^{13}C-selective dissociation of 1-chloro-1,1-difluoroethane *via* vibrational excitation of the C–C bond

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The ^{13}C-selective IR multiphoton dissociation of CF_2ClCH_3 *via* the vibrational excitation of the C–C bond produces $^{13}CF_2{=}CH_2$ and $CF_2{=}^{13}CH_2$; high ^{13}C selectivity and production yield can be attained at low laser fluence.

Despite frequent works on the ^{13}C-selective IR multiphoton dissociation of fluorinated methanes,[1–5] there have, so far, been few attempts to separate ^{13}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 ^{13}C-selective absorption of IR photons. The fluorinated methanes, however, have larger vibrational anharmonicity in the vibrational spectra and their effective ^{13}C-selective dissociation requires high laser fluence, which results in a higher energy consumption in the laser separation of ^{13}C isotope.[3,4] 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.[6,7] This is favourable for the absorption of IR photons and high ^{13}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 ^{13}C selectivity in the infrared multiphoton dissociation of fluorinated ethanes. High ^{13}C selectivity has been revealed only in the IR multiphoton dissociation of C_2F_5I by the ^{13}C-selective excitation of the $C{-}F_2$ stretching mode at an extremely low pressure.[8]

We report here the results on the ^{13}C-selective IR multiphoton dissociation of CF_2ClCH_3 by the excitation of the C–C stretching mode which is the ν_6 band located at 1134 cm^{-1}.[9,10] The ^{13}C isotope shifts for the C–C stretching modes of $^{13}CF_2ClCH_3$ and $CF_2Cl^{13}CH_3$ have not been reported yet and are generally estimated to be *ca.* 15–25 cm^{-1}. It is possible to excite selectively $^{13}CF_2ClCH_3$ and $CF_2Cl^{13}CH_3$ molecules by using the radiation of the 9R branch of a TEA CO_2 laser. In the present ^{13}C separation experiments, intense IR light pulses of a TEA CO_2 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^3. CF_2ClCH_3 at a pressure of 13.3 mbar was irradiated with 2000 laser pulses at a fluence of about 2 J cm^{-2} at the 9R(10) laser line (1071.88 cm^{-1}). The dissociated product detected by a gas chromatograph contained only 1,1-difluoroethene. The mass spectroscopy analysis indicated that ^{13}C was highly enriched in the products $^{13}CF_2{=}CH_2$ and $CF_2{=}^{13}CH_2$. We consider that the ^{13}C-selective dissociation channels of CF_2ClCH_3 can be attributed to a four-centred elimination of HCl from $^{13}CF_2ClCH_3$ or $CF_2Cl^{13}CH_3$,

$$^{13}CF_2ClCH_3 \xrightarrow{nh\nu} {}^{13}CF_2{=}CH_2 + HCl \qquad (1)$$

$$CF_2Cl^{13}CH_3 \xrightarrow{nh\nu} CF_2{=}^{13}CH_2 + HCl \qquad (2)$$

Table 1 cites a set of ^{13}C yields per pulse and ^{13}C concentrations of the CF and CH_2 fragments and the $CF_2{=}CH_2$ product. Under the mentioned photolytic condition, the ^{13}C concentration of $CF_2{=}CH_2$ could reach 40%. In principle, when the ^{13}C–C vibrational band is selectively excited, one carbon atom must maintain no ^{13}C selectivity. It dilutes the ^{13}C concentration of the product decomposed from the other reaction channel. So, the intrinsic ^{13}C decomposition selectivity from reactions (1) and (2) should be higher than those observed in the CF and CH_2 mass fragments.[†] We also found that decreasing the initial working pressure of CF_2ClCH_3 resulted in a decrease of ^{13}C concentration in the product. For instance, when we changed the pressure of CF_2ClCH_3 from 13.3 mbar to 6.7 mbar and maintained the same photolytic condition as mentioned above, the ^{13}C concentration in the $CF_2{=}CH_2$ 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_2ClCH_3 rather than the direct rupture of C–C, C–F or C–H bonds,[11] we added 2.7 mbar of oxygen into the reaction system containing 13.3 mbar of CF_2ClCH_3 as a radical scavenger. No evidence of the formation of oxygen-containing product was observed and oxygen did not obviously influence the ^{13}C selectivity in the $CF_2{=}CH_2$ product under the same photolytic conditions.

The excitation of the C–C bond of fluorinated ethanes generally can not give high ^{13}C selectivity and the maximum of the ^{13}C concentration in the product can attain only 50% at optimum selective excitation. We have demonstrated that a fairly high ^{13}C selectivity and yield in the ^{13}C-selective IR multiphoton dissociation of CF_2ClCH_3 can be attained at a low laser fluence of 2–3 J cm^{-2}. In the ^{13}C-selective dissociation of $CHClF_2$ which is a molecule investigated widely for ^{13}C separation, the optimum ^{13}C yield could be attained at 6–10 J cm^{-2} and the yield at 2.5 J cm^{-2} is only 1×10^{-3}.[1,4,5]

Table 1 ^{13}C yields and concentrations in IR multiphoton dissociation of CF_2ClCH_3

Pressure of CF_2ClCH_3 (mbar)	Laser fluence (J cm^{-2})	^{13}C concentration in mass fragments (%)		^{13}C concentration in $CF_2{=}CH_2$ (%)	^{13}C yield per pulse[a]
		CF	CH_2		
13.3	2.4	34	23	29	0.005
13.3[b]	2.0	46	34	40	0.003
6.7	2.0	27	21	24	0.004

[a] ^{13}C yield per pulse is defined as the ratio of 2 × ^{13}C molecules decomposed per pulse to ^{13}C molecules irradiated per puse. [b] 2.6 mbar of oxygen was added into the reaction cell.

Therefore, in the ^{13}C separation from the $CHClF_2$ system, the laser beam must be tightly focused and the resulting short photolytic zone limits the utilisation efficiency of photons. In the case of CF_2ClCH_3, a near parallel laser beam can be used to expand the effective photolytic zone several times and the ^{13}C yield must be enhanced.[5] We expect that CF_2ClCH_3 is a promising molecule for practicable ^{13}C separation.

Footnote

† Considering the ^{13}C concentration balance in the CF and CH_2 mass fragments of $CF_2{=}CH_2$, for 45% of ^{13}CF and 20% of $^{13}CH_2$ detected in the mass spectrum the branch ratio of reaction (1) to (2) should be between 0.8 and 4 and the nascent ^{13}C concentration in the CF_2 group originated from reaction (1) and in the CH_2 group produced from reaction (2) should be higher than at least 56 and 36%, respectively.

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