with a normal focus molybdenum-target X-ray tube operated at 2.0 kW (50 kV. 40 mA) [9]. A total of 1321 frames of data were collected using a narrow-frame method with scan widths of  $0.3^{\circ}$  in  $\omega$  and exposure times of 30 sec per frame using a crystal-to-detector distance of 6.015 cm (maximum  $2\theta$  angle 51.62°). The total data collection time was approximately 13 h. Frames were integrated with the Siemens SAINT program to yield a total of 14059 reflections, of which 2213 were independent ( $R_{int} = 0.0307$ , Laue symmetry 6/mmm,  $R_{sig} = 0.0179$ ) and 1993 were above  $4\sigma(F)$ . The unit cell parameters (at 153 K) of a = b = 16.5617(2), c = 15.4433(2) Å were based upon least-squares refinement of the three-dimensional centroids of 8192 reflections. The cell volume and density were 3668 Å<sup>3</sup> and 1.547 g cm<sup>-3</sup>, respectively. By assuming a merohedrally twinned trigonal specimen, twinning law  $(0 - 1 \ 0 - 1 \ 0 \ 0 \ 0 - 1)$  and space group  $P\overline{3}c1$ , Ru of position A is found at (1/3, 2/3, z) (site simmetry  $C_3\overline{3}$ ) and Ru of position B at (0, 0, 1/4) (site symmetry  $D_3\overline{3}2$ ) with a twin population of 0.501(3). The refinement of coordinates and anisotropic displacement parameters converged at  $R_1 = 0.0250$ , GOOF = 1.144 ( $\omega = 1/(\sigma^2 (F_o^2) +$  $(0.0090 \text{ P})^2 + 3.0338 \text{ P})$ , where  $P = (F_o^2 + 2F_o^2)/3$  for 1993 observations and 181 parameters (hydrogen atoms in calculated positions, d(C-H) = 0.95 Å).

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Fluorinated oxiranes are suitable candidates for such investigations because of the small and rigid ring structure and their strong infrared absorptions in the range of the CO<sub>2</sub> laser. Some work on the influence of substituents on the ring structure of highly fluorinated oxiranes has been reported,<sup>[5-8]</sup> but up to now monofluoroxirane has neither been prepared nor otherwise experimentally investigated. Two publications describe theoretical computations of the molecular structure of the monofluorooxirane.<sup>[9, 10]</sup> The anticipated shortening of the C-O bond at the fluorinated carbon atoms relative to the C-O bond length at the CH<sub>2</sub> carbon suggests the formation of a C-O double bond at the CHF side of the ring upon elimination of hydrogen fluoride. Both the structure and the proposed decomposition pathway have to be verified by experiment. We have found remarkably diverse phenomena in experiments with isotopic labeling. Furthermore, fluorooxirane should also be important in the chemical activation of fluoroethylene with oxygen atoms (<sup>1</sup>D oder <sup>3</sup>P).<sup>[11]</sup> In a general context, the calculation of the circular dichroism of substituted oxiranes,<sup>[12]</sup> the stereomutation at the carbon atom,<sup>[13]</sup> and parity selection<sup>[14]</sup> are of interest.

Fluorooxirane 2 and  $2,2-[^{2}H_{2}]$ -fluorooxirane 3 have been prepared according to Scheme 1, starting from chlorotrifluoroethylene. The preparation of the ester<sup>[15]</sup> and its reduction to the optically active (-)-alcohol following the diastereoisomer separation of chlorofluoroacetic acid have been reported.<sup>[16]</sup>

$$CF_{2} = CCIF \xrightarrow{\text{NaOEt}} CCIFH-CF_{2}OEt \xrightarrow{\text{H}_{2}SO_{4}} CCIFH-CO_{2}Et$$

$$1$$

$$1 \xrightarrow{\text{LiAIH}_{4}} CCIFH-CH_{2}OH \xrightarrow{\text{KOH}} H_{2}C \xrightarrow{\text{CHF}} CHF$$

$$2$$

$$1 \xrightarrow{\text{LiAID}_{4}} CCIFH-CH_{2}OH \xrightarrow{\text{KOH}} H_{2}C \xrightarrow{\text{CHF}} CHF$$

$$3$$

Scheme 1.

The last step is performed in analogy to the reaction of 2chloroethanol with potassium hydroxide to yield the unsubstituted oxirane already reported by Wurtz.<sup>(17)</sup> For the doubly deuterated isotopomer the ester 1 is reduced with lithium aluminium deuteride. The isotopic purity of the  $CD_2$  groups of the alcohol and the oxirane has been checked by infrared and mass spectroscopy to be at least 99%.

