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Yamauchi, Tomoya ; Barillon, Remi ; Balanzat, E. ; Asuka, Taku ; Izumi, Kentaro ; Masutani, Takashi ; Oda, Keiji

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Yields of CO_2 formation and scissions at ether bonds along nuclear tracks in CR-39

T. Yamauch[a,*], R. Barillon[b], E. Balanzat[c], T. Asuka[a],
K. Izumi[a], T. Masutani[a], K. Oda[a]

[a] Faculty of Maritime Sciences, Kobe University, 5-1-1 Fukaeminami-machi, Higashinada-ku, Kobe 658-0022, Japan
[b] IReS, Universite Louis Pasteur (UMR 7500), 67037 Strasbourg Cedex 2, France
[c] CIRIL, Unite mixte CEA-CNRS-ISMRA, 14070 Caen Cedex 5, France

Abstract

Yields of CO_2 gas formation and the scissions at ether bonds have been determined along ion tracks in CR-39 plastics. Thin CR-39 films with 15 μm thickness were irradiated by 130 MeV C-13 ions at 45 degree incidence up to 10^{13} ions/cm^2, and then IR spectra were obtained without removing the samples from the vacuum chamber. Absorption band for CO_2 was observed clearly around 2338 cm^{-2}, which absorbance increased proportional to the fluence up to $3x10^{12}$ ions/cm^2 and then saturated. Using a mole absorption coefficient for gaseous CO_2, the yield along the track was determined to be 7200 CO_2 molecules/μm. This means that G-value of CO_2 formation in CR-39 was about 3.6 molecules/100eV. Scission yield of ether bonds was found to be 11000 scissions/μm. This corresponds to G-value of about 5.5 scissions /100eV. These values suggest that the parts between the two carbonate ester bonds in each repeat unit of CR-39 can be segmented into two CO_2 and other small molecules along the nuclear tracks.

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Keywords: CR-39; track chemistry; carbon dioxide; G-value; segmentation

*Corresponding author.
Tel.: +81-78-431-6307; fax: +81-78-431-6369.
E-mail address: yamauchi@maritime.kobe-u.ac.jp

1. Introduction

In our recent papers, the present authors proposed an overview on the nuclear track formation process in CR-39 plastics as followings: (a) CO_2 gases were produced along particle trajectory as a result of the breaking of carbonate ester bonds in CR-39 main chain; (b) After the breaking, the CO_2 gases were diffused away and lower density region with chemically active end-points was formed simultaneously; (c) Subsequent chemical modifications, including a reaction with dissolved oxygen, derived OH group as new end-points in polymer network. As described here, we have paid much attention on the chemical phase of track formation process, which followed the physical one. We think that the speed of etchant penetrating along the track, namely track etching velocity, is controlled by the concentration of OH group that is a water attractive function, as well as by the track core size (Yamauchi, 2003; Yamauchi et al., 2003a, 2003c). These discussions were based on our own optical studies (Yamauchi et al., 1999b, 2000, 2001b, 2003a, 2003b) and those on the etching property of irradiated CR-39 under various conditions (Oda et al., 1997; Yamauchi et al., 1992, 2001a, 2001c, 2003d). This is, however, remained as a qualitative consideration or a speculation. As a whole, quantitative treatments are required to ensure the overview. Therefore, in this work the present authors have determined the yields of CO_2 gases formation and scissions at ether bonds along ion tracks in CR-39 plastics, as the first step for our goal.

