

Simulation of the Collisional Cooling Effect in a Quadrupole Ion Trap Mass Spectrometer

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Examination of the collisional cooling effect of the buffer gases on ion trapping and detection in an ion trap mass spectrometer has been undertaken by the SIMION 3D program. Computation for the kinetic energy of ions under various conditions was used to account for the effects of collisional cooling of ions. Several parameters that may affect the collisional cooling effects of ions are evaluated including the existence and the variation of pressure of the buffer gas; the temperature of the ion trap; the size of the inner radius of the ion trap electrodes; the mass to charge ratio of ions; the alternative buffer gases and the q_z values which establish the ion trap trapping environment.

INTRODUCTION

The ion trap mass spectrometer has been widely used in ion-molecule reactions¹⁻⁴ since 1983, the year it came on the market. The reason could be attributed to the advantages of the ion trap mass spectrometer: high sensitivity, nice resolution, fast scan rate, reasonable price and especially for its tandem mass capability.⁵⁻⁷ The existence of the buffer gas in the ion trap mass spectrometer is very important because it provides the function of collision deactivation of the ions and damps the trajectories of an ion's motion in the ion trap leading to a reduction of the kinetic energy of the ions. Therefore, the ion clouds could be more concentrated in the central area of the three dimensional electrodes of the ion trap, favoring the ejection of ions through the small holes on the end cap for detection. Thus, the resolution and sensitivity of the ion trap mass spectrometer can be greatly improved. Among all possible buffer gases that have been used in the ion trap, helium is the best choice, not only because it is inert to react with ions but also because the molecular weight of He is only 4 amu; after colliding with ions it does not change the moving directions of ions and it does not interfere with the detection of spectra either. Therefore, 1 mtorr of He is typically used in the ion trap to improve the sensitivity and resolution of the ion trap. The study of the collisional cooling effect is very important for the operation of the ion trap because a better understanding of this effect will provide a lot of useful information for the development of the quadrupole ion trap to become a more powerfully analytical instrument.

Some simulations in the ion trap mass spectrometer have been reported in the literature: Cooks et al. developed

the ITSIM (Ion Trap Simulation Program) to simulate the motions of ions in the ion trap.⁸ They used the discontinuous collision model for ions to collide with a buffer gas in order to calculate the collision probability for the pressure of the buffer gas and then compared it with a random number to determine whether the collision would take place or not. After collision, it assumed that the moving directions of ions would not change but that the kinetic energy of ions would decrease. The reducing values of kinetic energy of ions may range from 0 to $[(m_{\text{ion}} - m_{\text{buffer}})/(m_{\text{ion}} + m_{\text{buffer}})] \times \text{KE}$ eV, where KE represents the initial kinetic energy before collision. From the results of their simulation, the resolution of an ion trap spectrometer would effectively increase by the addition of a suitable amount of buffer gas inside the ion trap. Dunbar et al. applied Ar and SF₆ as possible alternative buffer gases to investigate under the condition of variation of pressure in order to examine the influence of different kinds of buffer gases on an ion's internal energy and the collisional cooling rate.⁹ Andre et al. used Gaussian function to calculate the ions' energy and their distribution in the three-dimensional electrodes of the ion trap after colliding with different kinds of buffer gases.¹⁰⁻¹² Wu and Brodbelt studied the collisional cooling effect by actually performing experiments in an ion trap mass spectrometer.¹³ They examined many factors that might affect the collisional cooling effect in the trap such as pressure of buffer gas, q_z value, cooling time and tickle voltage of CAD.

The purpose of this simulation is primarily concerned with the influence of a buffer gas on an ion's kinetic energy under various conditions to examine the collisional cooling effect. We used simulation methods to evaluate six parameters that may affect the collisional cooling of ions in the ion

trap including: the existence and the pressure of the buffer gas, the temperature of the ion trap, the radius of the ion trap electrodes, the mass to charge ratio of ions, the alternative buffer gases and the q_z values. A better understanding of these factors that may influence the ion trapping phenomena and ion energy will be discussed.

SIMULATION EXPERIMENT

The simulation program used in this study was the "SIMION 3D, version 6.0 program developed by the Lockheed Idaho Technologies Company.¹⁴ The calculations were performed on an IBM compatible personal computer (Pentium 166 MHz, 32 MB). The setting parameters of the three dimensional electrodes in the ion trap mass spectrometer are provided by this program. This program computed the RF voltage, velocity of ions, and kinetic energy of ions. The standard parameters were set as follows: voltage of the electron ionization source was 70 eV, initial kinetic energy of ions in the source region was 0 eV, number of ions was 50, $q_z = 0.5$, $a_z = 0$, and $r_0 = 1$ cm. The computation results were recorded by the computer and the items recorded include number of ions, mass of ion per charge, time of flight of ions, velocity and kinetic energy of ions. The recording time for all data started from the location where ions were generated in the ion source region to the time when they reached the detector. As to simulation for the collisional cooling effect of the condition of having the buffer gas inside the ion trap, since the original program did not provide the function, we had to write a series of programs and equations into the original program. For example, altering the collisional probability to relate with the temperature and pressure, setting the mass of the buffer gas to 4 amu for Helium buffer gas, and assuming that the buffer gas collided with the ions was elastic collision. The initial velocity of the buffer gas was set at zero, then the collisional probability was calculated from equation 1.^{15,16} According to the Langevin theory,¹⁷ the cross section of collision (σ) can be represented as equation 1 when a single charged ion collides with an atom or a molecule:

$$\sigma = \pi b_0^2 = (2\pi e/4\pi \epsilon_0 v) \times (\alpha_e/\mu)^{1/2} \quad (1)$$

where e is the electronic charge, ϵ_0 is the permittivity of free space, v is the relative velocity of the collision partners, μ is the reduced mass of the collision system and α_e is the elec-

tronic polarizability of the gas atom. From the collisional cross section, the probability of a collision per unit of time can be represented as:

$$P = nv\sigma \quad (2)$$

where P is the collisional probability, n is the number density of collision-gas atoms. Substituting σ value from equation 1 and using the ideal gas law to approximate n value and then to calculate the collisional probability, then the collisional probability can be represented as in equation 3:¹⁶

$$P = (e/2 \epsilon_0) \times (\alpha_e/\mu)^{1/2} \times (p/kT) \quad (3)$$

where p and T represent pressure and temperature of the collision-gas, respectively, and K is the Boltzmann constant. Random collisions were computed by the following procedures in this simulation program:

1. Set values of temperature, pressure, and mass of the buffer gas then use these parameters to calculate the collisional probability by using equation 3.
2. From the calculated collisional probability in procedure 1 to calculate the probability for determining whether the collision would occur or not by the following equation:

$$P' = 1 - e^{(-P)} \quad (4)$$

3. Generate a random number from 0 to 1 when calculating each time step.
4. Compare the probability of collision of each time step with the random number. If the probability of collision is larger than the random number, then the collision would occur.
5. After collision, the reduced factor on final velocity of ion is $(m_{ion} - m_{buffer})/(m_{ion} + m_{buffer})$, where m_{ion} represents mass of ion, and m_{buffer} stands for mass of buffer gas, respectively.⁸
6. Multiply the original velocity of the ion to the reduced factor $(m_{ion} - m_{buffer})/(m_{ion} + m_{buffer})$ on final velocity to get a new value, then store it as the new velocity of the ion.
7. The new velocity of the ion was transformed to the three-dimensional velocity then it was used to calculate the final kinetic energy of this ion by the program.

Since the original program doesn't provide the function for the condition for simulation of the existence of buffer gas in the ion trap, the original program was altered by using the RPN Language of HP calculator to write it as an AS-

CII file in order to perform the above procedures of simulation.

RESULTS AND DISCUSSION

For all the simulation experiments performed in this study, 50 ions of the same mass are used in the calculations. All ions are assumed to be positively, singly charged ions. In the simulation, one wants to simulate as many ions as in the real condition in an ion trap mass spectrometer. However, in this study, the interaction between ion/ion collisions was not considered since only a limited number of ions (50) are in the trap. If at higher ion densities, the Coulombic repulsive effects will become important for the ion trajectories and this may also lead to space charge effects. Thus, the ion-ion repulsion effects can not be ignored.

Mass dependence and the size of the inner radius of the ion trap electrodes on the collisional cooling effect

In the ion trap, the presence of the buffer gas can damp the trajectories of ions toward the center of the ion trap by reducing the kinetic energies of ions.¹³ Therefore, calculating the values of kinetic energy of ions can be used to represent the effect of collisional cooling effect. In order to examine the collisional cooling effect on different mass of

ions, several simulation experiments were performed by comparing the kinetic energies of ions under both with and without 1 mtorr He buffer gas in the ion trap for 50 ions of the same mass. The mass of ions was varied from 30 to 1000 amu. The temperature was maintained at 375 K, $a_z = 0$, and $q_z = 0.5$. The results are shown in Figs. 1-3. Fig. 1 shows the results for computation of the average kinetic energy of ions under normal ion trap inner radius (1 cm). When without 1 mtorr of He buffer gas in the ion trap, the kinetic energies of all ions (indicated by the lines with the solid circle mark) from 30 to 1000 amu were approximately the same (about 66.5 eV), i.e. no collisional cooling effect at all under this condition, all ions possess very high kinetic energy. However, under exactly the same condition but with 1 mtorr of He in the trap, we found that the kinetic energy of all ions (indicated by the lines with the solid triangle mark) was reduced especially for low mass ions (below 200 amu). Thus, the collisional cooling effect decreases with the increasing of mass. Similar trends for mass dependence on collisional cooling effect could be observed in Fig. 2 and Fig. 3. In both figures, the simulation experiments were performed under exactly the same condition except at different radius of the ion trap electrodes, i.e. $r_0 = 0.5$ cm and 0.25 cm in Fig. 2 and Fig. 3, respectively. The results in the three figures show similar trends. In Fig. 2 and Fig. 3, very similar cooling effects for the ions with m/z above 350 are ob-

