

Structure-sensitive dissociation scheme for three isomers of difluorobenzene

M. Nomura, G. Veshapidze, H. Shiromaru*, Y. Achiba, N. Kobayashi

Graduate School of Science, Tokyo Metropolitan University, Tokyo 192-0397, Japan

Received 18 February 2004; accepted 26 March 2004

Available online 6 May 2004

Abstract

Three isomers of difluorobenzene were multiply ionized by low-energy collisions with Ar^{8+} , and their subsequent dissociation was studied using position-sensitive time-of-flight (TOF) measurements combined with a coincidence technique. The vector correlation of the velocities of the two F^+ fragment ions was examined and found to be sensitive to the structure.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Isomers; Difluorobenzene; Time-of-flight; Position-sensitive

1. Introduction

To distinguish isomers using mass spectrometry, collision-induced dissociation (CID) is widely used (MS/MS); the most suitable isomer is deduced by comparing the observed fragmentation pattern with patterns compiled in databases [1–3]. Various commercial MS/MS instruments equipped with sophisticated computing systems are available, enabling the quick identification of target samples. However, the fragmentation pattern is not always a unique fingerprint of a molecule, since patterns do not differ drastically if the molecular structures are very similar. Many attempts to enhance the differences in the fragmentation patterns of isomers have been reported, including using high-energy collision-induced dissociation (CID) for isomeric sugars [4], and charge inversion mass spectrometry for C_2H_2 isomers [5]. In general, the relationship between the branching ratio of the fragment ions and the structure of the parent molecule is not straightforward. In this paper, we report an intuitive method to distinguish isomers, which uses position-sensitive time-of-flight (TOF) measurements, and present an example of how isomers are distinguished.

According to the database [6], the five prominent peaks observed in the mass spectra of difluorobenzenes are sorted by intensity as follows:

- 1,2-difluorobenzene, (ortho-difluorobenzene, hereafter ODFB); $m/e = 114$ (parent ion), 88, 63, 57, 50.
- 1,3-difluorobenzene, (meta-difluorobenzene, hereafter MDFB); $m/e = 114$ (parent ion), 63, 88, 57, 50.
- 1,4-difluorobenzene, (para-difluorobenzene, hereafter PDFB); $m/e = 114$ (parent ion), 63, 88, 57, 50.

Here, peaks due to isotopes are omitted. For these isomers, the major fragment ions are shared in common, and the order is quite similar for each. This is also true for the isomers of dichlorobenzene, for which a considerable difference is observed only in charge inversion mass spectra [7]. This means that the series of halogen-disubstituted benzenes is a good example of compounds that are not easy to distinguish using collision-induced fragmentation alone. To avoid the complexity due to isotopes, the isomers of difluorobenzene appear to be suitable targets.

If dissociation is faster than the time of molecular rotation and isomerization, the dissociation scheme should differ among the isomers. The dissociation of multiply ionized molecules may be a suitable reaction, since it is likely to be much faster than that induced by single ionization or collisional heating. Therefore, it might be possible to distinguish the isomers by analyzing the dissociation of multiply ionized molecules. Experimentally, the dissociation of multiply ionized molecules can be analyzed in detail by applying multiple coincidence measurement of the fragment ions. In addition, position-sensitive TOF measurements allow

* Corresponding author. Tel.: +81-426771111; fax: +81-426772525.
E-mail address: shiromaru-haruo@c.metro-u.ac.jp (H. Shiromaru).