Many important FT-IR studies have been carried out to understand the CO_2 production and/or releasing behaviors in CR-39 detectors irradiated by various kinds of ions or low-LET radiations (El-Shahawy et al., 1992; Chong et al., 1997; Saad et al., 2001; Malek et al., 1999&2002). The ejection of CO_2 gases from the bombarded CR-39 has also been detected using mass spectrometer (Rickards et al., 1992). A thin film of CR-39 can make it possible for us to assess the density of carbonate ester bonds in it using ordinal FT-IR spectrometers at desired ion fluences (Gagnardre et al., 1993; Darraud et al., 1994; Gerstener et al., 1999, Lounis-Mokrani et al., 2003; Phukan et al., 2003). The general reduction of the densities of CH_2, C-O-C and C-H bonds due to the irradiations has been observed (Darraud et al., 1994). It was also well ascertained that CO_2 gases in CR-39 film could be resolved on IR spectrum of transmission mode. Nevertheless, a few attentions are needed to make fairly quantitative measurements for CO_2 concentration in CR-39. The first is that the air should be purged from the optical path in FT-IR system to keep enough power intensity at the absorption band for CO_2. The second is that the measurements must be done quickly after the irradiation to prevent from significant escape of CO_2 (Yamauchi et al., 2003a). In this work, we have used the well-established FT-IR spectrometer that has been utilized at the medium energy line facility of the GANIL accelerator (for an example, Dehaye et al. 2003).

Unsaturated IR spectra of the thin CR-39 samples with a thickness of 15 μm have been attained, except C=O and O-C-O of carbonate ester bonds. Clear absorption band for CO_2 was observed around 2338 cm^{-2}, the absorbance increased proportional to

the fluence up to $3x10^{12}$ ions/cm^2 and then saturated. Based on a mole absorption coefficient of gaseous CO_2, its yield along the unit track length was determined. The yield could be converted to the G-values for CO_2 formation in CR-39 in this system, using the calculated stopping power. The reduction of ether bonds has been also observed clearly as a function of fluence. And the G-value for the scission of ethers was determined. The track core size was also estimated on the assumption that the core has cylinder like structure and all ether and carbonate ester bonds inside it will break. Comparing it with those obtained from different methods (Yamauchi et al., 1999, 2000, 2003c), it was found that the scissions of ether bonds were inferred to be dominant damages along the tracks in CR-39, as well as CO_2 formations. This indicates that the part between the two carbonate ester bond in each repeat unit of CR-39 can be segmented into two CO_2 and other small molecules composed by a few carbon atoms.

2. Experimental

Thin CR-39 films with 15 μm thickness were prepared by chemical etching from commercially obtainable pure CR-39 sheets with 100 μm (BARYOTRAK, Fukuvi chemical Industry Co., Ltd., Japan). The etchings were made in 6.25 N NaOH solution kept at 70 degree of C without steering. It took about 40 hours to reduce the thickness down to 15 μm. Subsequent to the etchings the samples were washed in ion-exchange water carefully and then dried in clean and dark space after blew-out the excess water on the surface. Handlings of thin CR-39 films with a normal forceps became difficult when their thickness is less than 10 μm. To obtain unsaturated IR spectra for carbonate ester bond in CR-39 in transmission mode, thinner samples are need below 5 μm.

Carbon ion irradiations were made using the medium energy line facility of the GANIL accelerator (Caen, France). At the end of this beam line, a FT-IR spectrometer was set. A special cell was equipped for irradiations and it enabled us to obtain FT-IR spectra without removing the samples from the cell. All irradiations were performed under vacuum with 130 MeV C-13 ions. Fluence rate was about $2x10^9$ ions/cm^2/sec.

3. Results and discussion

3.1 IR spectra

The IR spectrum of CR-39 film with 15 μm thickness before the irradiations is shown in Fig. 1. Except two strong absorption bands from carbonate ester bonds (>C=O and O-C-O), unsaturated spectrum was attained in a transmission mode. The bands from ether bonds are observed at 1030, 1099 and 1144 cm^{-1} in this spectrum (C-O-C). The assignments of these peaks were well summarized by Lounis-Mokrani (2003). We also confirmed them by semi-empirical quantum calculations using CAChe program (Fujitsu, Japan).

Fig. 2(a) and (b) show the IR spectra of irradiated CR-39 with a fluence of

$8x10^{12}$ ions/cm^2 and un-irradiated one. As shown in Fig. 2(a), after the irradiation the absorption band of OH group appears around at 3600 cm^{-1}. The band from CH_2 and CH_3 slightly modified in shape by the irradiation. Simultaneously, new significant absorption peak of CO_2 emerges at 2338 cm^{-1}. Other region of spectra is shown in Fig. 2 (b), indicating that most of all peaks are reduced with the increasing of absorbance at some valleys (indicating by * in this figure). Among these peaks, we paid our attention on the bands from ether at 1099 and 1144 cm^{-1}, which is a part of CR-39 main chain.