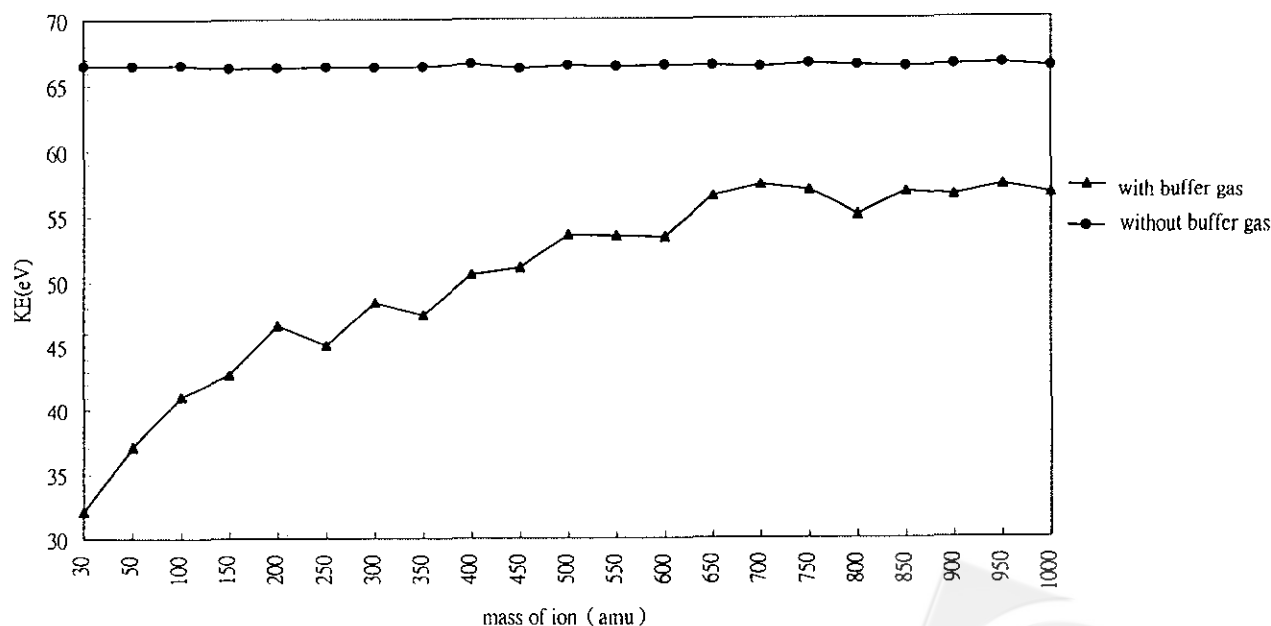


Fig. 1. Comparison of the kinetic energy variation as a function of mass under both with and without 1 mtorr of He buffer gas inside the ion trap for 50 ions of the same mass when the inner radius of ion trap was 1.0 cm (temperature = 375 K, $q_z = 0.5$).

served. This is because the reduced factor $(m_{\text{ion}} - m_{\text{buffer}})/(m_{\text{ion}} + m_{\text{buffer}})$ in step 5 and 6 of the simulation experiment reaches 0.98-0.99 for the ions with m/z above 350 to 1000. Thus, similar trends of the collisional cooling effect for heavier ions with m/z above 350 are observed. This proves that changing the size of the ion trap electrodes would not have any effect on the collisional cooling effect at

all: the kinetic energy of ions increased with the mass of ions. Thus, the collisional cooling effects decreased with the increment of ion mass.

The next goal is to further examine the relationship between the size of the three dimensional ion trap electrodes with the collisional cooling effect. The size of the ion trap depends on the inner radius (r_0) of the three dimensional ion

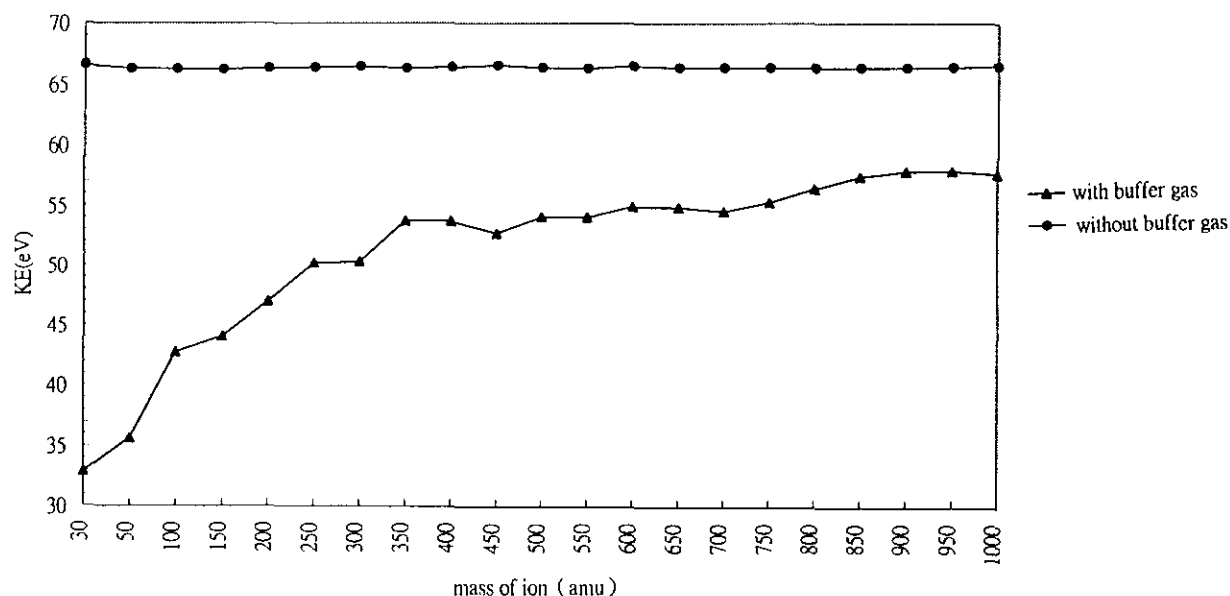


Fig. 2. Comparison of the kinetic energy variation as a function of mass under both with and without 1 mtorr of He buffer gas inside the ion trap for 50 ions of the same mass when the inner radius of ion trap was 0.5 cm (temperature \approx 375 K, $q_z = 0.5$).

