



## On the separation of enantiomers of 1,1,1,2-Tetrafluoroiodoethane by IR Multiphoton Excitation

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### Abstract

We report the first attempt to separate enantiomers of chiral molecules using IR-multiphoton excitation with circularly polarized light.  $\text{CF}_3\text{CHI}$  has been chosen as its IR-spectroscopy and its IR-photochemistry is well characterized by our previous work. A theoretical model based on a master equation is presented to predict the enantiomeric enrichment factor. Our experimental results show that the experimental sensitivity must be improved to reach the limit of the theoretical prediction.

### Introduction

The infrared laser chemistry of chiral molecules is of potential interest for some of the fundamental aspects of molecular chirality [1], including racemization dynamics, the possibility of chiral selection of diastereomers and enantiomers by multiphoton excitation, and the hypothetical influence of the weak nuclear interaction in chemistry. So far, only two classes of chiral compounds have been the subject of detailed studies concerning their infrared laser chemical properties, the chiral sulfoxides [2], and the (mono)fluorooxiranes [3, 4]. Our investigations of sulfoxides proved for the first time [6], that isotopic diastereoisomers can be separated by multiphoton excitation, due to their slightly different vibrational transition frequencies. However, the possibility of enantiomer enrichment by infrared laser radiation has not been investigated previously, mainly because of the difficulties related to highly accurate enantioselective analysis of racemic mixtures of the possible candidates. Now, for the chiral  $\text{CF}_3\text{CHI}$  these difficulties have been solved, analyzing the racemic mixtures before and after irradiation by means of chiral gas chromatography.

Tetrafluoroiodoethane has many advantages for experimental investigations of IR multiphoton excitation and laser chemistry. Its infrared laser chemistry [6] and spectroscopy were subject to previous studies, including a detailed analysis of the influence of a chiral, symmetry breaking coupling on the infrared spectra of the C-H chromophore [7, 8].  $\text{CF}_3\text{CHI}$  contains a strong infrared chromophore moiety (C-F) with an integrated band strength of  $G = 2.1 \text{ pm}^2$ . The low threshold energy of  $\tilde{E}_2 = 18400 \text{ cm}^{-1}$  for the C-I bond fission leads to a simple primary dissociation step in IR-laser chemistry.

### Theoretical Model for Enantiomeric Enrichment During IR-Multiphoton Excitation

Our theoretical treatment of the enantiomeric enrichment by infrared multiphoton excitation is based on the vibrational circular dichroism of the pumped chromophore vibration. Irradiation with circularly polarized (CP) light leads to a slightly more efficient excitation of one of the two enantiomers, giving rise to a higher product yield. This effect can be calculated approximately using the master equation [9, 10, 11]. Assuming that the difference in the efficiency of the multiphoton excitation with CP-light for the (R) and (S) enantiomers is essentially determined

by their different integrated band strengths  $G_{S,R}$ , we can apply the master equation with a modified rate coefficient for up-pumping, given by

$$K_{M+1,M} = \frac{CG(1 \pm g/2)I\rho'_M}{\Delta E\rho_M} \quad (1)$$

where the symbols have been defined previously in [9, 10, 11] and  $g$  is the (Kuhn) anisotropy factor [12, 13]

$$g = \frac{\Delta G}{G} = \frac{4R}{D} \quad (2)$$

$\Delta G$  represents the difference between the integrated band strengths of the vibration excited for (R) and (S) enantiomers, irradiated with circularly polarized light. In equation (2)  $g$  is furthermore related to the rotatory strength  $R$  and the dipole strength  $D$  of the vibration [14], molecular quantities which can be measured or calculated ab initio [15, 16, 17]. In equation (1) we assume the approximate validity of the chromophore principle [9, 10, 11] not only for  $G$ , but also for  $g$ , meaning that both quantities are constant over a wide range of excitation energies.

## Enantiomeric enrichment, experiment and theory

To investigate the possibility of chiral selection by infrared multiphoton excitation, we performed experiments irradiating racemic mixtures of tetrafluoroiodoethane with CP-radiation, using the laser lines 9R24 and 9R28 under various experimental conditions. The results are summarized in table 1. Within the experimental accuracy of our analytical method of typically 0.1%, no enantiomeric enrichment could be achieved. Experiments with higher total pressure where collisional deactivation should increase the selectivity because more photons are absorbed until the reaction threshold is reached again gave no significant deviation from the racemic ratio.

$\tilde{\nu}_{exc}/$ $cm^{-1}$	$P_{tot}/$ mbar	$F/$ $Jcm^{-2}$	$N$	$n$	Yield/ %	$\langle\langle e_1/e_2 \rangle\rangle$	$\Delta\langle\langle e_1/e_2 \rangle\rangle$
—	11	—	—	4	—	0.999	0.005
1083.3	11	0.7	8640	4	50	0.998	0.014
1083.3	11	0.5	13500	4	25	1.0032	0.0024
1083.5	11	0.6	23000	4	60	1.004	0.004
1074.7	11	0.7	9000	4	30	1.004	0.007
1074.7	11	0.6	18000	4	30	1.002	0.007
1074.7	11	0.5	37200	4	20	1.007	0.008
1074.7	27	1.4	5600	4	30	0.989	0.04
1074.7	43	1.9	2300	4	50	1.004	0.008
1074.7	17.8	1.1	10670	7	41	1.003	0.013

Table 1: Summary of the experiments on chiral selection of tetrafluoroiodoethane.  $N$ ,  $\tilde{\nu}_{exc}$  and  $F$  are the number of multi mode laser pulses, the excitation wavenumber, and the laser fluence in the experiments.  $P_{tot}$  is the total pressure (reactant: always  $p = 0.5$  mbar  $CF_3CHI$  plus additional  $N_2$ ), and  $n$  is the number of experiments. The first line represents the result of the analysis of the reactant without laser irradiation. For each experiment the reaction yield was determined by IR spectroscopy. The mean enantiomeric ratio  $\langle\langle e_1/e_2 \rangle\rangle$  was measured by chiral gas chromatography with the error  $\Delta\langle\langle e_1/e_2 \rangle\rangle$  given as 95% confidence interval.