3.2 CO_2 formation

Figure 3 shows that the net absorbance for CO_2 increases almost proportional to the fluence up to $3x10^{12}$ ions/cm^2 and then tends to decrease. The reduction at higher fluence should be caused by the release of CO_2 gases from CR-39 film. Ignoring the escape at the proportional fluence region, we obtained the simple relation between the fluence, F, and CO_2 absorbance, $Abs(CO_2) = 0.125x10^{-12}\ F$[ions/cm^2]. This formula gives us the changes in net absorbance by a single track. The net absorbance, *Abs*, is express as a product of mole concentration of the considering molecules, c [mole/cm^3], the thickness of the sample, t [cm], and mole absorption coefficient, ε [cm^2/mole], as following:

$$Abs = \varepsilon\, ct. \qquad (1)$$

In this measurement the effective thickness of sample was 0.0021 cm because the measurements were done at 45 degree to the surface. Using an attained specific mole absorption coefficient for gaseous CO_2 as $4.9x10^5$ [cm^2/mol], its yield along the single track was determined as 7200 [CO_2 molecules/μm]. Since the stopping power of 130 MeV C-13 ion in CR-39 is about 200 [keV/ μm], G-value of CO_2 formation in this system was calculated to be about 3.6 [CO_2/100eV]. The density of CR-39 is 1.32 [g/cm^3], so the averaged provided volume for each repeat unit is $3.45x10^{-10}$ μm^3. Within this volume, two CO_2 molecules can be produced. On the assumptions that the track core is cylindrical in shape and every carbonate ester bonds in the core emit CO_2 gases by breaking, the radius of track core was found to be 0.63 nm. In these estimations the escaping of CO_2 gases was not taken into account. If we had observed just half of the produced CO_2 gases, the G-values and the core radius will be re-calculated as 7.2 [CO_2/100eV] and 0.89 nm, respectively. For more precise measurements, we must observe the reduction of carbonate ester bond directly using thinner CR-39 films.

3.3 Scissions at ether bonds

Figure 4 indicates the changes in the net absorbance for ether bonds as a function of the fluence. These two peaks have almost same trend on the ion fluence, showing linear reduction up to $3x10^{12}$ or $4x10^{12}$ ions/cm^2, and at higher fluences the

reduction rates are decreased. Such fluence dependence could be attributable to the track overlapping at higher fluences and the overlapping should be negligible at the liner region less than $3x10^{12}$ ions/cm^2. The track overlapping model derived the core radius of about 1.2 nm for the critical fluence of $3x10^{12}$ ions/cm^2, above which the overlapping become statistically significant (Yamauchi et al., 1990, 2000, 2003c).

From the linearly decreasing region, we obtained the relation between the net absorbance of ether (1141 cm^{-1}) and the fluence, Abs(C-O-C)=1.4543-5.4662x10^{-14} F[ions/cm^2]. That of the other peak at 1099 cm^{-1} gave an equivalent relation. First, we obtained the mole absorption coefficient at the band of 1141 cm^{-1}as ε = 1.44x10^5 [cm^2/mol], based on this trend of the absorbance. Second, using Eq. (1) the scission yield of the ether bond along the single track was estimated to be 11000 [scissions/μm]. In this irradiation system, the G-value for the scission was found to be 5.5 [scissions/100eV]. Since each repeat unit of CR-39 has one ether bond, the track core radius was calculated to be 1.1 nm. This is similar to that attained by the track overlapping model mentioned above.

3.4 Track core structure

We have evaluated the track core size for various ions in CR-39 using the UV and the AFM methods (Yamauchi et al., 2003c). These examinations have been made for ions with energies at around Bragg peaks and the result was summarized as a function of the stopping power as shown in Fig. 5. As the first attempt, we compared the present results for 130 MeV C-13 ions with the previous ones. The core size from the ether bond scission agrees well the previous estimation. That from CO_2 formation gave smaller radius. But there is some possibility that some fraction of generated CO_2 gases escaped during irradiation before the IR measurements. It will close to others when we take into account the escaping effect.