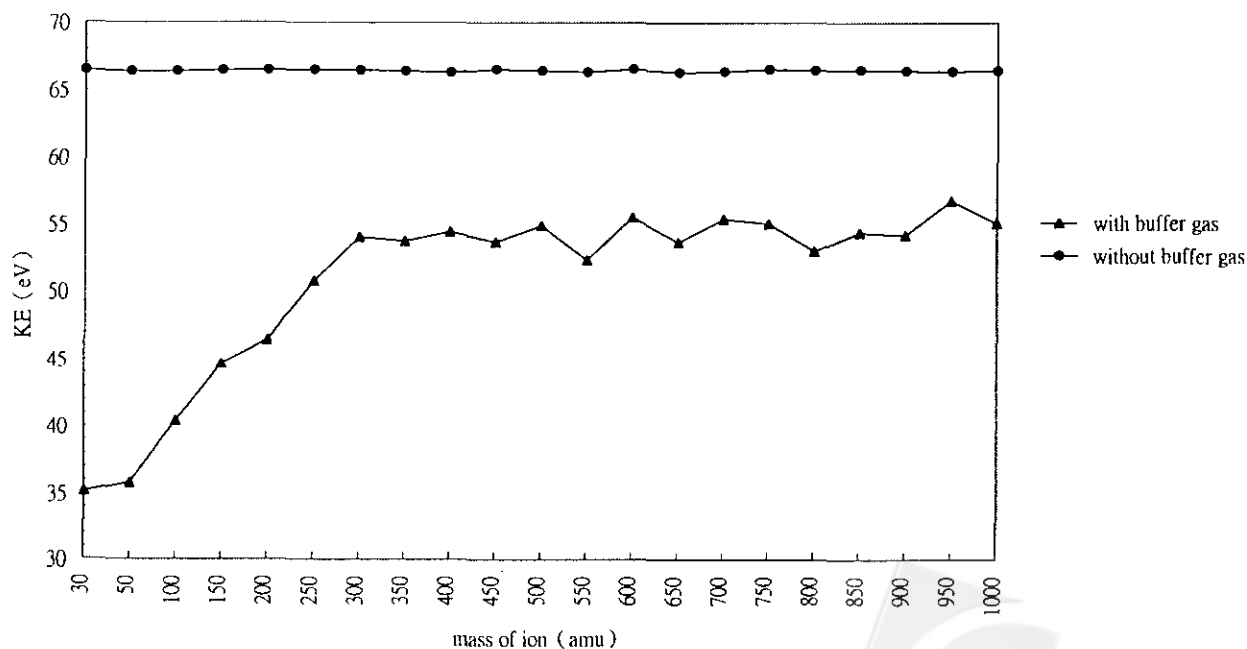


Fig. 3. Comparison of the kinetic energy variation as a function of mass under both with and without 1 mtorr of He buffer gas inside the ion trap for 50 ions of the same mass when the inner radius of ion trap was 0.25 cm (temperature = 375 K, $q_z = 0.5$).

trap electrodes, and the values of kinetic energy of ions can be used to represent the effect of collisional cooling effect. The simulation was performed by comparing the ion's kinetic energy when under the condition of with and without

the existence of 1 m torr of buffer gas inside the various inner radius of the ion trap electrodes. The results are shown in Figs. 4-5. Fig. 4 shows the kinetic energy distributions of ions when no buffer gas is inside the ion trap for 50 ions of

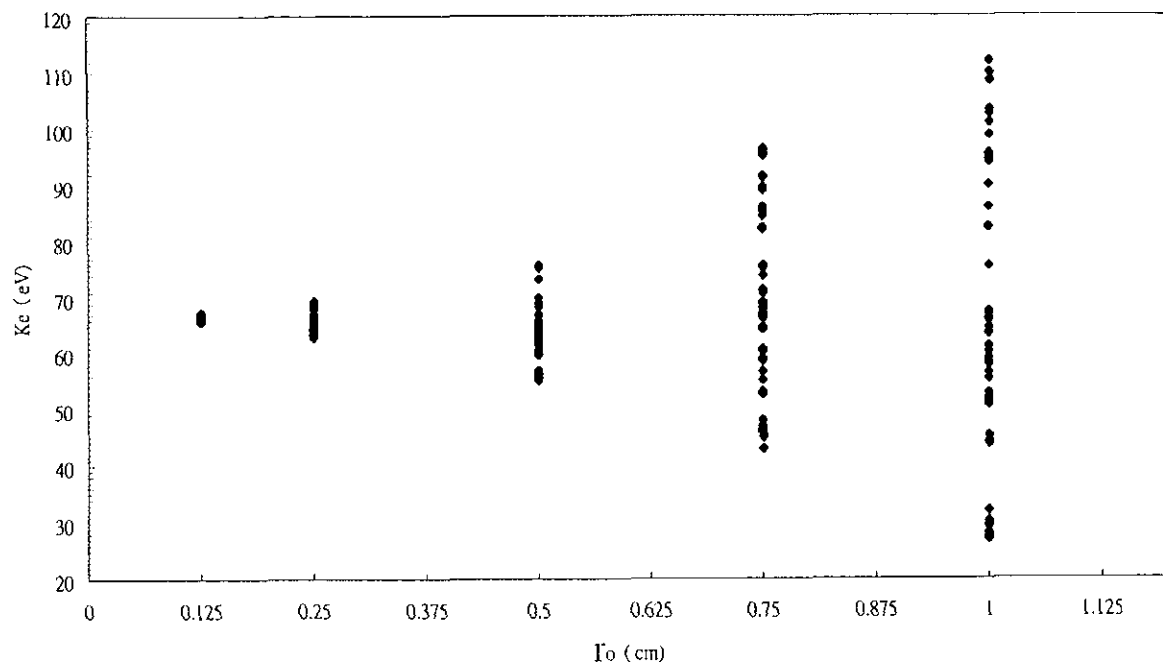


Fig. 4. Kinetic energy distributions of ions under the condition of without buffer gas inside the ion trap for 50 ions of m/z 150 at different inner radius of ion trap electrodes (temperature = 375 K, $q_z = 0.5$).

