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Enhancement of ion activation and collision induced dissociation by direct current potential in digital ion trap mass spectrometer

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ABSTRACT

The efficiency of collision induced dissociation (CID) is strongly dependent on the ion activation energy. In order to increase the ion kinetic energy during resonance ion excitation, a DC voltage was deduced by simply changing the duty cycle of digital power supply in this study using a digital linear ion trap. In this experiment, different DC potentials were obtained by choosing different duty cycles of main ion trapping digital waveform, and the waveforms applied to the x and y electrode pairs were kept complimentary during ion activation and CID period. The experimental results shown that the CID efficiency was significantly increased when the DC potential was increased. The observed ion internal energy was increased about 2.5 times, and the CID efficiency was increased from 68% to 93%. A calculation shows that the low mass cut off can also be reduced by 15% and it is in agreement with the experiment results.

1. Introduction

Among the different type of mass spectrometers, the ion trap mass analyzer plays an important role in performing mass analysis and tandem mass spectrometry [1,2], because of its special characters of ion storage, multiple-stage mass selected isolation, and mass analysis. Collision-induced dissociation (CID) of activated ion has become one of the most popular method for tandem mass analysis of chemical and biological molecule structures in mass spectrometry [3–6]. In an ion trap mass spectrometer (IT MS), CID is usually realized by coupling a small supplementary AC potential to the main radio frequency (RF) power [7,8]. When the frequency of this supplementary AC potential is equal to the secular frequency of a mass selected precursor ion, then the ion will be resonance excited and will absorb some energy from the electric field that increases the its velocity and kinetic energy [9]. Collisions of the high kinetic energy ion with the buffer gas molecules and/or atoms, such as helium, nitrogen or argon, will convert the kinetic energy into ion internal energy. Eventually, the ions with high internal energy will overcome the chemical bond energy barriers and form fragments. Obviously, in CID process, the ion internal energy must be sufficient to break chemical bonds and to produce efficient ion fragments [10,11]. To ensure a certain amount of internal energy is deposited into ions for fragmentation, the ion kinetic energy must be high enough through effective excitation. Furthermore, a higher kinetic energy will benefit more fragmentation efficiency and give more molecular structure information.

The technologies for increasing ion kinetic energy have been intensively investigated over the past decades [12–14]. A number of new methods of ion excitation were developed previously. For example, the thermally-assisted collision-induced dissociation (TA-CID) [13] can increase the initial internal energy of the precursor ions by heating the collision bath gas. The results showed that the ion kinetic energy and its dissociation efficiency could certainly be increased when ions collide with hotter bath gas and provide more structural information compared with traditional CID under the same conditions. Another method of increasing ion internal energy and dissociation efficiency can be realized by increasing the mass of the bath gas, because the collision between the precursor ion with heavier molecules will increase the energy conversion efficiency to internal excitation [15–17]. Danell et al. [16] found the use of argon could increase the CID efficiency. However, the use of heavier bath gas can lead to the distinct loss of mass resolution.

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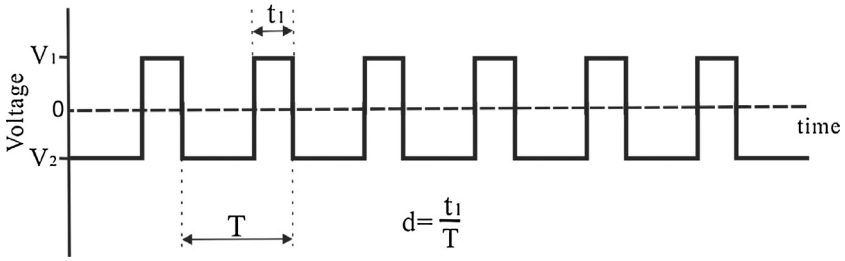

Fig. 1. Schematic diagram of the rectangular waveform voltage. T is the period of the waveform, t_1 is the width of the high voltage excursion, and $d = t_1/T$ is the duty cycle.

To apply DC potential for accelerating ions in ion traps to increase CID efficiency has been another hot topic in recent years. Many new methods were introduced and investigated. For example, a long quadrupole DC pulse was used in the technology named boundary activated dissociation (BAD) to move ions to the stability boundary and the ions can absorb more RF electric energy before colliding with the neutral gas molecules [18,20]. On the other hand, Prentice and Tolmachev et al. [19,21] used a long dipolar DC pulses in a 3D and a linear ion trap, respectively, for increasing ion kinetic energy and CID efficiency. They explained that a dipolar DC moved ions from the ion trap center, where RF fields are smallest, to the regions close to electrodes, where the RF field is higher. The ions can absorb more electric energy at this higher RF quadrupole fields from the main RF trapping voltage. They also presented a model that relates dipolar DC operating conditions to the effective internal temperature to which the precursor ion can be elevated [21]. Microsecond time-scale DC pulses can also be used to excited ions for increasing CID efficiency [22–26]. Plass [27] has simulated and explained the effects of a dipolar DC on the ion kinetic energy change inside ion trap. McLuckey's group [19,28–32] found that all of the ion accumulation efficiency, mass analysis, ion isolation, ion/ion reaction, ion activation and tandem mass spectrometry performance can be improved by applying a dipolar DC potential to the exit end-cap electrode, which utilize a monopolar DC field [29] and a dipolar DC field [30].