Figure 1 shows the gas-phase infrared spectra of 2 and 3 in the region important for  $CO_2$ -laser excitation. For the normal mode assignment of the fundamentals and to characterize the compounds, the equilibrium geometry and the infrared spectra have been calculated ab initio (Gaussian'94, MP2) with basis sets of increasing size up to triple-zeta with additional polarization functions (C,F,O: 5s4p2d; H: 3s3p<sup>[19]</sup>). The experimental and ab initio wavenumbers in Table 1 show differences of the order of a few percent. The sequences of strong and weak absorptions are identical for experiment and ab initio theory. The strongest absorptions are due to the C-F chromophore at 1100 (3) and 1125 cm<sup>-1</sup> (2).

The rotational structure of the vibrational bands has been resolved in the spectra recorded on our BOMEM-DA002 Fourier-transform infrared spectrometer with an instrumental bandwidth of 0.004 cm<sup>-1</sup> (FWHM, apodized). In an iterative

## Synthesis, Structure, High-Resolution Spectroscopy, and Laser Chemistry of Fluorooxirane and 2,2-[<sup>2</sup>H<sub>2</sub>]-Fluorooxirane\*\*

#### Hans Hollenstein, David Luckhaus, Jörg Pochert, Martin Quack,\* and Georg Seyfang

Dedicated to Professor Edgar Heilbronner on the occasion of his 75th birthday

Fundamental questions concerning symmetry, structure, and dynamics of chiral molecules beyond classical structural concepts<sup>[1]</sup> may in future be answered by spectroscopy and laser chemical investigations.<sup>[2]</sup> For this purpose, small chiral molecules that can be investigated by reaction dynamics and by gasphase IR and UV spectroscopy with rotational resolution have to be found. Only few examples of this type have been reported, for instance CHBrClF<sup>[3]</sup> or the substituted thiiran-1-oxides.<sup>[4]</sup>

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## COMMUNICATIONS

Table 1. Experimental fundamental wavenumbers  $\tilde{v}_{exp}$ , harmonic wavenumbers  $\omega_{ai}$  calculated ab initio, and band strengths G of 2 and 3 [a].

	C <sub>2</sub> H <sub>3</sub> FO <b>2</b>									
No.	cm <sup>-1</sup>	$\frac{G_{ai}}{\text{pm}^2}$	$\frac{\tilde{v}_{exp}}{cm^{-1}}$	$\frac{G_{exp}}{pm^2}$	Assignment	$\frac{\omega_{ai}}{\mathrm{cm}^{-1}}$	$\frac{G_{ai}}{pm^2}$	cm <sup>T</sup>	Gese pm <sup>2</sup>	Assignment
1	3289	0.02	3078		v-CH <sub>2</sub>	3235	0.07	3053	0.02	v-CF-H
2	3235	0.06	3050	0.11 [b]	v-CF-H	2457	0.02	2203	0.02	v-CD <sub>2</sub>
3	3176	0.04	3011		v-CH <sub>2</sub>	2304	0.03	2193	0.02	v-CD <sub>2</sub>
4	1541	0.28	1479	0.15	δ-CH <sub>2</sub>	1444	0.96	1406	0.6	δ-COC
5	1427	0.66	1383	0.38	δ-CF-H	1328	0.25	1293	0.20	δ-CF-H
6	1319	0.33	1284	0.21	δ-COC	1189	0.07	1150		δ-CF-H
7	1188	0.87	1156		δ-CF-H	1116	1.79	1101	1.48 [c]	v-CF
8	1163	0.47	1135	1.14 [c]	δ-CH <sub>2</sub>	1069	0.22	1044		δ-CD <sub>2</sub>
9	1148	0.9	1126		v-CF	1000	0.59	982	0.26	δ-CD <sub>2</sub>
10	1098	0.05	1085		δ-CH,	875	0.28	867	0.15	_
11	985	0.93	968	0.52	_	831	0.50	820	0.7 [d]	δ-COC
12	881	1.39	867	0.71	δ-COC	816	0.49	803	. ,	_
13	786	0.45	755	0.29	δ-COC	696	0.35	684	0.26	-
14	511	0.15	510	0.07	δ-CF	487	0.14	488	0.16	δ-CF
15	434	0.25	432	0.13	δ-CF	389	0.24	386	0.21	δ-CF

[a]  $G = \int \sigma(\vec{v}) d \ln \hat{v}$  where  $\sigma$  represents the absorption cross-section. Range of integration for overlapping bands [cm<sup>-1</sup>]: [b] 2961-3134. [c] 1078-1177. [d] 1020-1190. [e] 760-847. The values  $\vec{v}_{exp}$  represent the approximate band positions, except for the fundamentals analyzed in Table 2. The assignments of local symmetry coordinates are given in the last column.  $\delta$  represents a deformation and v a stretching vibration.