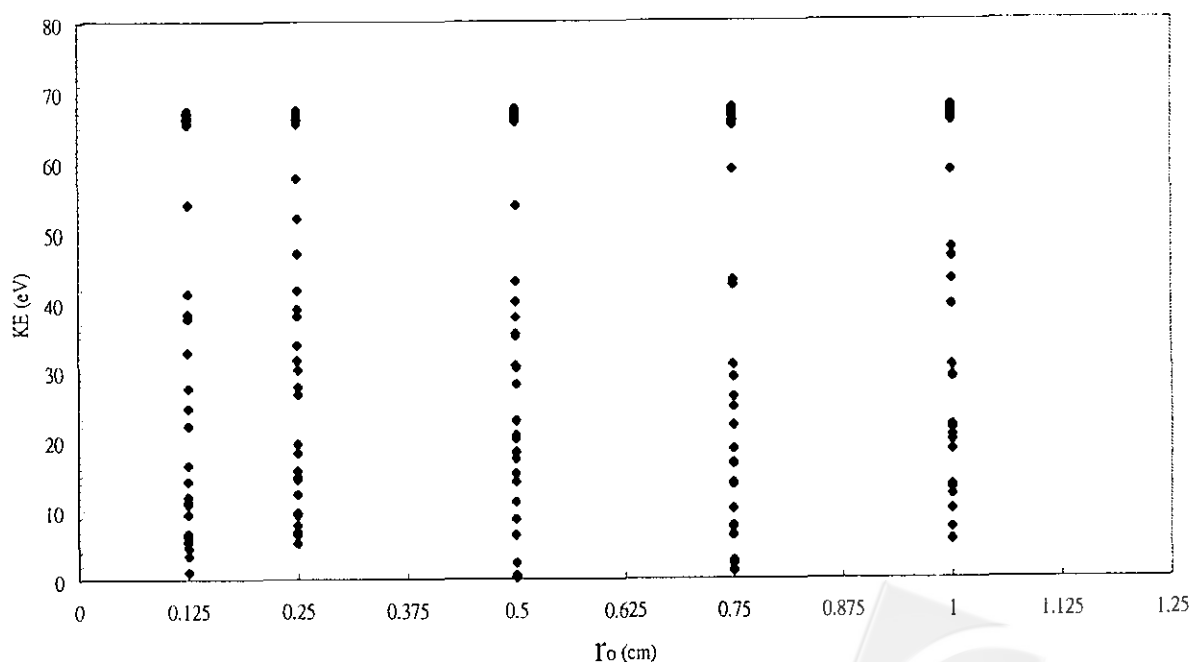


Fig. 5. Kinetic energy distributions of ions under the condition of 1 mtorr He buffer gas inside the ion trap for 50 ions of m/z 150 at different inner radius of ion trap electrodes (temperature = 375 K, $q_z = 0.5$).

the same mass (150 amu) under various inner radius of ion trap electrodes (temperature = 375 K, $q_z = 0.5$). The results show that when the inner radius of the ion trap was smaller, the distribution of an ion's kinetic energy would be narrower. Moreover, when the inner radius of the ion trap electrodes (r_0) is equal to 0.25 cm, the kinetic energies of all ions are almost all concentrated at the same point (about 62 eV). This is because when the inner radius is smaller, the flying route for ions to reach the detector is shorter and thus the flying time of ions becomes shorter too. Thus, the distributions of kinetic energy were narrower. When the inner radius became larger, the time that ions stay in the ion trap electrode will be longer, the impact that ions experienced from the RF electrical field will be larger, and the flying time will be longer too. For the condition of no buffer gas to collide with the ions for damping their trajectories, the trajectories of ions will disperse in the whole space of the three dimensional trap electrodes. In contrast to Fig. 4, Fig. 5 is under the condition of with 1 mtorr of He buffer gas in the trap, 50 ions of m/z 150 under various inner radius conditions. In this figure one could observe that the collisional cooling effect of He causes the kinetic energy of ions distributed from 0-70 eV because the kinetic energy of some ions may be reduced by the existence of the He buffer gas. When the inner radius changed from 0.125 to 1 cm. According to the above mentioned two type experiments, one can make a conclusion that when the inner radius of the ion trap varied, the collisional cooling effect of the buffer gas would

not being affected at all.

Effect of q_z on collisional cooling effect

The effect of storing ions at different values of the stability parameters q_z on collisional cooling effect was evaluated by comparing the kinetic energy of ions when they were under the conditions of both with and without buffer gas inside the ion trap. The q_z value is defined by the following equation:

$$q_z = 8eV/mr_0^2\omega^2 \quad (5)$$

and it is related to the radiofrequency (RF) voltage applied to create the quadrupole field in the ion trap in which ions are trapped. The average kinetic energy of ions is related to q_z . When q_z increases, the frequency of ion's motion will be affected. The q_z parameter directly influence ion's kinetic energy.¹³ Fig. 6 shows kinetic energy variation as a function of q_z values for 50 ions of m/z 250 (temperature = 375 K, pressure of He = 1 mtorr). Both curves in the figure show similar trends: the kinetic energy under both conditions increases slightly with the q_z values no matter whether it has a buffer gas inside the trap or not.

