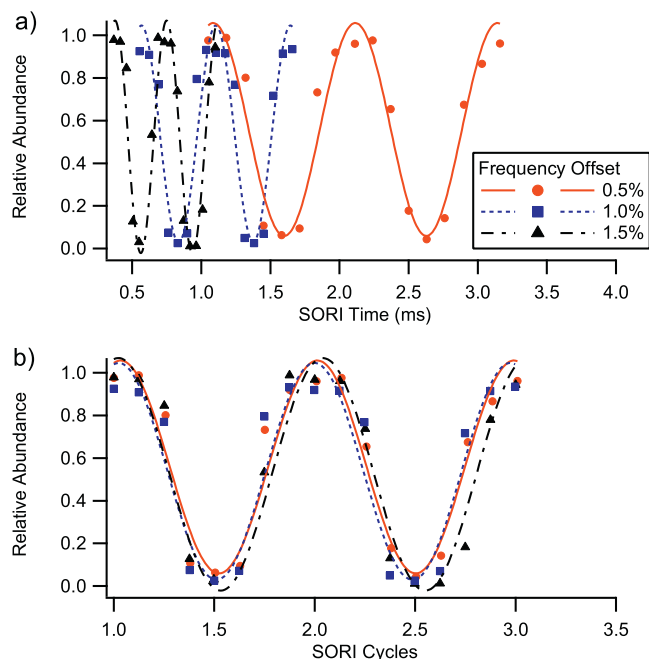
In Fig. 2, the energy deposited in the ions via low-energy collisions alone is not sufficient to cause much dissociation of the ions; dissociation is observed because of residual kinetic energy due to a non-integer number of SORI cycles. Fig. 3 shows that the effect is also important at higher SORI energy deposition levels from 5 to 20 ms of SORI excitation. In Fig. 3, the slow collisional heating of the ions due to multiple low-energy collisions is sufficient to cause significant dissociation of the parent ion, and a parent ion survival curve is generated. However, if the SORI excitation event durations are non-integer multiples of the SORI cycle, the survival curve is strongly affected.

Fig. 3 also shows a decrease in dissociation 0.1 ms above integer values, becoming more prominent after several SORI cycles have occurred. The inset in Fig. 3 highlights these points especially well. The exact cause of this decrease in dissociation is not known. It could be caused by a slight error in the off resonance frequency applied, which would accumulate and become more prominent over multiple cycles. If this is the case then setting the distance off resonance as we have could be a means for more accurate determination of either the distance off resonance or, if the excitation frequency is well defined, the resonance frequency of the excited ions. A second possible explanation is that the ions are brought into coherence by the excitation resulting in space charges that cause the resonance frequency to shift slightly.

The results above were all reproduced using the  $18c6-Cs^+$  complex, and the same behavior is seen. When integer multiples of  $1/\Delta f$  are chosen, little to no dissociation is seen. However, when non-integer multiples are chosen the complex begins to fragment.



**Fig. 3.** Dissociation curve of  $[mc5 + LiCs]^{2+}$  when excited 1 kHz below resonance at various SORI-CID event lengths from 1 to 20 ms at 22 V (peak-to-peak, measured at the output of the amplifier). Integer values are shown as filled circles and non-integer values are shown as empty circles. Decreased dissociation can be seen at 14.1, 15.1, and 16.1 ms (shown in the overlay).



**Fig. 4.** Dissociation curves for 18-crown-6- $\text{Cs}^+$  with varying excitation frequency offsets, 0.5% (0.95 kHz), 1.0% (1.81 kHz), and 1.5% (2.73 kHz) of the resonant frequency (181.6 kHz). The continuous curves are sinusoidal fits to the data. (a) When plotted vs. the length of the SORI event, the variation in parent ion abundance depends on the frequency offset. (b) When plotted vs. the number of SORI cycles, all three frequency offsets give similar results.

Overall the dissociation is sinusoidal with nearly complete dissociation occurring halfway through a SORI cycle. Experiments were also performed at 0.5%, 1.0%, and 1.5% off-resonance. When these dissociation curves are plotted against time (Fig. 4a) the sinusoidal trend is evident at each frequency offset, but the time scales vary as expected because the SORI period varies with the frequency offset. In fact, once the dissociation curves are normalized by  $1/\Delta f$  and plotted against SORI cycles (Fig. 4b) they show good agreement with each other and are comparable with the results from the mc5 complex. This demonstrates that activated ion dissociation due to residual kinetic energy occurs over a range of frequency offsets and is compelling evidence for the dissociation mechanism described above.

#### 4. Conclusions

The experimental systems shown in this paper were chosen to highlight the energetic effects of phase mismatch in SORI-CID experiments. In particular, we used SORI events that are shorter, and have higher amplitudes, than are typically applied. Under the conditions we employed, a substantial fraction of the collisions occur after the SORI event, making our results especially sensitive to residual energy. Further, the chemical systems we examined are weakly bound. However, we expect the effects demonstrated here to be general, especially when the residual kinetic energies at non-integer numbers of SORI cycles are greater than the binding energy for the ion under study.

If comparison of dissociation energies is the goal, care should be taken when choosing the lengths of SORI events so that they are integer multiples of the SORI cycle time; otherwise, large errors are likely. As with any phase error, the effects are cumulative so may be more apparent at longer times. Conversely, deliberately setting the length of the SORI excite to a non-integer multiple of the SORI cycle is a means for imparting additional energy to the ions, combining slow heating via multiple collisions during SORI with a harder

collision from residual kinetic energy at the end of the event. As a reviewer has noted, it is likely these effects will show some molecular size dependence. Larger molecules will be slower to activate due to RRKM effects, and radiative cooling could also come into play. As is well known, if the molecule radiatively cools more quickly than the collisional activation rate, it may not be possible to deposit sufficient energy in a large ion to cause dissociation. In such cases, it is desirable to carry out the activation quickly, and the “activated ion collision-induced dissociation” demonstrated here may help.

#### Acknowledgments

We are grateful for financial support from the National Science Foundation (CHE-0957757) and to IBC Advanced Technologies Inc. for providing a sample of mc5.

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