In the simulation a master equation was applied for different values of  $g$  and no significant influence from possible nonlinear intensity effects (case C, [10, 11]), even at very low laser

intensities ( $I < 5\text{MWcm}^{-2}$ ), was observed. An almost linear dependence of the static yield ratio as a function of the anisotropy factor  $g$  is found for different laser fluences. The slope is close to one for all laser fluences. Therefore the effect of chiral selection by multiphoton excitation scales linearly with the anisotropy factor  $g$  or the vibrational circular dichroism  $\Delta G$ :

$$\frac{P_{app}^R - 1}{P_{app}^S - 1} \propto g \propto \Delta G \quad (3)$$

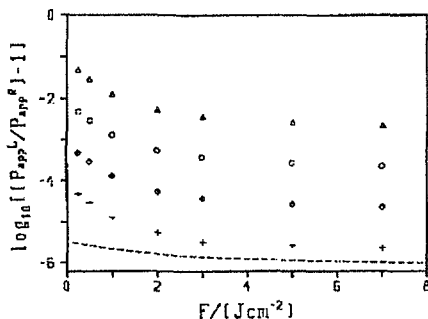


Figure 1: Ratios of apparent yields  $P_{app}^R, P_{app}^S$  in logarithmic scale are given as a function of laser fluence for different values of the anisotropy factor  $g$ . (Symbols,  $g$ ; ( $\Delta$ ):  $4.76 \cdot 10^{-2}$ ; ( $\circ$ ):  $4.76 \cdot 10^{-3}$ ; ( $\circ$ ):  $4.76 \cdot 10^{-5}$ ; (+):  $4.76 \cdot 10^{-6}$ . The hypothetical single photon selectivity is given as dashed line ( $g = 4.76 \cdot 10^{-6}$ ).

This finding is consistent with the usual stepwise excitation of the reactant in infrared laser chemistry, whereas for direct absorption of  $n$  photons one might expect a scaling with  $(\Delta G)^n$ . Figure 1 shows the fluence dependence of the static yield ratio for different anisotropy factors. Here, increasing enantiomeric separations are observed for decreasing laser fluences. These data can be compared to the hypothetical single photon case which are shown for the smallest value of  $g$  as a broken line in the figure. Concerning chiral selection, single and multiphoton excitation of tetrafluoroiodoethane differ by a factor of 15 for small laser fluences ( $F = 0.25 \text{ Jcm}^{-2}$ ). This enhancement is comparable with the number of absorbed IR-photons. For higher laser fluences contributions from the steady state regime are more important and the chiral selection approaches the value for single photon excitation.

To simulate a realistic experiment, we have calculated the vibrational circular dichroism of tetrafluoroiodoethane ab initio. For the  $\nu_{C-F}$  chromophore vibration a value of  $g = 6.75 \cdot 10^{-5}$  was obtained [17]. If one chooses a laser fluence of  $F = 0.5 \text{ Jcm}^{-2}$ , one finds that a maximum enantiomeric excess is obtained with the number of laser pulses chosen to be  $N_{max} = 2286$ . We then get static yields of  $P_{app}^R = 1.094060 \cdot 10^{-2}$  and  $P_{app}^S = 1.093610 \cdot 10^{-2}$ . The calculated enantiomeric excess is  $ee = 2.1 \cdot 10^{-4}$ , one order of magnitude beyond the sensitivity of our experiments using chiral gas chromatography with an uncertainty of about  $\Delta ee = 2.5 \cdot 10^{-3}$ .

## Summary

We have previously determined for the first time hyperfine state selected product distributions in IR-multiphoton excitation with the examples  $\text{CF}_3\text{I}$ ,  $\text{C}_6\text{F}_5\text{I}$  and  $\text{CF}_3\text{CHF}_1$  [6]. Here, several

major new results were obtained for the chiral compound  $\text{CF}_3\text{CHF}_1$ . A first experiment was performed, resulting in enantiomer separation below the sensitivity of our analytical technique. In principle one can think of increasing the sensitivity, for example by averaging individual gas chromatograms. Parallel to the experiment, enantiomer enrichment was calculated, implementing the vibrational circular dichroism into the statistical theory of multiphoton excitation. The simulation of a realistic experiment, based on the vibrational circular dichroism calculated ab initio revealed that the effect is expected to be below the sensitivity of our current experimental conditions. The calculation points to the fact, that chiral selection in the limit of case B [10] is approximately linear with respect to the number  $n$  of photons absorbed. A larger effect would be expected in case C [10], i.e. for a smaller chiral molecule such as fluorocyclohexane [3, 4].

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