Inside the track core, all of the ether bonds and most of carbonate ester bond will break. This means that the parts of polymer chain between two carbonate ester bonds (-O-(C=O)-O-CH_2-CH_2-O-CH_2-CH_2-O-(C=O)-O-) should be segmented into small molecules composed by one or two carbon atoms including CO_2. The unique sensitivity of CR-39 may be attributable to such relatively long part segmentation.

4. Conclusion

The yields for CO_2 formation and scissions at ether bond in CR-39 plastics have been obtained along the single track of 130 MeV C-13 ion using the on-line FT-IR measurements. The yield along the single track and the G-values of CO_2 formation were 7200 [CO_2 /μm] and 3.6 [molecules/100eV], respectively. In this estimation, the escape of the gases during irradiation was ignored. The scission yields and the G-value for the ether bond were 11000 [scissions/μm] and 5.5 [molecules/100eV], respectively. The

assessed track core size was found to be concordant those obtained by the different methods previously.

Based on the present study, we must re-write our overview on the nuclear track formation process in CR-39 as followings: (a) The parts between the two carbonate ester bonds should be segmented into small molecule, including CO_2 gases, along particle trajectory; (b) After the segmentation, the CO_2 gases were diffused away and lower density region with chemically active end-points was formed simultaneously (The role of the other small molecules are unknown); (c) Subsequent chemical modifications, including a reaction with dissolved oxygen, derived OH group as new end-points in polymer network. Further studies should be performed to understand the segmentation and the release or possible additional reaction of these active small molecules.

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Figure captions

Fig. 1 IR spectrum of thin CR-39 film with a thickness of 15 μm. The measurement was made at 45 degree to the sample surface on a transmission mode.

Fig. 2 IR spectra of thin CR-39 film before and after the irradiation with 130 MeV carbon-13 ions at a fluence of $8x10^{12}$ ions/cm^2. (a) at wavenumber between 2000 and 4000cm^{-1}; (b) at wavenumber between 500 and 2000cm^{-1}.

Fig. 3 Changes in the net absorbance of CO_2 gas with ion fluence.

Fig. 4 Reduction of the net absorbance at ether absorption band against ion fluence.

Fig. 5 Track core radius assessed from yields of CO_2 gas formation and scissions of ether. The curve was derived from the different methods (see Yamauchi et al. 1999, 2000, 2003c).

