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## Diffusion mechanisms in the Fe<sub>3</sub>Si alloys<sup>\*</sup>

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**Abstract:** In this paper, the possible reasons for the high thermal vacancy concentration and the low migration barriers for the Fe atom diffusion in the stoichiometric D0<sub>3</sub> structure Fe<sub>3</sub>Si have been discussed. The high thermal vacancy concentration was attributed to the compression of Fe - Fe atomic pairs and the tension of Fe - Si atomic pairs in Fe<sub>75</sub>Si<sub>25</sub>. The deformations (compression or tension) of the atomic pairs increase the interatomic potentials and thus decrease the enthalpies of vacancy formation. The low migration barriers for the Fe atom diffusion in Fe<sub>75</sub>Si<sub>25</sub> were related to the symmetric property of the triangular barriers. Additionally, it was considered that the Si atoms in Fe<sub>3</sub>Si could probably migrate via nearest-neighbour jumps without disturbing the long-range order of atomic arrangements, provided that during the diffusion process the residence time on the antistructure sites is very short.

**Keywords:** Self-diffusion; D0<sub>3</sub> - Fe<sub>3</sub>Si alloys; Thermal vacancy; Migration barriers

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### 1 Introduction

With the only exception that the small impurity or minority atoms can move by the interstitial mechanism, it is mostly the vacancy that is held responsible for the diffusion of atoms in the ordered alloys<sup>[1]</sup>. It was generally considered that the minority atoms in the ordered alloys, such as the Si atoms in Fe<sub>3</sub>Si, cannot migrate randomly via the nearest-neighbour (NN) jumps, because this mechanism may generate more and more antisite defects and hence the order of alloy would be destroyed<sup>[2,3]</sup>. In this case, diffusion of the Si atom can only take place via direct jumps to further distant sites on sublattices with Si atoms, or via mechanisms involving more than one elementary jump process, e. g. the six-jump cycle mechanism<sup>[4,5]</sup>.

In our opinions<sup>[6]</sup>, however, it is probable, not

only possible, that the Si atoms migrate via NN jumps in Fe<sub>3</sub>Si without disturbing the long-range order, and involving no unique jump process. Since the residence time of the Si atoms on the antistructure sites could be so short that there are a very few of Si atoms on the 'wrong' sublattices measured at any time. Furthermore, the majority atoms Fe can also migrate to the antistructure sites via NN jumps, although there are NN sites belonging to the Fe atoms.

But the theoretical problems of atomic diffusion in the Fe<sub>3</sub>Si alloys are far from solved. Mössbauer spectroscopy experiments by Sepiol and Vogl have shown that diffusion of the Fe atoms in Fe<sub>75</sub>Si<sub>25</sub> is astonishingly much faster than that of Fe diffusion in Fe-rich Fe<sub>3</sub>Si, or in pure BCC iron<sup>[7-9]</sup>. In other words, the less the Fe content of Fe<sub>3</sub>Si is, the faster the diffusion of Fe atoms would be. By contrast, self-diffusivity of Si is a

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great deal slower and much less sensitive to the Si content. Herein we try to analyze the diffusion mechanisms to explain the interesting results of previous experiments.

## 2 Thermal formation of vacancies in Fe<sub>3</sub>Si

Thermal vacancies and the effective vacancy formation enthalpies of Fe<sub>3</sub>Si with the D0<sub>3</sub> structure have been investigated by the positron-lifetime spectroscopy method<sup>[10]</sup>. High vacancy concentration was deduced for the stoichiometric alloy Fe<sub>75</sub>Si<sub>25</sub> from the trapping of positrons. At about 750 K the trapping rate in Fe<sub>75</sub>Si<sub>25</sub> reaches saturation, while at which temperature the off-stoichiometric alloy Fe<sub>79</sub>Si<sub>21</sub> contains nearly no vacancies (Fig. 1), although an extrapolation of the vacancy concentration of Fe<sub>79</sub>Si<sub>21</sub> also yields in the percent range near the melting temperature<sup>[10,11]</sup>.

