

# <sup>13</sup>C-selective dissociation of 1-chloro-1,1-difluoroethane via vibrational excitation of the C–C bond

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The <sup>13</sup>C-selective IR multiphoton dissociation of CF<sub>2</sub>ClCH<sub>3</sub> via the vibrational excitation of the C–C bond produces <sup>13</sup>CF<sub>2</sub>=CH<sub>2</sub> and CF<sub>2</sub>=<sup>13</sup>CH<sub>2</sub>; high <sup>13</sup>C selectivity and production yield can be attained at low laser fluence.

Despite frequent works on the <sup>13</sup>C-selective IR multiphoton dissociation of fluorinated methanes,<sup>1–5</sup> there have, so far, been few attempts to separate <sup>13</sup>C by the isotopically selective excitation of fluorinated ethanes. In the studied fluorinated methanes, the C–F stretching vibration modes are generally excited for the <sup>13</sup>C-selective absorption of IR photons. The fluorinated methanes, however, have larger vibrational anharmonicity in the vibrational spectra and their effective <sup>13</sup>C-selective dissociation requires high laser fluence, which results in a higher energy consumption in the laser separation of <sup>13</sup>C isotope.<sup>3,4</sup> In the case of fluorinated ethanes, the vibrational anharmonicity is relatively small and the role of the rotational 'bottleneck' for the multiphoton absorption at lower levels is insignificant.<sup>6,7</sup> This is favourable for the absorption of IR photons and high <sup>13</sup>C decomposition yield by using a lower laser fluence. However, fluorinated ethanes have more complicated vibrational bands than methanes, actually, it is not easy to obtain high <sup>13</sup>C selectivity in the infrared multiphoton dissociation of fluorinated ethanes. High <sup>13</sup>C selectivity has been revealed only in the IR multiphoton dissociation of C<sub>2</sub>F<sub>5</sub>I by the <sup>13</sup>C-selective excitation of the C–F<sub>2</sub> stretching mode at an extremely low pressure.<sup>8</sup>

We report here the results on the <sup>13</sup>C-selective IR multiphoton dissociation of CF<sub>2</sub>ClCH<sub>3</sub> by the excitation of the C–C stretching mode which is the ν<sub>6</sub> band located at 1134 cm<sup>-1</sup>.<sup>9,10</sup> The <sup>13</sup>C isotope shifts for the C–C stretching modes of <sup>13</sup>CF<sub>2</sub>ClCH<sub>3</sub> and CF<sub>2</sub>Cl<sup>13</sup>CH<sub>3</sub> have not been reported yet and are generally estimated to be ca. 15–25 cm<sup>-1</sup>. It is possible to excite selectively <sup>13</sup>CF<sub>2</sub>ClCH<sub>3</sub> and CF<sub>2</sub>Cl<sup>13</sup>CH<sub>3</sub> molecules by using the radiation of the 9R branch of a TEA CO<sub>2</sub> laser. In the present <sup>13</sup>C separation experiments, intense IR light pulses of a TEA CO<sub>2</sub> laser were focused into a cylindrical Pyrex reaction cell with a length of 10 cm and an inner diameter of 2.5 cm. The laser pulse was composed of a main spike of 100 ns containing 60–70% of the total energy and a tail of 2 μs. The focused laser beam could be recognised as homogeneous along the beam direction and the effective photolytic zone was 2.5 cm<sup>3</sup>. CF<sub>2</sub>ClCH<sub>3</sub> at a pressure of 13.3 mbar was irradiated with 2000 laser pulses at a fluence of about 2 J cm<sup>-2</sup> at the 9R(10) laser line (1071.88 cm<sup>-1</sup>). The dissociated product detected by a gas chromatograph contained only 1,1-difluoroethene. The mass spectroscopy analysis indicated that <sup>13</sup>C was highly enriched in the products <sup>13</sup>CF<sub>2</sub>=CH<sub>2</sub> and CF<sub>2</sub>=<sup>13</sup>CH<sub>2</sub>. We consider that the <sup>13</sup>C-selective dissociation channels of CF<sub>2</sub>ClCH<sub>3</sub> can be attributed to a four-centred elimination of HCl from <sup>13</sup>CF<sub>2</sub>ClCH<sub>3</sub> or CF<sub>2</sub>Cl<sup>13</sup>CH<sub>3</sub>,

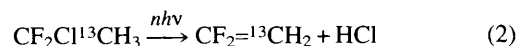
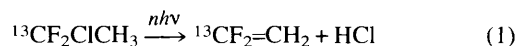