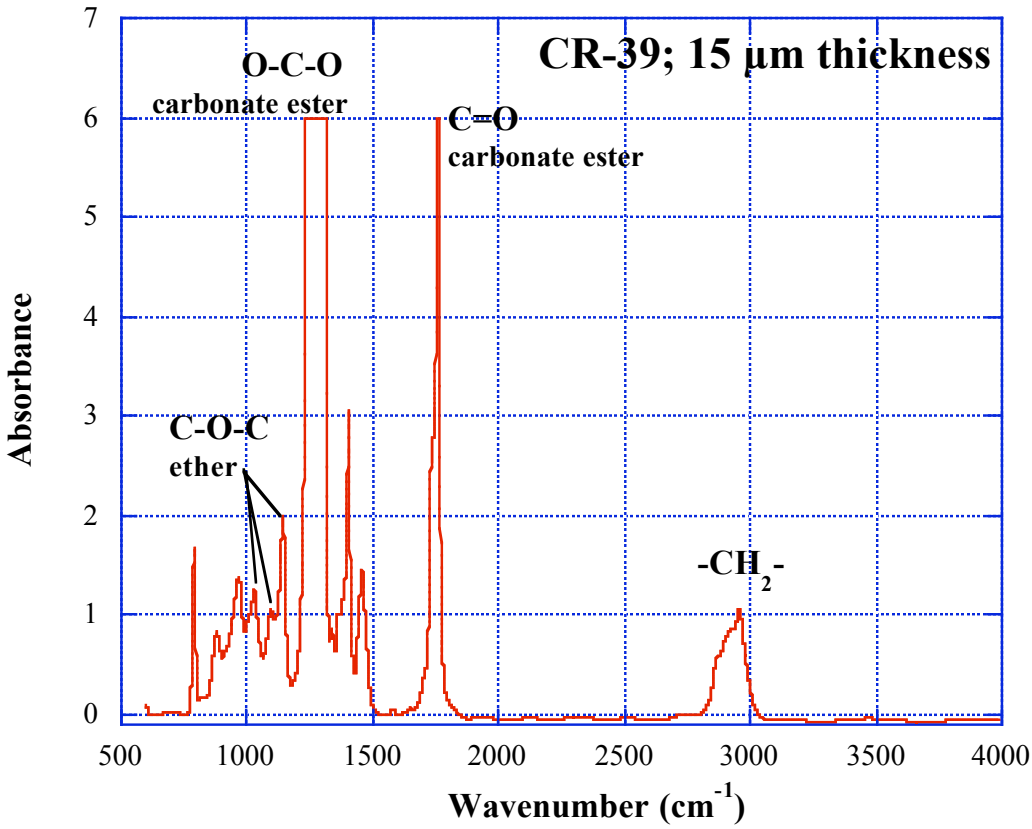
CR-39; 15 µm thickness
O-C-O
carbonate ester
C=O
carbonate ester
C-O-C
ether
-CH2-
Absorbance
Wavenumber (cm-1)
0
1
2
3
4
5
6
7
500
1000
1500
2000
2500
3000
3500
4000

Fig. 1

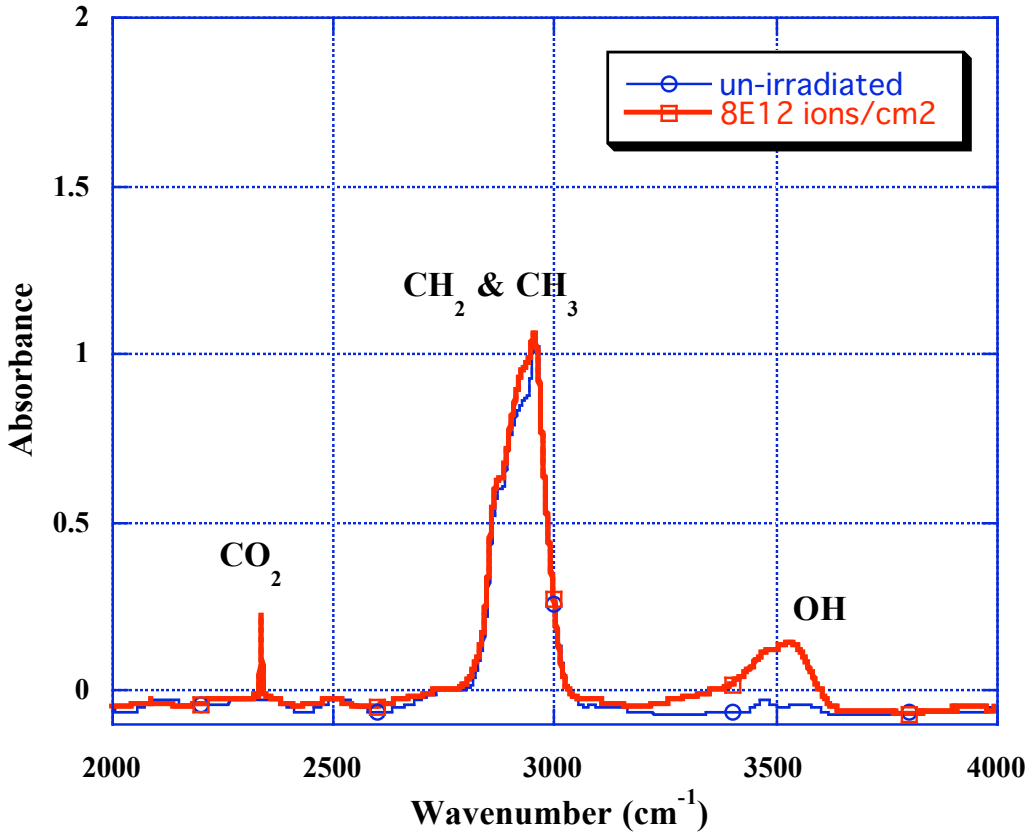
un-irradiated
8E12 ions/cm2
CH2 & CH3
CO2
OH
Absorbance
Wavenumber (cm-1)
2
1.5
1
0.5
0
2000
2500
3000
3500
4000