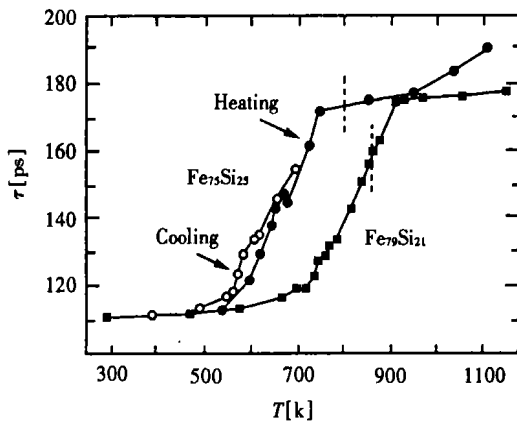


Fig. 1 Temperature variation of the mean positron lifetime  $\tau$  in Fe<sub>75</sub>Si<sub>25</sub> (measured between 5 and 24 h after the temperature change) and Fe<sub>79</sub>Si<sub>21</sub>. The dashed lines indicate the ferromagnetic order-disorder transitions at  $T_c^{[10]}$

Generally, the vacancy concentrations in alloys are higher than the vacancy concentrations in pure metals<sup>[12]</sup>, yet how can we understand the sensitive relationship between the vacancy concentrations and the alloy compositions for the Fe<sub>3</sub>Si alloys?

As Shown in Fig. 2, the D0<sub>3</sub> structure is an ordered BCC structure with three different sublattices  $\alpha$ ,  $\gamma$ , and  $\beta$ . In Fe<sub>75</sub>Si<sub>25</sub>, the Fe atoms are located on two different sites  $\alpha$  and  $\gamma$ , and the Si atoms on  $\beta$ . It is shown that the cluster of one Fe atom on  $\gamma$  site with eight nearest-neighbour Fe atoms on  $\alpha$  is enclosed in the

net of Si atoms on  $\beta$  (Fig. 3). Since the equilibrium bonding distance  $r_1$ ,  $r_2$  of Fe - Fe and Fe - Si atompairs respectively are not equal, the enclosed structure may result in the deformation in the whole crystal lattice. The deformed interatomic distance  $R_1$ ,  $R_2$  of Fe - Fe and Fe - Si atompairs respectively should

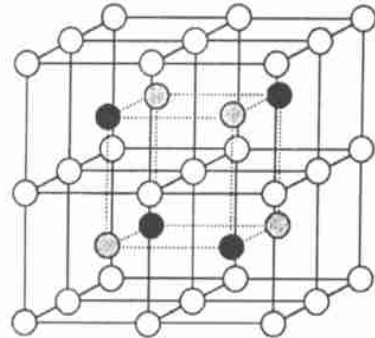


Fig. 2 Unit cell of the D0<sub>3</sub> structure Fe<sub>3</sub>Si with full order. The Fe atoms occupy open circles ( $\alpha$  sites) and grey circles ( $\gamma$  sites) and the Si atoms occupy black circles ( $\beta$  sites)

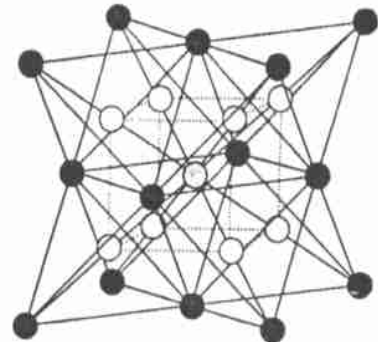


Fig. 3 In the Fe<sub>3</sub>Si matrix with full order, the cluster of one Fe atom on  $\gamma$  site with eight nearest-neighbor Fe atoms on  $\alpha$  is enclosed in the net of Si atoms on  $\beta$  sites

satisfy the geometrical restriction

$$R_1 = R_2 = r \tag{1}$$

For values of  $|r_1 - r_2| \ll r_1$ , the elastic deformation energy  $E_1$  of the Fe - Fe atompairs can be approximately given by

$$E_1 = k_1 \frac{(r - r_1)^2}{2} \tag{2}$$

and the elastic deformation energy  $E_2$  of the Fe - Si atompairs

$$E_2 = k_2 \frac{(r - r_2)^2}{2} \tag{3}$$

where  $k_1$  (or  $k_2$ ) is the force constant of the Fe - Fe (or Fe - Si) atompairs<sup>[13]</sup>.

