Ionization Efficiency from Matrix Surface Bombarded with Xe, Ar, and He Beams

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The ionization efficiency under fast atom bombardment conditions with liquid matrix have been studied. The dependence of fast atoms, Xe, Ar, and He, for the ionization efficiency from the surface of matrix solution bombarded with 6 keV atom beams has been rationalized from the standpoint of elastic/inelastic collisions between a fast atom and a matrix molecule in the surface layer. A relationship between ionization efficiency and atomic mass, which was formulated by a collision theory, predicted a tendency that the efficiency approaches asymptotically to a finite value with increasing atomic mass. The curves for the ionization efficiency *versus* atomic mass, obtained by using a few compounds, were in agreement with the theoretical prediction in the tendency.

1. Introduction

The relationship between ionization efficiency and the mass of fast atom was first reported by Martin *et al.*[1] in order to optimize the experimental conditions for fast atom bombardment mass spectrometry (FABMS). The order of ionization efficiency for the noble gases used was Xe>Ar>Ne. They explained the relationship by which a plot of ion yield versus momentum was linear. The relative momenta of the noble gases are 2.6 for Xe, 1.4 for Ar, and 1.0 for Ne. However, the ion formation from the matrix surface bombarded with fast atom should be rationalized by the energetics and dynamic events in the collisions between fast atom and matrix molecules. The Monte Carlo molecular dynamic calculations for a glycerol solution indicated that a fast primary ion (5 keV/Ar^-) creates a hole deeper than the 10Å surface thickness.[2] The author called the hole a "cavity" as a dense gas-like phase and have presented the cavity model for FAB ionization.[3] The quantity directly relating to the ionization efficiency is the cavity size which means the number of molecules in a cavity. Here we rationalize the ionization efficiency with 6 keV Xe, Ar and He beams from the viewpoint of the elasticity of two-body collision between a fast atom and a matrix molecule. A relationship between the ionization efficiency and atomic mass will be presented to rationalize the experimental results.

2. Experimental

The experiments were performed with a JEOL JMS-DX303 double-focusing mass spectrometer of an electric-magnetic (E-B) sector forward geometry with a JEOL JMA-DA5100 data system (Tokyo, Japan). The FAB gun emission current was 20 mA. The fast atoms used were Xe, Ar, and He. The fast atom was generated from the atomic ions which were accelerated to 6 kV. The source pressure used for each noble gases was 6×10^{-6} Torr. The conditions of ion beam focus and ion detection were common for each noble gases. The mass resolution was 2000. The liquid matrices used were *m*-nitrobenzyl alcohol (NBA) and glycerol (G). The chemicals of NBA, G, methyl stearate, and sinapinic acid were purchased from Tokyo Kasei (Tokyo, Japan), and were used without further purification. The sample (40 μg) was dissolved in 5 μl of matrix, and the 2 μl matrix solution was loaded onto a stainless steel tip. The reproducibility of spectral patterns was confirmed over 1st to 5th scans, and the spectra were averaged over 2nd to 4th scans.

3. Results and Discussion

3.1 Formulation for the ionization efficiency

In general, the ionization efficiency of i-th ion species, y_i, may be given by the product of the gas-phase population of analyte, n, in ionizing cell and the probability for i-th ion formation, w_i, under a given ionization method as follows:

$$y_i = w_i \cdot n \quad (1 \geq w_i \geq 0) \qquad (1)$$

In the case of positive-ion electron ionization method, the population n corresponds to the concentration of gaseous sample which is supplied by using appropriate inlet systems into the ionizing cell and the probability w_i is a function of electron energy and ionization energy of analyte for the formation of molecular ions $M^{+\cdot}$.

In the case of positive-ion FAB method, the population n corresponds to the number of matrix and analyte molecules emitted from the matrix surface as a result of bombardment by energetic atoms and the probability w_i is a function of the proton affinities of matrix and analyte molecules for the formation of protonated molecules $[M+H]^+$. For a given FAB condition, a most important quantity for the ionization efficiency seems to be gaseous population n. The n directly relates to the rate of sputtering of the neutral and ionic species from the matrix surface by atom bombardment. According to the cavity model,[3] the collision between a fast atom A_{fast} and a matrix molecule in the surface layer, B_{surf}, as an earliest event brings about the formation of a cavity or hole in the matrix surface layer consisting of several 10–100 molecules thickness.