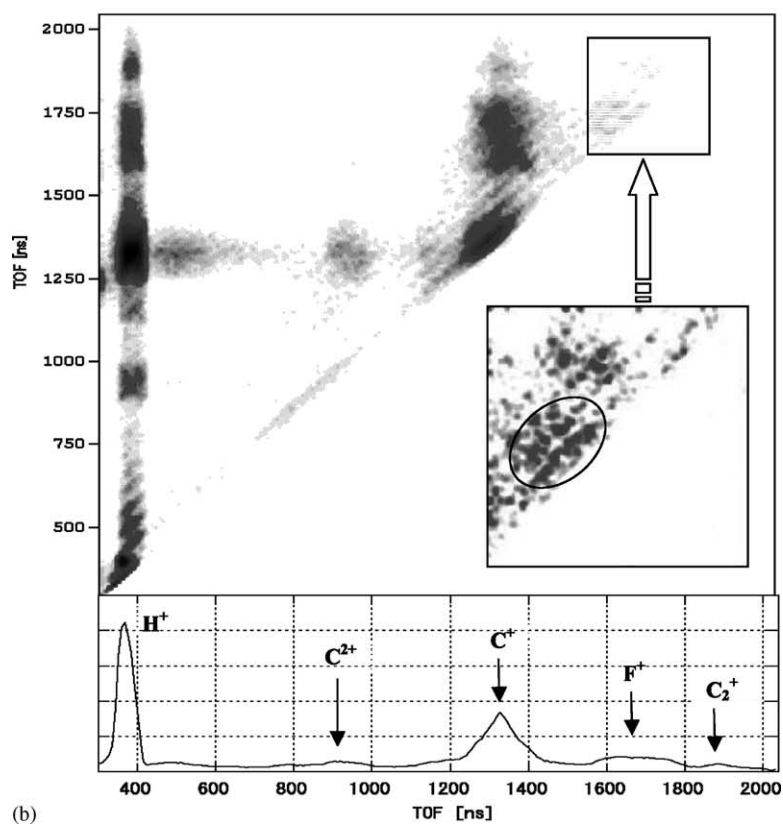
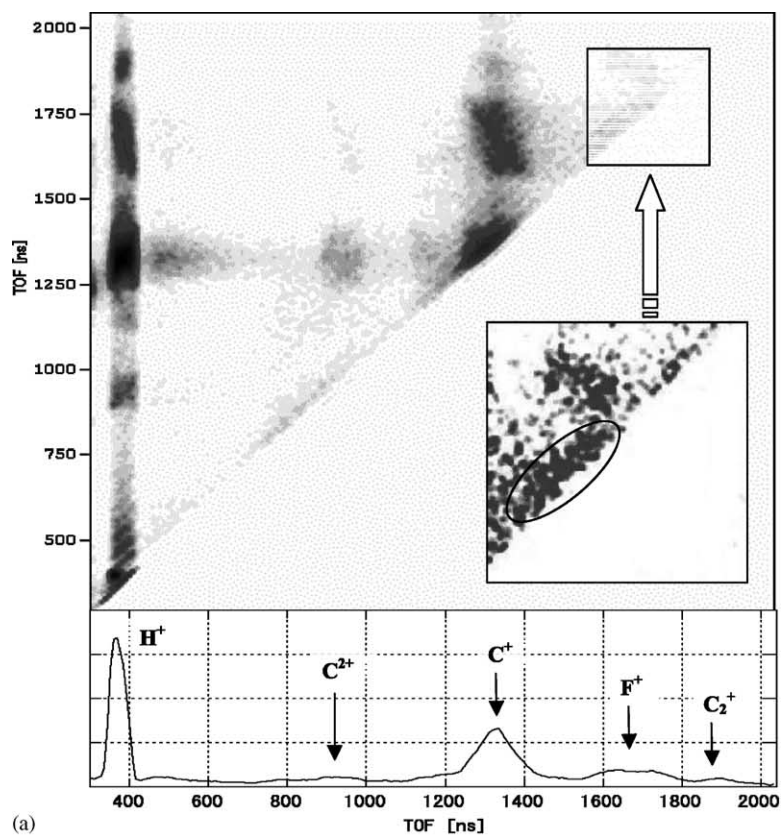


Fig. 1. TOF coincidence maps for ODFB (a), MDFB (b), and PDFB (c). The maps at an expanded scale are inserted in which the contrast is enhanced. The ($F^+ F^+$) island is indicated by the ellipse in each expanded map. The TOF spectra and the assignment of the peaks are shown below the maps.