Considering the quantity ratio of Fe - Fe and Fe - Si atompairs is 1 : 1 in Fe<sub>75</sub>Si<sub>25</sub>, the real interatomic distance  $r_0$  can be given by the harmonic deformation function

$$r_0 = r \left| \frac{\partial(l_1 + l_2)}{\partial r} \right| = 0$$

i. e.

$$r_0 = \frac{k_1 r_1 + k_2 r_2}{k_1 + k_2} \tag{4}$$

Substituting in Eq. (2) and (3) shows that

$$E_1 = k_1 \frac{(r_1 - r_0)^2}{2} \tag{5}$$

and

$$E_2 = k_2 \frac{(r_2 - r_0)^2}{2} \tag{6}$$

where  $E_1$ ,  $E_2$  are the deformation energy of Fe - Fe and Fe - Si atompairs, respectively, resulting from the harmonic deformation of atompairs in Fe<sub>3</sub>Si matrix with full order (Fig. 4).

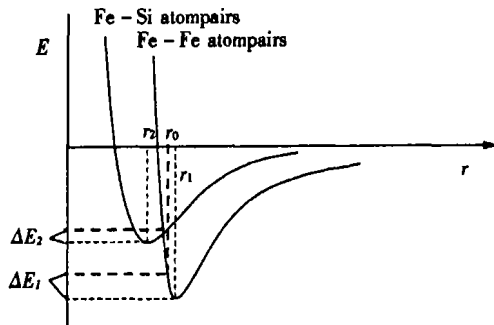


Fig. 4 Interatomic potential function  $E$  of Fe - Fe atompairs and Fe - Si atompairs plotted versus interatomic distance  $r$ .  $r_0$  is the deformed interatomic distance of Fe - Fe and Fe - Si atompairs in Fe<sub>75</sub>Si<sub>25</sub>

The deformation energies  $E_1$  and  $E_2$  increase the potential energies of Fe and Si atoms and thus attribute to the easier formation of vacancies in Fe<sub>75</sub>Si<sub>25</sub>. If the Fe content increases in Fe<sub>3</sub>Si, the enclosed structure of Fe<sub>75</sub>Si<sub>25</sub> matrix would be destroyed and the average deformation energies in the whole crystal would decrease to the local lattice-distortion energies. Therefore, thermal vacancies in Fe<sub>3</sub>Si also decrease.

### 3 Self-diffusion in Fe<sub>3</sub>Si

For Fe<sub>75</sub>Si<sub>25</sub>, the resulting value from high temperature <sup>57</sup>Fe Mössbauer spectroscopy of the Fe self-diffusivity is strikingly high; it amounts to  $5 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$  already at 993 K, but a factor of 5 to 10 lower for the off-stoichiometric alloy Fe<sub>80</sub>Si<sub>20</sub><sup>[10]</sup>. Radiotracer investigation by Gude and Meher<sup>[14]</sup> also indicates that Fe diffusion in Fe<sub>3</sub>Si is strongly dependent on the composition; with increasing Fe content the Fe diffusivity decreases rapidly. But diffusion of Si (simulated by <sup>71</sup>Ce) is much less affected by the composition (Fig. 5), i. e. the diffusion of both components is obviously not 'coupled'<sup>[15]</sup>.

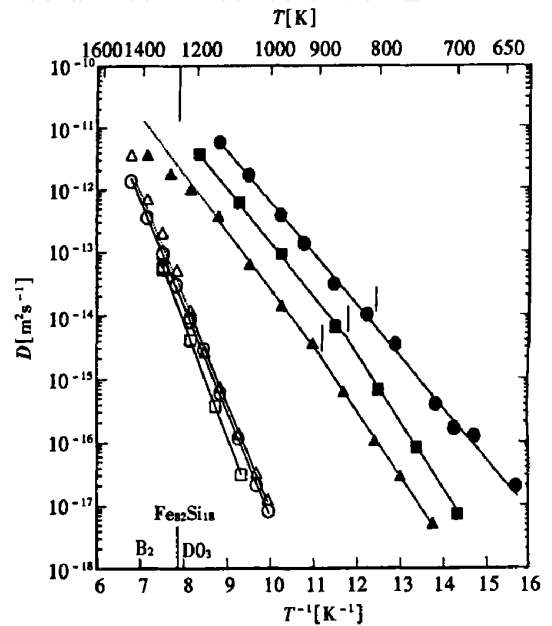


Fig. 5 Temperature dependence of Fe and Ge diffusion in Fe<sub>3</sub>Si alloys of three different compositions. One  $D$  value for Si diffusion has also been measured. The Curie temperatures have been indicated by vertical line segments<sup>[15]</sup>