In digital ion trap (DIT) technology, ion trapping and excitation can be carried out by scanning the rectangular waveform frequency or the waveform period [33–36]. In a previous CID study with DIT, there are several examples of CID that are used in the DIT, such as a sinusoidal dipole excitation waveform with a fixed frequency [37], changing the duty cycle of the resonance excitation waveform or the associated frequency [25,38]. It was suggested that variation of the duty cycle of the digital trapping waveform allows readily introduction of a DC component for BAD experiment [25], however such a convenient application has not been practically implemented in neither a 3D nor a linear digital ion trap.

In this study, we present a new method for ion excitation and CID experiments in a digital linear ion trap mass spectrometer. In this method, while the dipole excitation was still applied in the x direction, a quadrupole DC component was obtained by changing the duty cycle of main digital waveform power to assist the CID process. Rather than using a traditional DC power supply, a certain amount of DC voltages can be obtained by simply manipulating the duty cycle of ion trapping waveform, and this DC voltage was applied between the x and y electrode pairs.

By using this method, we found that both CID efficiency and low mass cutoff (LMCO) effect could be significantly improved. The process was fully controlled by software, without any hardware modifications in digital ion trap mode. The method will supply another method of DC enhanced ion activation and CID. The advantages of this method include simplifying the tandem mass spectrometry procedure, increasing the CID efficiency, and improving the low mass cutoff effect.

Table 1
CID efficiencies with d ranging from 46.09375% to 53.90625%.

d (Duty cycle)	DC (v)	Duration (ms)	T (us)	CID efficiency
50%	0	40	1.705	68.2%
50.78125%	3.126	40	1.680	76.8%
51.5625%	6.256	40	1.625	84.5%
52.34375%	9.396	40	1.585	88.2%
53.125%	12.549	40	1.550	90.4%
53.90625%	15.721	40	1.515	93.6%

2. Method

2.1. Direct current (DC) produced by digital waveform potential

A DC voltage can be deduced when the duty cycle of rectangular waveform is deviated from 50%, assuming a periodic rectangular waveform voltage is generated by switching amplitudes between a higher voltage level V_1 and a lower voltage level V_2. So, a DC potential can be produced by this periodic rectangular waveform voltage if its duty cycle is not 50% as shown in Eq. (1) and Fig. 1. Duty cycle, in terms of d, is defined as the ratio between t_1 and the total period T of the waveform applied as shown Fig. 1. The DC and RF voltages, i.e. U and V, can be expressed with V_1, V_2 and d as Eq. (1) [36] below:

$$U = dV_1 + (1-d)V_2$$
$$V = 2(V_1 - V_2)(1-d)d \quad (1)$$

In this study, V_1 and V_2 are of the same amplitudes but with opposite phases, $V_1 = -V_2$, so the relationship between U and d can be expressed as Eq. (2):

$$U = (2d-1)V_1 \quad (2)$$

Obviously, a positive DC potential U, or negative DC potential voltage −U can be produced if d is deviated from 50%, $U > 0$ if $d > 50\%$, and $U < 0$ if $d < 50\%$. In the case where a linear ion trap was used, as in this study, U and V in Eq. (1) are normally defined for the net DC and AC voltage components on the x pair of electrode, and the DC and AC components on the y pair are the same value but take opposite sign. Table 1 listed some DC components at different experimental conditions.

3. Experimental

All experiments were performed on a homemade three-stage differential pumping vacuum system, the same as that described in previous works [37–39]. A ceramic-based rectilinear digital ion trap with $x_0 \times y_0 = 6\,\text{mm} \times 5\,\text{mm}$ was used. Previous studies gave the effective field radius of this geometry of $r_0 = 5.3\,\text{mm}$. Helium gas was used as an ion-cooling buffer gas as well as a collision gas, and the gas pressure was measured by a gauge outside the trap. The background pressure is around 1×10^{-5} Torr and the pressure will rise to $5–8 \times 10^{-5}$ Torr. Helium gas was introduced through a needle valve. During mass scan the ejected ions were finally detected