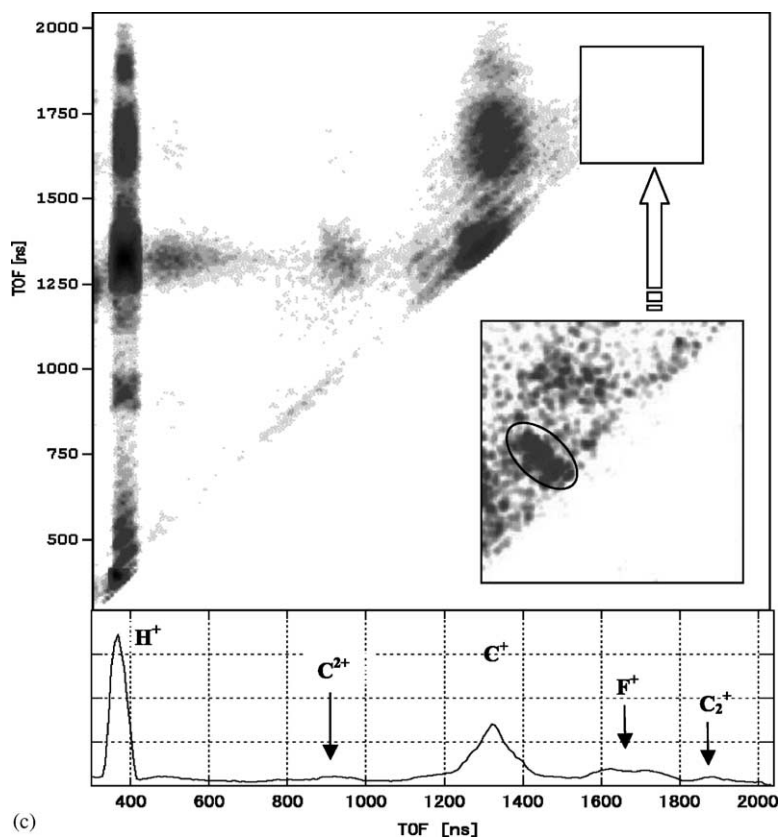
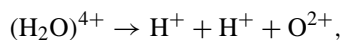


Fig. 1. (Continued).

analysis of the 3-dimensional velocity vectors of the fragment ions, and their vector correlation. The method of determining molecular structure from a trajectory analysis of the fragment ions is referred to as “Coulomb explosion imaging (CEI)” [8]. The feasibility of this technique has been demonstrated mainly for ionic species; for example, the stereostructure of a protonated positive acetylene ion was obtained in this way [9]. Concerning the application of CEI to neutral species, few vector correlation studies for fragment ions have been reported. Werner et al. reported position-sensitive TOF measurements for water molecules and the vector correlations of the fragment ions produced by the reaction:



were compared with those expected from a simple Coulomb explosion model [10,11]. In the first case, the experimental results deviated considerably from the Coulombic scheme. Nevertheless, the isomers, if any, could still be distinguished by their vector correlation pattern. For the latter case, the deviation from the Coulomb explosion model was much smaller.

Multiple-ionization of molecules is also possible by using X-ray or ultra short pulse laser. Applying position-sensitive TOF technique, the velocity (or momentum) vectors of fragment ions were analyzed in detail, and both the

near-Coulombic and non-Coulombic dissociation were observed, depending on the way of the excitation [12–15].

Previously, we reported position-sensitive TOF studies, combined with a multiple coincidence technique, for the fast dissociation of simple molecules multiply ionized by collisions of highly charged atomic ions [16–20]. From a series of experiments, we concluded that the fragmentation of a multiply charged molecular ion can be approximated by the Coulomb explosion, if the target molecules are fairly small and highly ionized. This means that a trajectory analysis of the fragment ions can provide information on the structure of the parent molecule; i.e., Coulomb explosion imaging is applicable to simple molecules.

Very recently, the dissociation of highly charged benzene was studied and the velocity vectors of the dissociating fragment ions were found to be coplanar. This means that the trajectories of fragments conserve the “memory” of initial planar structure of the parent molecule, even in a relatively large molecule like benzene. This study examined the dissociation of highly charged difluorobenzene, focusing on the vector correlation of the two F^+ fragment ions.

2. Experimental

The target molecules were multiply ionized by collision with 120 keV Ar^{8+} extracted from a 14.25-GHz electron

cyclotron resonance (ECR) ion source [21], and the fragment ions were detected using a position- and time-sensitive detector [22,23]. TOF measurements were triggered by the detection of the Auger electron(s) promptly emitted from the projectile after collision. This triggering system leads to a bias in the results, as will be described later. Commercial ODFB, MDFB, and PDFB were used after they had been subjected to a conventional degassing procedure.

To determine the initial velocity vectors of the fragments, it is desirable to detect all of them, since in that case the initial position of the dissociation can be determined numerically based on the conservation of momentum. For large molecules, many of the fragment ions should be detected in coincidence while the finite detection efficiency seriously reduces the number of multiple coincidence events. In this study, the TOF tube was 173.5 mm long, and the acceleration voltage was 2.4 kV, to achieve a satisfactory compromise between mass resolution and collection efficiency. These parameters permit recording of an acceptable number of events in which two ions are detected in coincidence, whereas the number of higher-fold coincidence events is very small.