$\left. \begin{matrix} \text{Fe}_{75}\text{Si}_{24} : \\ \text{Fe}_{79}\text{Si}_{21} : \\ \text{Fe}_{82}\text{Si}_{18} : \end{matrix} \right\} ^{59}\text{Fe}; \quad \left. \begin{matrix} \text{Fe}_{76}\text{Si}_{24} : \\ \text{Fe}_{79}\text{Si}_{21} : \\ \text{Fe}_{82}\text{Si}_{18} : \end{matrix} \right\} ^{71}\text{Ce} \quad \blacktriangledown \text{Fe}_{76}\text{Si}_{24} : ^{31}\text{Si}$

Upon deviation from the stoichiometric composition to the iron rich side, maybe the thermal vacancy concentration decreasing account for the decrease of the self-diffusivity of Fe in Fe<sub>3</sub>Si. However, it fails to explain the 'decoupled' diffusion of the Si atoms. Furthermore, Mössbauer experiments imply that in the off-stoichiometric alloy Fe<sub>80</sub>Si<sub>20</sub> or Fe<sub>82</sub>Si<sub>18</sub>, there are

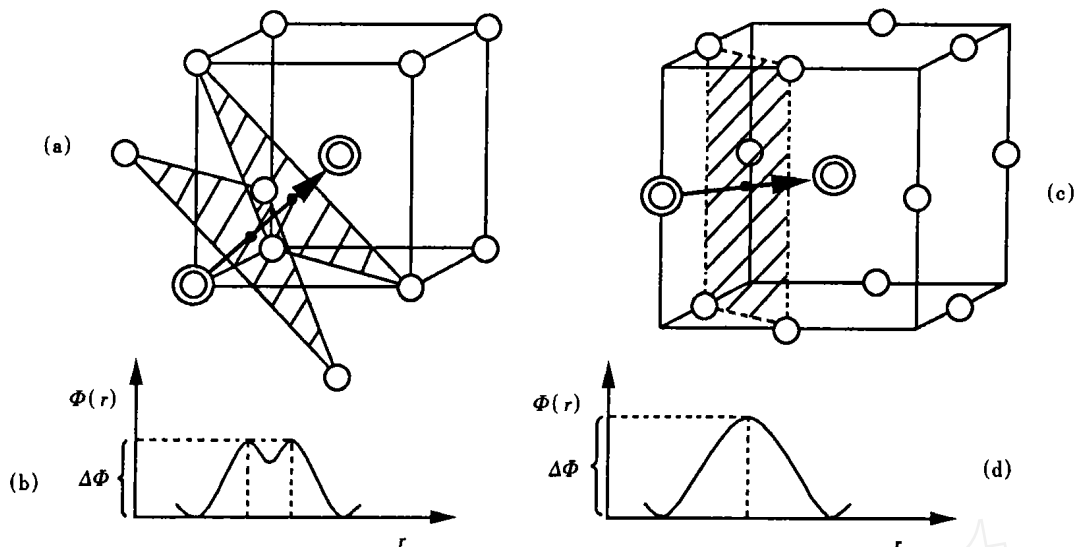


Fig. 6 (a)(b) For an atom migration in the BCC structure via an NN jump there are two barriers of triangular shape to overcome, while (c) (d) for an NN jump in the FCC structure the gate is the four atoms at the halfway point

significantly more jumps between the  $\alpha$  and  $\beta$  sites than jumps between the  $\beta$  and  $\gamma$  sites<sup>[7,16]</sup>.

So it remains herein an open problem for discussion that why the Fe atoms jumping to the antistructure sites in  $Fe_3Si$  becomes dominating when leaving stoichiometry versus the Fe - rich side.