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The rate of cavity formation is equal to the flux of fast atom, J_a (atoms/cm^{2}s), so that the rate of sputtering from the matrix surface, dN/dt (particles/cm^{2}s), may be given by the product of the flux and the number of molecular species in a cavity, n_c (particles/cavity), as follows:

$$dN/dt = J_a \cdot n_c \quad (2)$$

The gaseous population n corresponding to the number of matrix and analyte molecules emitted from the matrix surface is directly proportional to the rate of sputtering as follows:

$$n = c_1 \cdot J_a \cdot n_c \quad (3)$$

where c_1 represents a proportional constant. The beam flux J_a is relating to the emission current, so that the population n is determined by the number of molecules in a cavity, n_c. The estimation of the quantity n_c is an aim in this paper.

Considering the situation that an energetic atom A_{fast} with kinetic energy $E_{ao} = m_a \cdot (v_{ao})^2/2$ collides with a stationary matrix molecule B_{surf} of mass m_b, the initial kinetic energy E_{ao} can be transformed into kinetic energies $E_{a1} = m_a \cdot (v_{a1})^2/2$ and $E_{b1} = m_b \cdot (v_{b1})^2/2$, and internal energy ΔE_b as follows:

$$E_{ao} = m_a \cdot (v_{a1})^2/2 + m_b \cdot (v_{b1})^2/2 + \Delta E_b \quad (4)$$

where ΔE_b represents the increments of internal energy in the matrix molecule B_{surf}. In the case of $\Delta E_b = 0$, the event is an elastic collision which means that total kinetic energy is conserved before and after the collision. On the other hand, the condition of $\Delta E_b > 0$ represents the event is an inelastic collision. The maximum increments of internal energy, $\Delta E_{b,max}$, which is transferred into B_{surf} due to the inelastic collision can be given by the same expression as that of center-of-mass collision energy E_{cm} as follows[4]:

$$\Delta E_{b,max} = E_{ao}[m_b/(m_a + m_b)] \quad (5)$$

The term in right-hand side, E_{ao}, corresponds to laboratory collision energy E_{lab}.

The internal energy increments ΔE_b will be utilized to ionize and degrade the matrix molecules like a gas-phase FAB process,[5] so that the conversion of initial kinetic energy E_{ao} into internal energy seems to be disadvantageous for a phase explosion or cavity formation through collision cascade. For an effective sputtering of molecular species from the matrix surface, the initial energy E_{ao} have to convert into the work for cavity formation as highly as possible, ΔW_c, not into internal energy of molecules. In other words, the conversion of the initial energy E_{ao} into the work ΔW_c means that E_{ao} converts into the kinetic energies of matrix molecules in the cavity, as shown in the second term of expression (6):

$$E_{ao} = m_a \cdot (v_{a1})^2/2 + \Delta W_c + \Delta E_b \quad (6)$$

where the work ΔW_c can be divided into the kinetic energy term for matrix molecules after collision and latent heat for the formation of a cavity, q, as follows:

$$\Delta W_c = \Sigma_i m_{bi} \cdot (v_{bi1})^2/2 + q \quad (7)$$

Using the expression (5), here we define the minimum value which is convertible to the work for cavity formation as follows:

$$\Delta W_{c,min} = E_{ao} - \Delta E_{b,max} = E_{ao}[1 - m_b/(m_a + m_b)] \quad (8)$$

Since the cavity size may increase with increasing the value of $\Delta W_{c,min}$, it is reasonable to assume that the quantity n_c is proportional to $\Delta W_{c,min}$, *i.e.*,

$$n_c = c_2 \cdot \Delta W_{c,min} \quad (9)$$

where c_2 represents a proportional constant. Applying (8) and (9) to the expression (3) for the gaseous population n, we can obtain a relationship between n and the mass of fast atom m_a as follows:

$$n = c_1 \cdot c_2 \cdot J_a \cdot E_{ao}[1 - m_b/(m_a + m_b)] \quad (10)$$

Using the basic expression (2), consequently, the ionization efficiency of i-th ion species, y_i, under FAB conditions may be given as follows:

$$y_i = w_i \cdot c_1 \cdot c_2 \cdot J_a \cdot E_{ao}[1 - m_b/(m_a + m_b)] \quad (1 \geq w_i \geq 0) \quad (11)$$