From the x - y position and the TOF of each fragment ion, the initial 3-D velocity vector was calculated by assuming that a collision occurred at the specific position determined from an analysis of the results for the Ar target. Since the acceleration field did not affect the x - and y -components of the velocity vector, these values were simply determined from the x - y position on the detector and the TOF of each fragment ion. The z -component was calculated from the TOF itself. Note that the diameter of the projectile beam in the collision area was about 2 mm. This means that the uncertainty in the initial position of the dissociating molecule was relatively large as compared to the case in which all of the fragment ions are detected.

3. Results and discussion

Fig. 1a–c show the double coincidence maps for ODFB, MDFB, and PDFB, respectively. In each figure, ($F^+ F^+$) coincidence island is indicated by ellipses. The shapes of the islands differ considerably, indicating that the dissociation scheme differs among these isomers.

The correlation of the velocity vectors of the fragment ions gives much more information. To examine the vector correlation of two F^+ , we used $\cos\theta$, which is defined using $\vec{v}(F_1) \cdot \vec{v}(F_2) = |\vec{v}(F_1)| \times |\vec{v}(F_2)| \cos\theta$, where $\vec{v}(F_1)$ and $\vec{v}(F_2)$ are the initial velocity vectors of the two fragments, and θ is the angle between them. The histograms of $\cos\theta$ obtained for ODFB, MDFB, and PDFB are shown in Fig. 2a–c, respectively. As the figures show, the vector correlation clearly differentiates the isomers. In all cases, $\vec{v}(F_1)$ and $\vec{v}(F_2)$ are strongly correlated. The peak appears at around $\cos\theta = 0.5$, -0.5 , and -1 for ODFB, MDFB, and PDFB, respectively. These values match the cosines of the angles between the two C–F bonds, i.e., $\cos\theta = 0.48$,

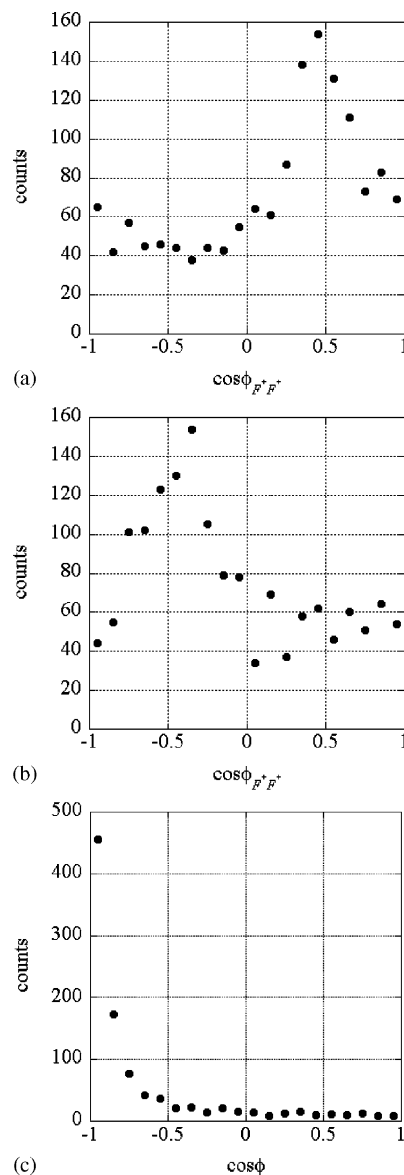


Fig. 2. Histograms of $\cos\theta$ (see text) obtained for ODFB (a), MDFB (b), and PDFB (c).

-0.52 , and -1 for ODFB, MDFB, and PDFB, respectively. Note that the ($F^+ F^+$) double coincidence events analyzed in this study include all the possible dissociation events in which F^+ and F^+ are detected in coincidence. Therefore, these dissociation events may involve many additional ions.