Examination of collisional cooling effect for alternate buffer gases

The use of alternate buffer gases other than He has been reported in the literature.¹⁸⁻²¹ Since the role of the buff-

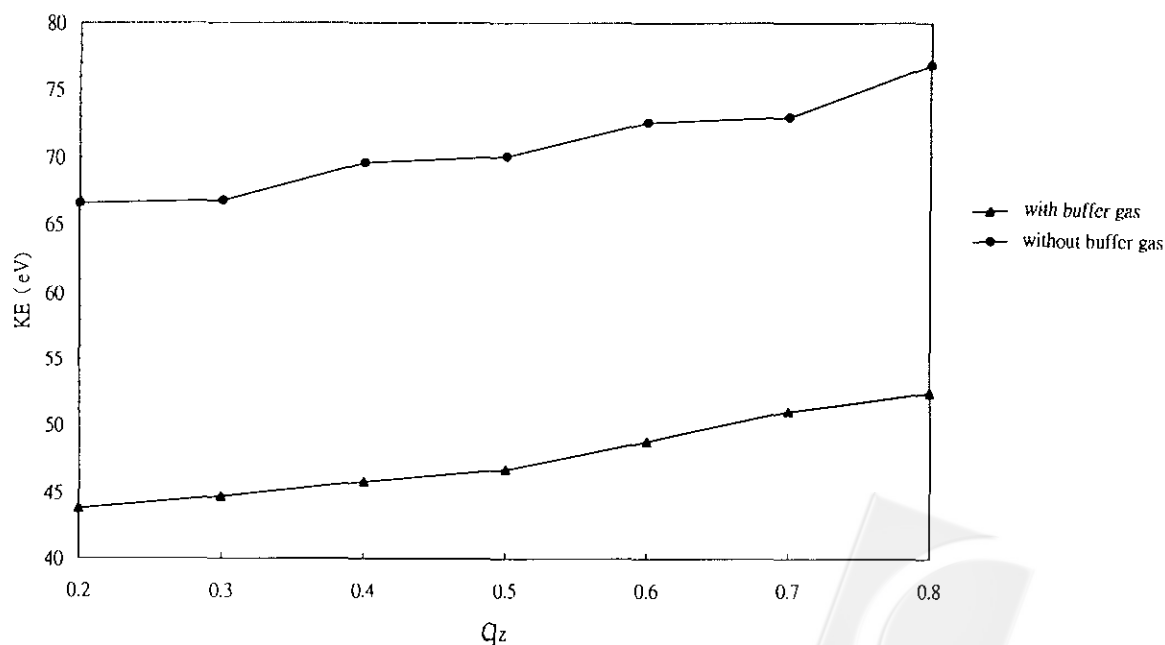


Fig. 6. Kinetic energy variation as a function of q_z values for 50 ions of m/z 250 (temperature = 375 K, pressure of He = 1 mtorr).

er gas is to remove the kinetic energies of ions through ion/neutral collisions, the better target gas should be the one which can remove more kinetic energies of ions after collisions. Therefore, in order to investigate the collisional cooling effect for alternate buffer gases, we applied a simulation method to examine several different kinds of buffer gases including helium (4 amu), nitrogen (28 amu), argon (40 amu), and SF₆ (146 amu). Since from step 5 and 6 of the simulation experiment, one knows that the average energy exchanged per collision depends on the relative masses of ion and buffer gas. Thus, the reduction of the kinetic energies of ions (ΔKE) vs. mass of buffer gas is plotted in Fig. 7. Fig. 7 shows reduction of kinetic energy with different kinds of buffer gases in comparison both with and without the 1 mtorr buffer gas in the ion trap for 50 ions of m/z 200 (temperature = 375 K, the inner radius of the ion trap = 1 cm, $q_z = 0.5$). The Y-axis represents the reduced value of kinetic energy (ΔKE) under the condition of comparing with and without the existence of 1 mtorr buffer gas inside the ion trap. When the mass of buffer gas was heavier, the collisional cooling effect was better. This is because when ions collide with the heavier buffer gases, they are able to remove more kinetic energy from ions. This figure shows that for using nitrogen, Ar and SF₆, the reduction of kinetic energy is approximately the same (about 24–26 eV). However, for He it is 19.477 eV. This is because the collisional probability for a heavier buffer gas to collide with an ion is smaller than

with a lighter buffer gas. It is also because of the μ value which in collisional probability equation influences the collisional probability. From the results we know that He is the worst choice since it reduces the least kinetic energy for all ions. SF₆ is the best choice (26.352 eV). Ar and N₂ got exactly the same results. This is because the Langevin Collision Theory is used to model the binary collisions. This theory is known to underestimate the ion-neutral cross-section when the ion energy is greater than a few eV. However, an initial 70 eV of energy of ion was used in the simulation. Therefore, the similarity of ΔKE between N₂ and Ar can be seen in Fig. 7.

Effect of buffer gas pressure on collisional cooling effect

Set the temperature at 375 K but in different pressures to observe the collisional cooling effect of the buffer gas. When the pressure is reduced, the amount of the buffer gas will be less, and the energy to move the ion will be small. When the pressure is increased, the buffer gas increases also, and the energy to move the ion will be raised. Fig. 8 shows the results of collisional cooling effect by changing the pressure of the buffer gas under the condition of 50 ions of equal mass; the buffer gas was He and the temperature was set at 375 K. According to the following equation: from equation 3 one knows that the collisional probability is proportional to the pressure of the buffer gas. Therefore, when