Fig. 2(a)

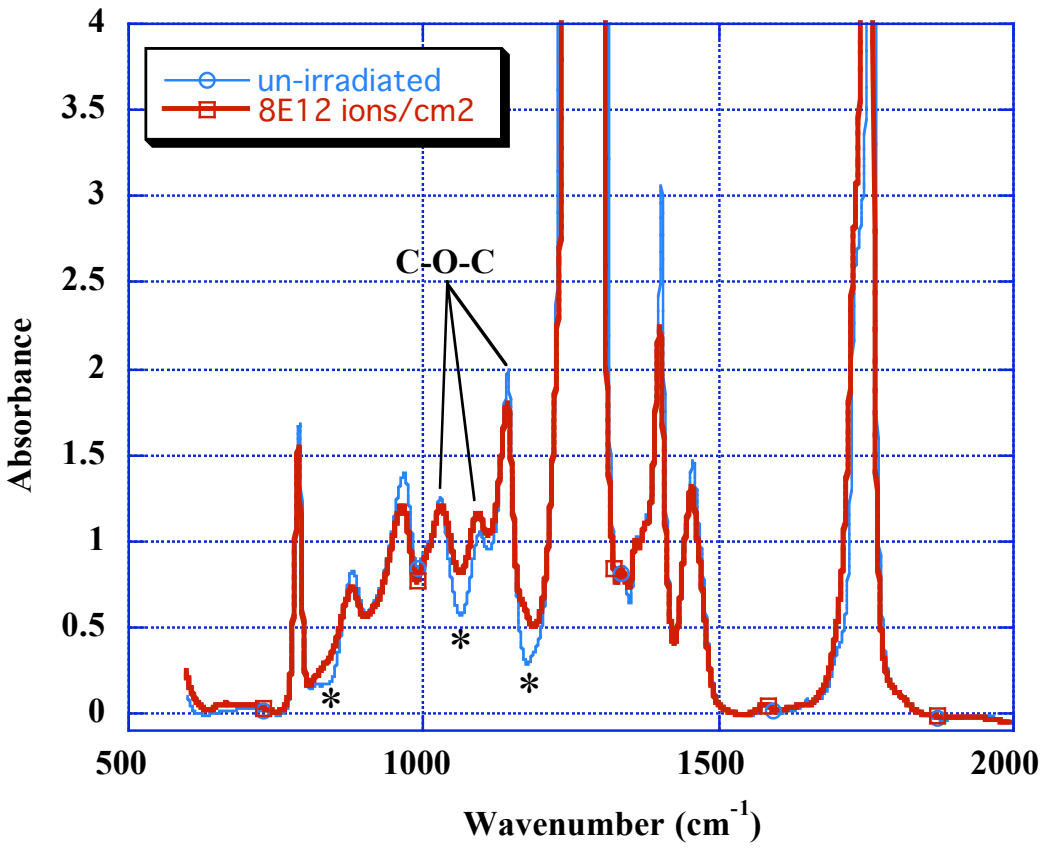
un-irradiated
8E12 ions/cm2
C-O-C
Absorbance
Wavenumber (cm-1)
4
3.5
3
2.5
2
1.5
1
0.5
0
500
1000
1500
2000
*
*
*

Fig. 2(b)