As mentioned before, using Auger electron detection for TOF measurements leads to the following bias: since the number of Auger electrons depends strongly on the number of electrons captured by a projectile, the probability of detecting Auger electrons, i.e., the probability of triggering, is a function of the number of electrons captured. This means that the observed distribution of the charge states of the parent molecule, which equals the number of electrons captured by the projectile, should be different from that expected from the relative cross-section of multiple electron

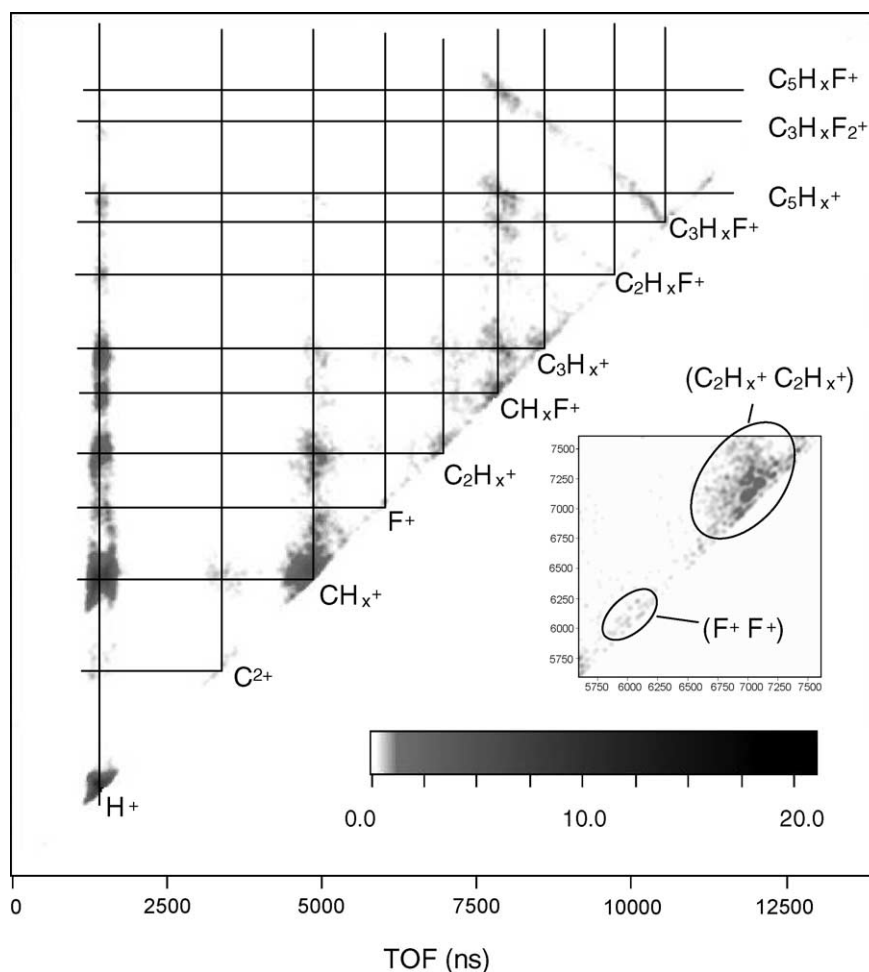


Fig. 3. TOF coincidence map obtained for MDFB using projectile detection as a trigger. The inset is a map at an expanded scale.

capture. As a result, the higher charge states of the parent molecule would be enhanced in this study.

To demonstrate the preference in the higher charge states due to our measurement system, an alternative TOF coincidence measurement was performed, using projectile detection as the start trigger. The projectile was also Ar^{8+} and the collision energy was the same as for the position-sensitive TOF measurements. The target molecule was MDFB. The double coincidence map is shown in Fig. 3, in which the darkness of the islands is a measure of the corresponding branching ratio, unlike the case in Fig. 1. Relative intensity of the islands is significantly different between these figures: $(\text{F}^+ \text{F}^+)$ islands are enhanced and $(\text{C}_2\text{H}_x^+ \text{C}_2\text{H}_x^+)$ islands are suppressed in Fig. 1a–c. This trend is consistent with the expected bias mentioned above because the probability of multiple bond breaking and atomic ion formation would increase with the charge state.

In fact, the collision of Ar^{8+} and CS_2 yields detectable amounts of highly charged molecular ions up to $(\text{CS}_2)^{10+}$, and $(\text{CS}_2)^{5+}$ to $(\text{CS}_2)^{8+}$ are major channels when the TOF measurements are triggered by the Auger electrons [13]. It is reasonable to assume that the charge states higher than

5+ are the main contributor, and that many additional fragment ions would dissociate just after the multiple ionization of difluorobenzene.

Assuming the crude approximation that the above mentioned additional positive charge would be distributed equally over the rest of the molecule and the direction of the dissociating fragments would be simply determined from the sum of the Coulombic repulsive force for the point charges, most of the repulsive forces would cancel out, except for those along the C–F bonds. For PDFB, the positive charges may be distributed symmetrically with respect to the two C–F bonds; therefore, F^+ would be kicked in the direction of the C–F bond. In fact, the histogram for PDFM shows a very sharp correlation, as shown in Fig. 2c. The histograms for ODFB and MDFB show rather broad peaks; the broadness is likely related to the fact that the C–F bonds are not aligned along the axis of symmetry.