Table 1 cites a set of <sup>13</sup>C yields per pulse and <sup>13</sup>C concentrations of the CF and CH<sub>2</sub> fragments and the CF<sub>2</sub>=CH<sub>2</sub> product. Under the mentioned photolytic condition, the <sup>13</sup>C concentration of CF<sub>2</sub>=CH<sub>2</sub> could reach 40%. In principle, when the <sup>13</sup>C–C vibrational band is selectively excited, one carbon atom must maintain no <sup>13</sup>C selectivity. It dilutes the <sup>13</sup>C concentration of the product decomposed from the other reaction channel. So, the intrinsic <sup>13</sup>C decomposition selectivity from reactions (1) and (2) should be higher than those observed in the CF and CH<sub>2</sub> mass fragments.† We also found that decreasing the initial working pressure of CF<sub>2</sub>ClCH<sub>3</sub> resulted in a decrease of <sup>13</sup>C concentration in the product. For instance, when we changed the pressure of CF<sub>2</sub>ClCH<sub>3</sub> from 13.3 mbar to 6.7 mbar and maintained the same photolytic condition as mentioned above, the <sup>13</sup>C concentration in the CF<sub>2</sub>=CH<sub>2</sub> product dropped from 40 to 25%.

In order to further prove that the dissociation channel under the excitation of the intense IR laser is the elimination of HCl from CF<sub>2</sub>ClCH<sub>3</sub> rather than the direct rupture of C–C, C–F or C–H bonds,<sup>11</sup> we added 2.7 mbar of oxygen into the reaction system containing 13.3 mbar of CF<sub>2</sub>ClCH<sub>3</sub> as a radical scavenger. No evidence of the formation of oxygen-containing product was observed and oxygen did not obviously influence the <sup>13</sup>C selectivity in the CF<sub>2</sub>=CH<sub>2</sub> product under the same photolytic conditions.

The excitation of the C–C bond of fluorinated ethanes generally can not give high <sup>13</sup>C selectivity and the maximum of the <sup>13</sup>C concentration in the product can attain only 50% at optimum selective excitation. We have demonstrated that a fairly high <sup>13</sup>C selectivity and yield in the <sup>13</sup>C-selective IR multiphoton dissociation of CF<sub>2</sub>ClCH<sub>3</sub> can be attained at a low laser fluence of 2–3 J cm<sup>-2</sup>. In the <sup>13</sup>C-selective dissociation of CHClF<sub>2</sub> which is a molecule investigated widely for <sup>13</sup>C separation, the optimum <sup>13</sup>C yield could be attained at 6–10 J cm<sup>-2</sup> and the yield at 2.5 J cm<sup>-2</sup> is only 1 × 10<sup>-3</sup>.<sup>1,4,5</sup>

**Table 1** <sup>13</sup>C yields and concentrations in IR multiphoton dissociation of CF<sub>2</sub>ClCH<sub>3</sub>

Pressure of CF <sub>2</sub> ClCH <sub>3</sub> (mbar)	Laser fluence (J cm <sup>-2</sup> )	<sup>13</sup> C concentration in mass fragments (%)		<sup>13</sup> C concentration in CF <sub>2</sub> =CH <sub>2</sub> (%)	<sup>13</sup> C yield per pulse <sup>a</sup>
		CF	CH <sub>2</sub>		
13.3	2.4	34	23	29	0.005
13.3 <sup>b</sup>	2.0	46	34	40	0.003
6.7	2.0	27	21	24	0.004

<sup>a</sup> <sup>13</sup>C yield per pulse is defined as the ratio of 2 × <sup>13</sup>C molecules decomposed per pulse to <sup>13</sup>C molecules irradiated per pulse. <sup>b</sup> 2.6 mbar of oxygen was added into the reaction cell.

Therefore, in the  $^{13}\text{C}$  separation from the  $\text{CHClF}_2$  system, the laser beam must be tightly focused and the resulting short photolytic zone limits the utilisation efficiency of photons. In the case of  $\text{CF}_2\text{ClCH}_3$ , a near parallel laser beam can be used to expand the effective photolytic zone several times and the  $^{13}\text{C}$  yield must be enhanced.<sup>5</sup> We expect that  $\text{CF}_2\text{ClCH}_3$  is a promising molecule for practicable  $^{13}\text{C}$  separation.

#### Footnote

† Considering the  $^{13}\text{C}$  concentration balance in the  $\text{CF}$  and  $\text{CH}_2$  mass fragments of  $\text{CF}_2=\text{CH}_2$ , for 45% of  $^{13}\text{CF}$  and 20% of  $^{13}\text{CH}_2$  detected in the mass spectrum the branch ratio of reaction (1) to (2) should be between 0.8 and 4 and the nascent  $^{13}\text{C}$  concentration in the  $\text{CF}_2$  group originated from reaction (1) and in the  $\text{CH}_2$  group produced from reaction (2) should be higher than at least 56 and 36%, respectively.

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