As we know, for an atom diffusion in the BCC structure via an NN jump there are two barriers of triangular shape to overcome; while for an NN jump in the FCC structure the gate is the four atoms at the halfway point (Fig. 6)<sup>[17]</sup>. In a successful jump, when the atom moves from the average position by thermal activation, its potential energy  $\Phi(r_0)$  increases to a maximum  $\Phi(r_0) + \Delta\Phi$  at the barrier and then decreases. This maximum is the least height for a certain path which defines the saddle point of the function  $\Phi(r)$  and the height of the potential barrier  $\Delta\Phi$ . In the pure BCC (or FCC) structure, the potential energy function  $\Phi(r)$  described by this potential-barrier model is perfectly symmetric (Fig. 6 (b), (d)).

For the ordered alloys, the geometric characteristics of the potential function of atom migrations via NN jumps are much complicate. In the  $Fe_3Si$  alloy with full order, when the Fe atom jumps from the  $\alpha$  to the  $\gamma$  sublattice it has to overcome the first barrier of triangular shape consisting of three Si atoms and the second of three Fe atoms (Fig. 7).

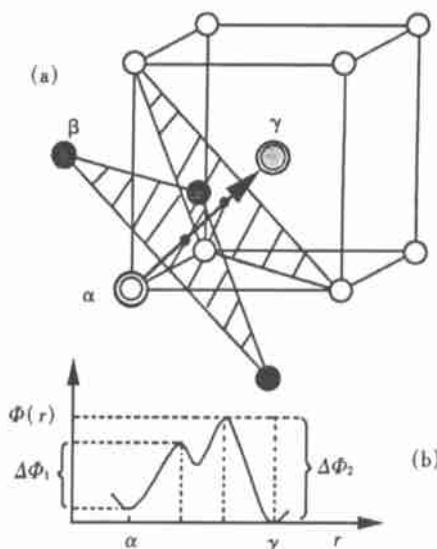


Fig. 7 In the stoichiometric  $D0_3$  structure  $Fe_3Si$ , the Fe atom jumps from the  $\alpha$  to  $\gamma$  sublattice to overcome the first barrier of triangular shape consisting of three Si atoms on  $\beta$  sites and the second of three Fe atoms on  $\alpha$  sites

This jumping path, symmetric in geometry, could be referred to as 'rapid passage' for the Fe atoms diffusion in  $Fe_{75}Si_{25}$ . In  $Fe_{75}Si_{25}$ , each Si atom relates to 24 rapid passages for the Fe atoms jumping between the  $\alpha$  and  $\gamma$  sites, i.e. the  $\beta$  sublattice or the Si atoms net provides the triangular-barriers as the rapid passages for Fe diffusion. In  $Fe_{76}Si_{24}$ , however, there are 4 to 12 percent of the rapid passages substituted by the higher migration barriers of triangular shape with only one or two Si atoms (Fig. 8 (a) (b)). In  $Fe_{80}Si_{20}$ , 20 to 60