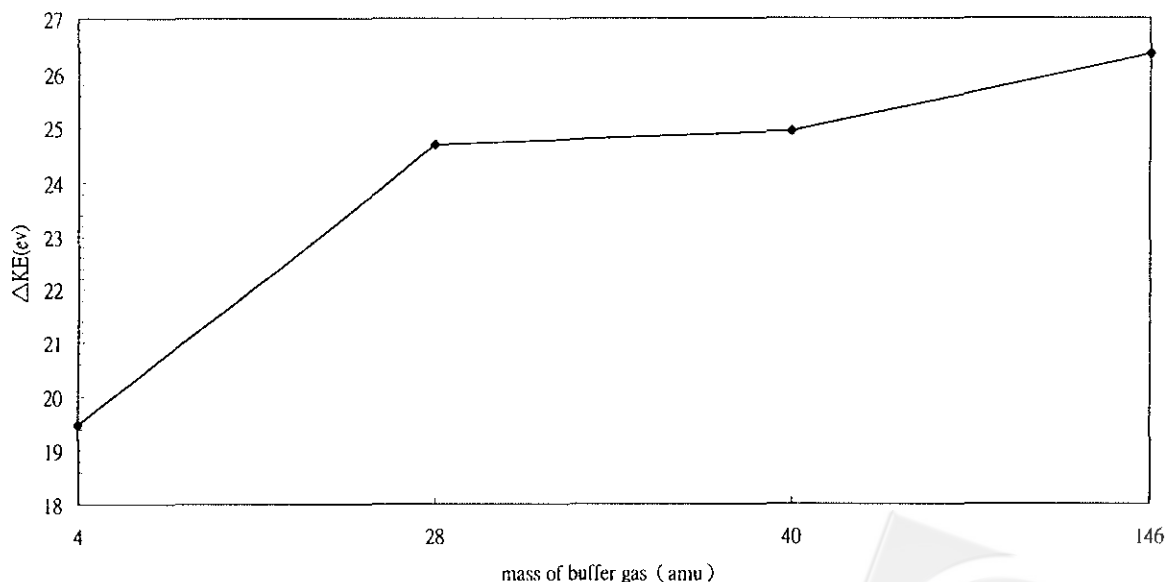


Fig. 7. Reduction of kinetic energy at different kinds of buffer gases in comparison of both with and without the 1 mtorr buffer gas in the ion trap for 50 ions of m/z 200 (temperature = 375 K, the inner radius of the ion trap = 1 cm, $q_z = 0.5$).

the pressure increases, the number of atoms of the buffer gas inside the ion trap would increase, thus the collisional probability would be larger and the kinetic energy of ions could be reduced after collisional deactivation by the buffer gas. Fig. 8 shows the simulation results of kinetic energy variation as a function of pressure of the He cooling gas for 50 ions of m/z 100 (temperature = 375 K, the inner radius of the ion trap electrodes = 1 cm, $q_z = 0.5$). The results are in

agreement with the above-mentioned phenomenon. The kinetic energy of ions is 66.5 eV when without any He buffer gas inside the ion trap. As the pressure increases the curve goes down, i.e. the kinetic energy of ions decrease. The collisional cooling effect shows a linear relationship with the He pressure. This phenomenon is in agreement with the experimental results of Wu and Brodbelt.¹³ When the He pressure equals 1 mtorr, the kinetic energy of ions is reduced to

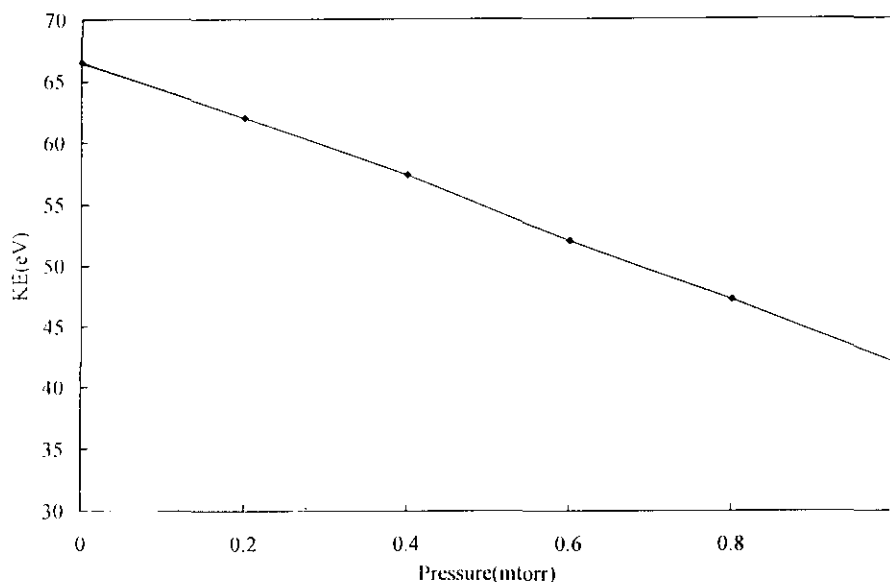


Fig. 8. Kinetic energy variation as a function of the pressure of the He cooling gas for 50 ions of m/z 100 (temperature = 375 K, the inner radius of the ion trap electrodes = 1 cm, $q_z = 0.5$).