The curves for y_i *versus* m_a were simulated as shown in Fig. 1, by fixing each parameters as follows:

$E_{ao} = 1$, $m_b = 153$, $w_i = 1$, $c_1 = 1$, $c_2 = 1$,
$J_a = 1$; $m_a = 1$–150 (for Fig. 1a),
$E_{ao} = 1$, $m_b = 153$, $w_i = 1$, $c_1 = 1$, $c_2 = 1$,
$J_a = 1$; $m_a = 1$–500 (for Fig. 1b).

The result obtained from theoretical consideration predicts that the ionization efficiency sputtered from matrix surface approach asymptotically to a limited value of $w_i \cdot c_1 \cdot c_2 \cdot J_a \cdot E_{ao}$ with increasing atomic mass m_a of fast atoms.

3.2 Ionization efficiency from NBA and G surfaces with Xe, Ar, and He bombardment

Positive-ion FAB mass spectra of neat matrices NBA and G were obtained with 6 keV Xe, Ar, and He beams. The FAB mass spectra of NBA with Xe and He beams are shown in Fig. 2, though these spectra were already reported.[3] The FAB mass spectra of G with Xe, Ar, and He beams are shown in Fig. 3. Although the FAB mass spectra with Xe and Ar beams were almost the same in pattern for both compounds, the relative abundances of the cluster ions $[M+H+nM]^+$ ($n \geq 1$) with Ar were slightly lower than those of the cluster ions with Xe beam. The FAB mass spectra with He beam were quite different from those with Xe and Ar beams. A most

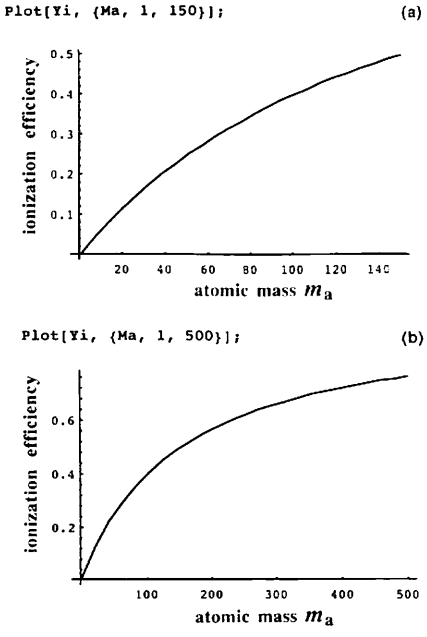

Fig. 1. Curves for ionization efficiency y_i *versus* atomic mass m_a, simulated from the expression (11) in the atomic mass ranges of (a) 1–150 and (b) 1–500.

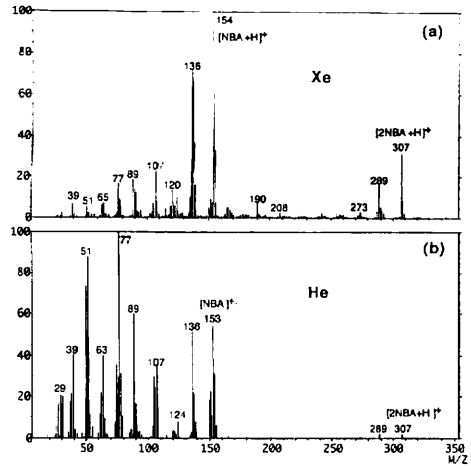

Fig. 2. FAB mass spectra of neat *m*-nitrobenzyl alcohol with 6 keV (a) Xe and (b) He beams.