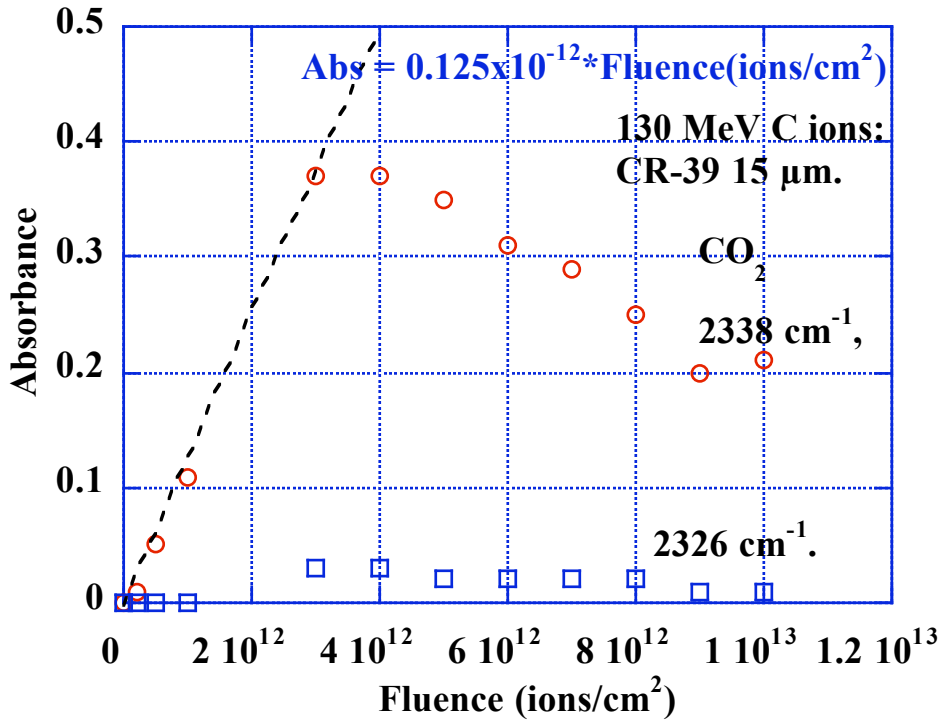
Abs = 0.125x10-12*Fluence(ions/cm2)
130 MeV C ions;
CR-39 15 µm.
CO2
2338 cm-1,
2326 cm-1.
Absorbance
Fluence (ions/cm2)
0
0.1
0.2
0.3
0.4
0.5
0
2 10^12
4 10^12
6 10^12
8 10^12
1 10^13
1.2 10^13

Fig. 3

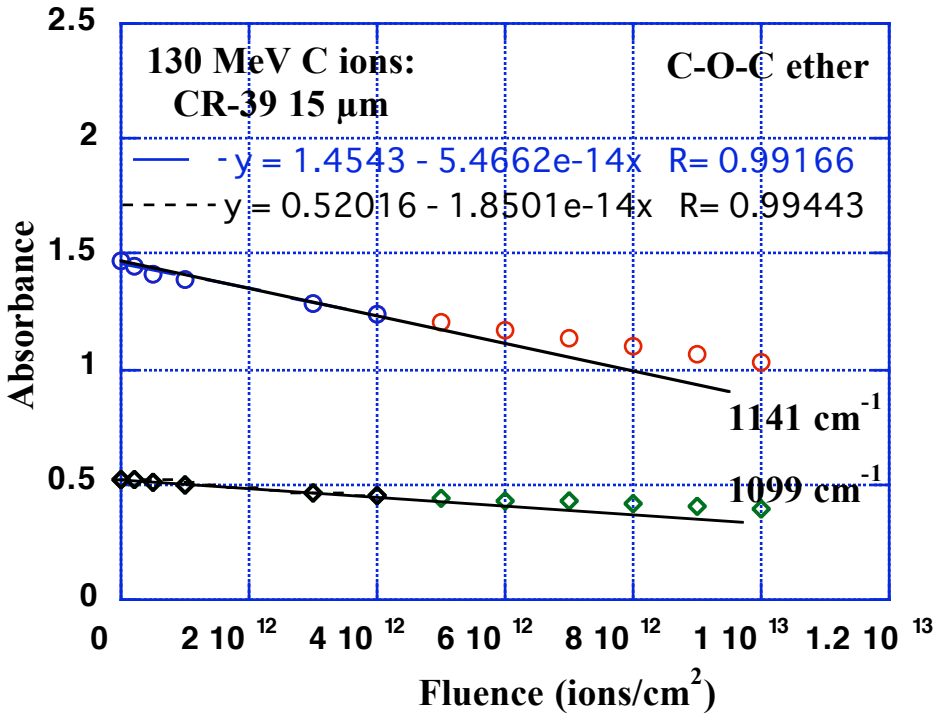
130 MeV C ions:
CR-39 15 µm
C-O-C ether
y = 1.4543 - 5.4662e-14x R= 0.99166
y = 0.52016 - 1.8501e-14x R= 0.99443
1141 cm-1
1099 cm-1
Absorbance
Fluence (ions/cm2)
0
0.5
1
1.5
2
2.5
2 10 12
4 10 12
6 10 12
8 10 12
1 10 13
1.2 10 13