In conclusion, our results demonstrate the applicability of position-sensitive TOF measurements for distinguishing isomers. More detailed analysis of the coincidence events, including classical calculations of the ion-trajectories, is now under way.

Acknowledgements

This work was partly supported by grants-in-aid from the Ministry of Education, Culture, Sports, Science and Technology of Japan (14204062, 15035213).

References

- [1] F.W. McLafferty, *Tandem Mass Spectrometry*, John Wiley, New York, 1983.
- [2] K. Biemann, H.A. Scoble, *Science* 237 (1987) 992.
- [3] R.A. Yost, C.G. Enke, *Anal. Chem.* 51 (1979) 1251A.
- [4] J.H. Scrivens, A.T. Jackson, K.R. Jennings, R.C.K. Jennings, N.J. Overall, *Int. J. Mass Spectrom.* 230 (2003) 201.
- [5] S. Hayakawa, K. Tomozawa, T. Takeuchi, K. Arakawa, N. Morishita, *Phys. Chem. Chem. Phys.* 5 (2003) 2386.
- [6] NIST Chemistry WebBook, NIST Standard Reference Database Number 69 (2003) (<http://webbook.nist.gov/chemistry/formser.html>).
- [7] S. Hayakawa, K. Taguchi, R. Kotani, K. Arakawa, N. Morishita, *J. Mass Spectrom. Soc. Jpn.* 49 (2001) 219.
- [8] Z. Vager, R. Naaman, E. Kanter, *Science* 244 (1989) 426.
- [9] E.P. Kanter, Z. Vager, G. Both, D. Zajfman, *J. Chem. Phys.* 85 (1986) 7487.
- [10] U. Werner, K. Beckord, J. Becker, H.O. Lutz, *Phys. Rev. Lett.* 74 (1995) 1962.
- [11] U. Werner, K. Beckord, J. Becker, H.O. Folkerts, H.O. Lutz, *Nucl. Instrum. Method.* B98 (1995) 385.
- [12] M. Lavollee, V. Brems, *J. Chem. Phys.* 110 (1999) 918.
- [13] U. Ankerhold, B. Esser, F. von Busch, *J. Phys.* B30 (1997) 1207.
- [14] S. Hsieh, J.H.D. Eland, *J. Phys.* B30 (1997) 4515.
- [15] A. Hishikawa, H. Hasegawa, K. Yamanouchi, *Chem. Phys. Lett.* 361 (2002) 245.
- [16] J.H. Sanderson, T. Nishide, T. Kitamura, H. Shiromaru, Y. Achiba, N. Kobayashi, *Phys. Rev. A* 59 (1999) 4817.
- [17] T. Nishide, F.A. Rajgara, T. Kitamura, H. Shiromaru, Y. Achiba, N. Kobayashi, *Phys. Scripta* T92 (2001) 415.
- [18] T. Kitamura, T. Nishide, H. Shiromaru, Y. Achiba, N. Kobayashi, *J. Chem. Phys.* 115 (2001) 5.
- [19] F.A. Rajgara, M. Krishnamurthy, D. Mathur, T. Nishide, T. Kitamura, H. Shiromaru, Y. Achiba, N. Kobayashi, *Phys. Rev. A* 64 (2001) 032712(10).
- [20] H. Shiromaru, T. Nishide, T. Kitamura, F.A. Rajgara, J.H. Sanderson, Y. Achiba, N. Kobayashi, The physics of electronic and atomic collisions. In: Y. Ichikawa, K. Okuno, H. Tanaka, A. Yagishita, M. Matsuzawa (Eds.), *AIP Conference Proceedings* 500, 1999, pp. 636.
- [21] H. Tanuma, J. Matsumoto, T. Nishide, H. Shiromaru, N. Kobayashi, *J. Chinese Chem. Soc.* 48 (2001) 389.
- [22] T. Mizogawa, M. Sato, Y. Awaya, *Nucl. Instrum. Methods Phys. Res. A* 366 (1995) 129.
- [23] T. Mizogawa, H. Shiromaru, M. Sato, Y. Ito, *Int. J. Mass. Spectrom.* 215 (2002) 141.