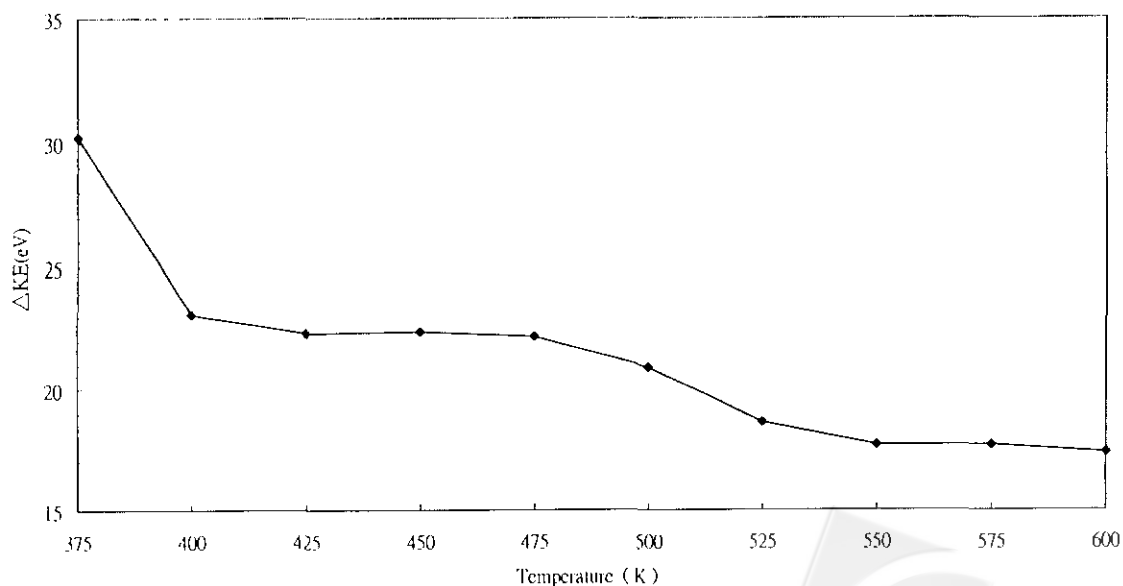


Fig. 9. Variation of reduction of kinetic energy as a function of temperature for 50 ions of m/z 100 ($q_z = 0.5$, the inner radius of ion trap = 1 cm, He pressure = 1 mtorr).

the small value of 42.0 eV.

Effect of temperature on collisional cooling

Investigation for the collisional cooling effect of a buffer gas with the variation of temperature was plotted in Fig. 9. It shows the results for the collisional cooling effect with variation of reduction of kinetic energy as a function of temperature for 50 ions of m/z 100 under various temperatures from 375-600 K. The He pressure was 1 mtorr, $q_z = 0.5$. The longitudinal axis (ΔKE) represents the kinetic energy change value; whether under the condition of with or without buffer gases. Since collisional probability is inversely proportional to temperature ($p \propto 1/T$), when the temperature increases, the collisional probability decreases; note that this means the number of collisions with the neutral He buffer gas would be reduced. However, the kinetic energy of ions would become larger at high temperature because the average kinetic energy of ions would rise at higher temperatures. Thus, the collisional probability between ions with ions in fact might be increased. Our simulation results show that the collisional cooling effects decrease with temperature: at 375 K, ΔKE was 30.23 eV, showing the largest collisional cooling effect; and then it drops with the increasing of temperature. At 600 K, ΔKE is reduced to the smallest value of 17.39 eV, i.e. the collisional cooling effect of buffer gases reaches the smallest value.

CONCLUSION

According to all simulation results obtained above, the existence of buffer gas inside the ion trap or not would dramatically influence the kinetic energy of ions and thus greatly affect the collisional cooling effects. The standard 1 mtorr of He buffer gas would be the best choice. All the simulation results are in good agreement with the experiment results found by Wu and Brodbelt.¹³ Also, variation of the operational parameters in the ion trap and using different kinds of buffer gas affect the collisional cooling effect in the ion trap.

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Key Words

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REFERENCES

1. Wu, H.-F.; Brodbelt, J. S. *J. Am. Soc. Mass Spectrom.* **1993**, *4*, 718-722.
2. Wu, H.-F.; Brodbelt, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 6418-6426.
3. Wu, H.-F.; Brodbelt, J. S. *J. Inclu. Phenom. Mole. Recog. in Chem.* **1994**, *18*, 37-44.
4. Wu, H.-F.; Brodbelt, J. S. *Inorg. Chem.* **1995**, *34*, 615-621.
5. Brodbelt, J. S.; Cooks, R. G. *Spectra* **1988**, *11*, 30-40.
6. Louris, J. N.; Cooks, R. G.; Syka, J. E. P.; Kelly, P. E.; Stafford, G. C. Jr.; Todd, J. F. J. *Anal. Chem.* **1987**, *59*, 1677-1685.
7. Louris, J. N.; Brodbelt, J. S.; Cooks, R. G.; Glish, G. C.; Berkel, G. J. V.; McLuckey, S. A. *Int. J. Mass Spectrom. Ion Processes* **1990**, *96*, 117-137.
8. Reiser, H. P.; Julian, R. K.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Processes* **1992**, *121*, 49-63.
9. Huang, F.-S.; Dunbar, R. C. *J. Am. Chem. Soc.* **1989**, *111*, 6497-6500.
10. Vedel, F.; Andre, J.; Vedel, M.; Brincourt, G. *Phys. Rev.* **1983**, *A27*, 2321-2330.
11. Vedel, F.; Andre, J. *Phys. Rev.* **1984**, *A29*, 2098-2101.
12. Andre, J.; Schermann, J. P. *Phys. Lett.* **1973**, *45A*, 139-140.
13. Wu, H.-F.; Brodbelt, J. S. *Int. J. Mass Spectrom. Ion Processes* **1992**, *115*, 67-81.
14. Dahl, D. A. Idaho National Engineering Laboratory, Idaho Falls, ID, 1995, Version 6.0.
15. March, R. E.; Todd, J. F. J. "Practical Aspects of Ion Trap Mass Spectrometry", vol. 1, CRC Press: Boca, New York, London, Tokyo, **1995**.
16. Su, T.; Bower, M. T. *J. Chem. Phys.* **1973**, *58*, 3027.
17. Gioumousis, G.; Stevenson, D. P. *J. Chem. Phys.* **1958**, *29*, 294.

18. Schey, K. L.; Kentamaa, H. I.; Wysocki, V. H.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Processes* **1989**, *90*, 71.
19. Nystrom, J. A.; Bursey, M. M.; Hass, J. R. *Int. J. Mass Spectrom. Ion Processes* **1983/1984**, *55*, 263.
20. Bursey, M. M.; Nystrom, J. A.; Hass, J. R. *Anal. Chim. Acta* **1984**, *159*, 275.
21. Bursey, M. M.; Nystrom, J. A.; Hass, J. R. *Anal. Chim. Acta* **1984**, *159*, 265.