Fig. 4

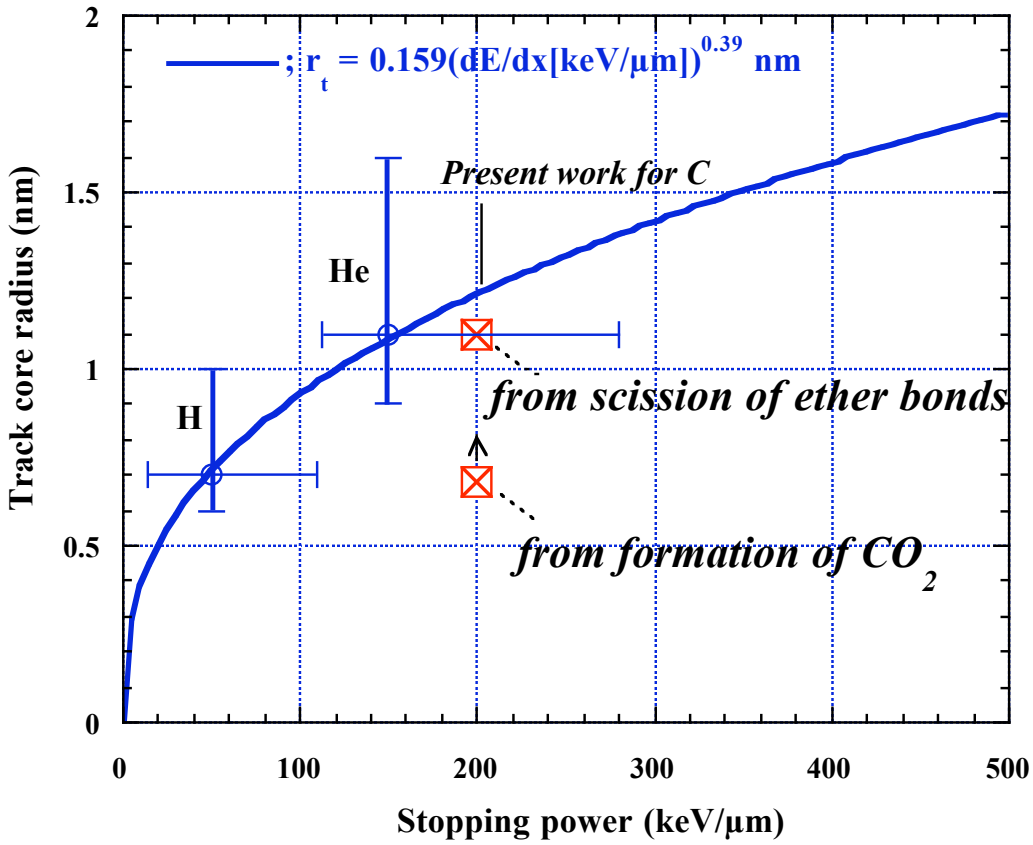
; r_t = 0.159(dE/dx[keV/μm])$^{0.39}$ nm
Present work for C
He
H
from scission of ether bonds
from formation of CO_2
Track core radius (nm)
Stopping power (keV/μm)
0
0.5
1
1.5
2
0
100
200
300
400
500

Fig. 5