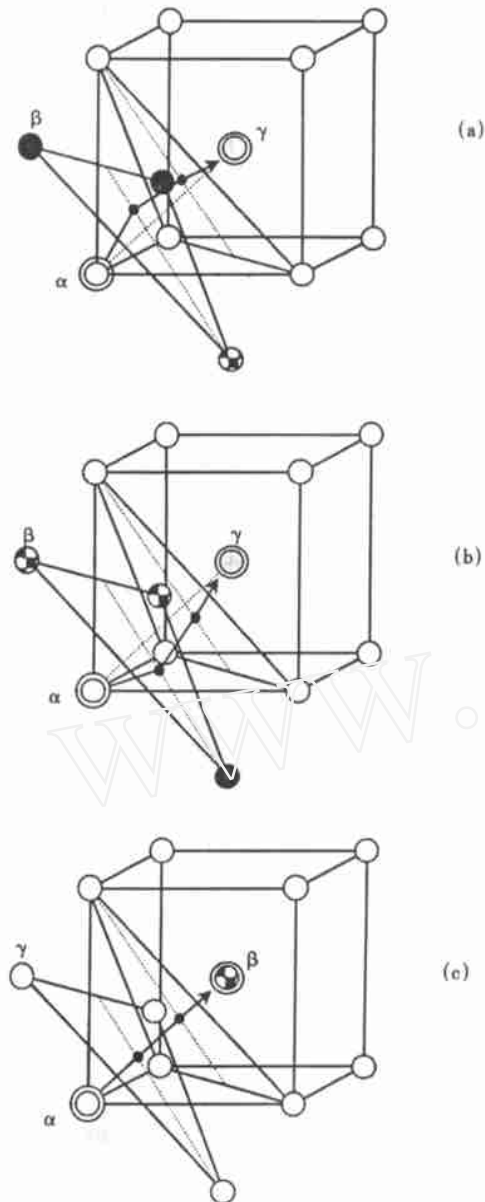


Fig. 8 In the off-stoichiometric  $D0_3$  structure  $Fe_3Si$ , it is thought that energy barriers of triangular shape (a) with two Si atoms or (b) with one Si atom for the Fe atoms jumping between  $\alpha$  and  $\gamma$  sites be higher than (c) the barriers with six Fe atoms for the Fe atoms jumping between  $\alpha$  and  $\beta$  sites. The mosaic circles are  $\beta$  sites occupied by Fe

percent of the rapid passages are destroyed. In other words, the migration barriers for Fe diffusion in  $Fe_3Si$  are much sensitive to the Fe content. If the potential barriers with one or two Si atoms are higher than that with six Fe atoms for the Fe atom jumps between the  $\alpha$  and  $\gamma$  sublattice, Fe diffusion in  $Fe_{80}Si_{20}$  may prefer to the  $\alpha$ - $\gamma$  model rather than the  $\alpha$ - $\beta$  model, as proved by the results of Mössbauer experiments<sup>[7]</sup>.

By contrast, the barriers for the Si atoms diffusion in  $Fe_{80}Si_{20}$  are less affected by the change of composition. Yet the potential energy of the Si atoms on  $\beta$  sites is higher according to the change of NN atoms around the  $\beta$  sites. This change would increase the residence time of the Si atoms on  $\beta$  sites and thus contribute to the Si atoms taking effective jumps, i. e. it should contribute to the self-diffusivity of Si in  $Fe_{20}Si_{80}$ <sup>[6]</sup>. Therefore, when the  $D0_3$  order decreases the Si self-diffusivity would be less affected or even accelerated, though the thermal vacancies decrease a lot (Fig. 5).

## 4 Summary

Geometric discussions on the atompairs and migration barriers indicate that the potential energy barriers for the Fe atoms diffusion in  $Fe_3Si$ , as well as the thermal vacancy concentrations, are closely sensitive to change of the composition. So the low migration barriers should also attribute to the extremely high diffusion coefficient of Fe in  $Fe_{75}Si_{25}$ .

The minority Si in  $Fe_3Si$  could probably migrate via NN jumps only if the residence time on the antistructure sites is very short. In the off-stoichiometric  $Fe_3Si$  alloys the longer residence time of Si on  $\beta$  sites contribute to its taking effective jumps. Therefore the self-diffusivity of Si in  $Fe_3Si$  is much less affected or even accelerated when leaving stoichiometry versus the iron rich side. The discussions explain the results of previous experiments.

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## Multiphoton ionization dissociation mechanism of 2- Butanone

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**Abstract:** Multiphoton ionization dissociation (MPID) mechanism has been studied on 2 - butanone molecule resonated via ( $n_o, 3d$ ) state by 3 photons. The main MPID products are  $C_2H_3O^+$  and  $CH_3CH_2^+$ , the intensity of  $C_2H_3O^+$  is 1 ~ 4 times larger than that of  $CH_3CH_2^+$ , and some minor ions  $C_2H_2^+$ ,  $C_2H_3^+$  and  $CH_3^+$  are also observed in the whole experimentally spectral region, where as no parent ion is observed. The mass-selected resonance-enhanced multiphoton ionization dissociation spectra take a similar feature, but the laser power indexes of the fragmental ions are different from each other. Based on the experimental results, the multiphoton ionization dissociation mechanism is made out to accord with "molecular ion ladder model". The producing mechanism of the main ions has been discussed in detail according to "ladder switching".

**Keywords:** 2-butanone; Multiphoton ionization dissociation; Ladder switching; Time-of-flight mass spectrum