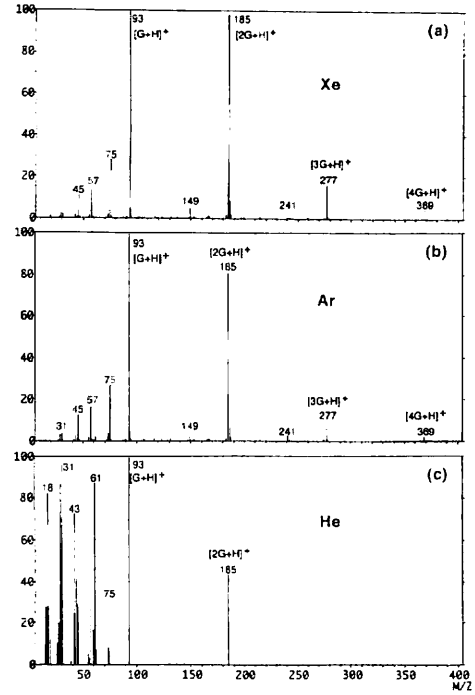

Fig. 3. FAB mass spectra of neat glycerol with 6 keV (a) Xe, (b) Ar, and (c) He beams.

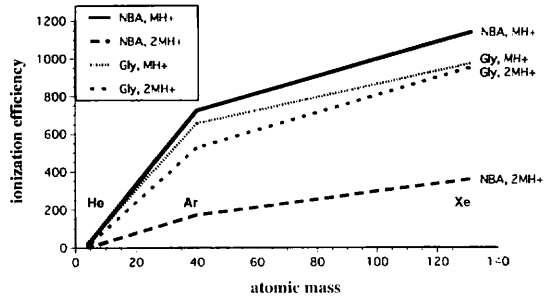

Fig. 4. Absolute abundances for the monomeric and dimeric ions of *m*-nitrobenzyl alcohol and glycerol with 6 keV Xe, Ar, and He beams.

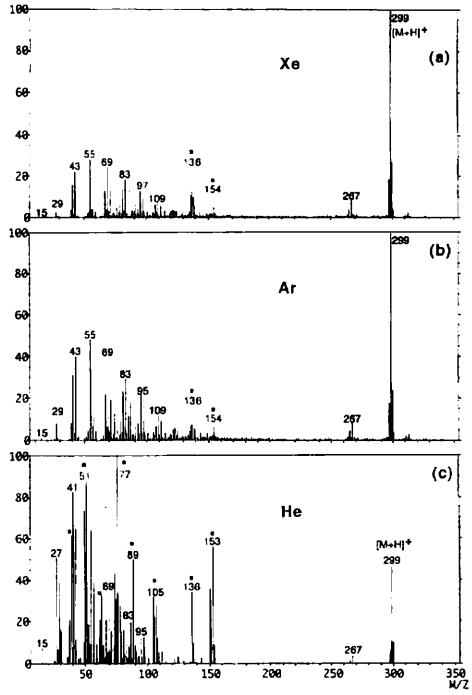

Fig. 5. FAB mass spectra of methyl stearate obtained by using *m*-nitrobenzyl alcohol matrix, with 6 keV (a) Xe, (b) Ar, and (c) He beams.

significant characteristic in the spectra with He was the appearance of intense and abundant fragment ions. It is particularly of interest in connection with the conversion of fast atom kinetic energy E_{a0} into the internal energy ΔE_b of matrix molecules that the FAB mass spectrum of NBA shows a peak that corresponds to the molecular ion $M^{+\cdot}$ at *m/z* 153, as well as intense fragment ions.[3] These characteristics with He beam indicate that stronger inelastic collisions leading to electronic and vibrational excitations occur on the matrix surface than with Xe and Ar beams. This indication is consistent with the theoretical considerations described above.

The peak abundances of the protonated molecules $[M+H]^+$ and dimeric ions $[2M+H]^-$ for NBA and G are plotted against the atomic masses of He, Ar and Xe (Fig. 4). The ionization efficiency was estimated by using the values as printed in the FAB mass spectral data. The values are correspond to absolute peak abundances. Since the expression (11) predicts that the efficiency y_i approaches asymptotically to the value of $w_i \cdot c_1 \cdot c_2 \cdot J_a \cdot E_{a0}$ with increasing atomic mass m_a, the resulted curves in Fig. 3 are in agreement with the theoretical prediction in a tendency.

3.3 Ionization efficiency from the surface of NBA solutions of methyl stearate and sinapinic acid with Xe, Ar, and He bombardment

Furthermore, the FAB mass spectra of methyl stearate and sinapinic acid were obtained with Xe, Ar and He beams. In all the spectra, asterisks indicate the background peaks originating from the NBA matrix. The FAB mass spectrum of methyl stearate with He beam showed intense and abundant matrix peaks (*), while the spectra with Xe and Ar beams mainly showed the peaks originating from analyte at *m/z* 299, 267, 109, 97, 83, 69, 55, 43, 29, and 15, as shown in Fig. 5. The relative abundances of analyte fragment ions at *m/z* 109, 95, 83, 69, 55, 43 or 41, 29 or 27, and 15 to the protonated molecule $[M+H]^+$ at *m/z* 299 were highest

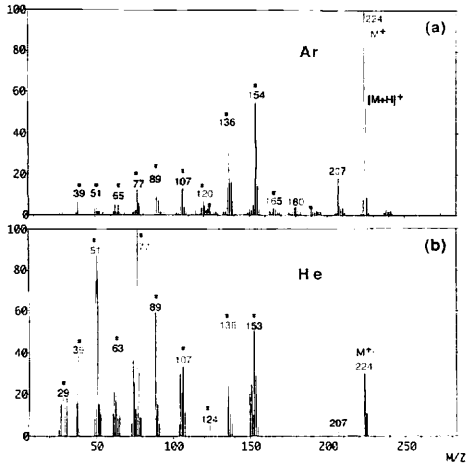

Fig. 6. FAB mass spectra of sinapinic acid obtained by using glycerol matrix, with 6 keV (a) Ar and (b) He beams.

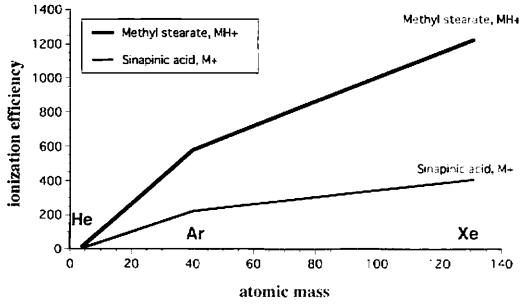

Fig. 7. Absolute abundances for the molecular-related ions of methyl stearate and sinapinic acid with 6 keV Xe, Ar, and He beams.

when He beam was used. The spectrum with He beam demonstrated that the fast atom kinetic energy E_{a0} was mainly used to form matrix molecular ion $M^{+\cdot}$ at *m/z* 153 and to form the fragment ions of matrix and analyte.

Since the FAB mass spectra of sinapinic acid with Xe and Ar beams were almost the same in pattern, the spectra with Ar and He beams are shown in Fig. 6. Whereas the spectra with Xe and Ar beams showed preferential peaks that correspond to molecular ion $M^{+\cdot}$ at *m/z* 224 and protonated molecule $[M+H]^+$ at *m/z* 225, the spectrum with He beam showed intense matrix peaks (*). This observation can be explained by following descriptions. The high energy He atoms first collide with matrix molecules as a solvent, so that the kinetic energy E_{a0} may be mainly converted into the internal energy of matrix molecules according to the relation (5). In this case, the energy E_{a0} is utilized for the ionization and fragmentation of matrix molecules and the ionization efficiency from matrix surface will give the lowest value because the energy E_{a0} can not be utilized for the formation of cavity.

The ionization efficiency of $[M+H]^+$ for methyl stearate and $M^{+\cdot}$ for sinapinic acid are plotted against the atomic masses of He, Ar, and Xe (Fig. 7). The curves obtained are consistent with the curves simulated in Fig. 1 in the tendency.

4. Conclusion

The mechanism for the ion formation under FAB conditions is really complicated owing to the instantaneous dynamic events such as high-energy atom/molecule collisions, energy conversion through collision cascade in condensed phase, explosive phase transition, and ion/molecule reactions. Here we tried to rationalize the ionization efficiency from the surface of matrix solution bombarded with fast Xe, Ar, and He beams, by formulating a relationship between the ionization efficiency and atomic mass of fast atom. The ionization efficiency was correlated to a degree of the elastic collision between a fast atom and a matrix molecule. The theoretical expression derived for the relationship between the ionization efficiency and atomic mass successfully explained the experimental results for a few compounds treated here.

References

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