Figure 1. Gas-phase infrared spectra of 2 and 3 in the spectral region of the emissions of the CO<sub>2</sub> laser. Experimental conditions: 9 mbar 3 and 5 mbar 2, pathlength 18 cm. Resolution:  $0.1 \text{ cm}^{-1}$ . The positions of the laser frequencies used for excitation and the integration ranges for the evaluation of the integrated band strengths *G* are indicated by lines. The maximum values of the absorbance ( $A \approx \ln I_0/I$ ) are close to 4 for 3 and 1 for 2.

procedure,<sup>[20]</sup> the simulated rovibrational structure was fitted to experiment (Figures 2 and 3). The rotational and centrifugal distortion constants of both fluorooxiranes were determined. The vibrational ground-state constants were determined by a separate fit to combination differences. The good correspondence between calculated and experimental rotational constants provides evidence for the identity and the structure of the prepared molecules. Although this type of proof is rather usual for the identification of unstable species, for example in radioastronomy,<sup>[21]</sup> it can also be applied in exceptional cases for the characterization of newly synthesized compounds.<sup>[22]</sup> Table 2 lists the calculated and experimentally determined parameters. For the determination of the experimentally improved  $r_0$ -structure, the ab initio geometry is used as a starting point, and the bond lengths and bond angles of the heavy atoms (C,O,F) are fitted to the experimental rotational constants. The C-H distances are taken from the correlation between stretching frequency and bond length<sup>[23]</sup> and the angles from the ab initio calculation (MP2/TZ2P). An additional investigation of the effect of H/D substitution on the rotational constants showed that the chosen



Figure 2. Experimental (bottom) and simulated rovibrational structure (top) of the 968 cm<sup>-1</sup> band of 2 (parameters from Table 2). Experimental conditions: 5 mbar 2, pathlength 18 cm, resolution  $0.004 \text{ cm}^{-1}$ .



Figure 3. Detail of Figure 2, showing the perfect agreement of experimental (bottom) and simulated rovibrational structure (top).

 $r_0$  CH/D bond lengths are optimal with respect to the deviation between experimental and calculated rotational constants. The resulting structure is shown in Figure 4. While the CH and CD  $r_0$  structures are slightly different in general,<sup>[24]</sup> this is not important at the level of accuracy achieved here.

When irradiated at small pressures in the gas phase with infrared laser light, fluorooxirane decomposes unimolecularly after

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Table 2. Experimental rovibrational parameters from the analysis of the high resolution spectra of 2 and 3 and rotational constants calculated ab initio [a].

		C <sub>2</sub> H <sub>3</sub> FO 2		C <sub>2</sub> D <sub>2</sub> HFO <b>3</b>				
	v = 0	$v_{11} = 1$	v <sub>12</sub> = 1	v = 0	$v_9 = 1$	$v_{\gamma} = 1$		
A	0.6703127(6)	0.6685743(3)	0.668578(2)	0.584192(2)	0.584139(6)	0.5842373(2)		
В	0.2449829(6)	0.2446638(3)	0.244492(1)	0.2273402(6)	0.227369(2)	0.2268587(1)		
С	0.2139151(5)	0.2134613(2)	0.213565(1)	0.1978526(4)	0.197488(1)	0.1972001(1)		
$D_J/10^{-6}$	0.109(1)	0.1071(4)	0.108(3)	0.092(2)	0.08(1)	0.0882(4)		
$D_{JK}/10^{-6}$	0.235(6)	0.256(2)	0.25(2)	0.18(1)	0.27(8)	0.133(2)		
$D_{\rm K}/10^{-6}$	0.974(7)	0.984(3)	0.89(5)	0.69(6)	0.14(3)	0.715(3)		
$d_1/10^{-7}$	-0.23(1)	-0.257(5)	-0.06(3)	-0.11(1)	~ 0.16(7)	-0.105(3)		
$d_2/10^{-8}$	0.13(5)	0.14(3)	-0.2(1)	-0.14(7)	-0.1(2)	-0.20(1)		
<i>v</i> <sub>o</sub>	0	968.21267(5)	866.637(3)	0	982.0232(3)	1101.32909(3)		
N <sub>data</sub>	2417 [b]	3628	878	2300 [c]	1883	2616		
$d_{\rm rms}/10^{-3}$	0.554	0.918	4.504	0.651	4.398	0.706		

[a] All values (except  $N_{data}$ ) are given in cm<sup>-1</sup>. Rotational constants calculated ab initio are given in cm<sup>-1</sup>: for 2  $A_c = 0.670755$ ,  $B_c = 0.245158$ ,  $C_c = 0.213635$ ; for 3:  $A_c = 0.584162$ ,  $B_c = 0.227693$ ,  $C_c = 0.197700$ . Combination differences: [b] 2010 from the analyses of  $v_{11}$  and 407 from  $v_{12}$ . [c] 1119 from  $v_9$  and 1181 from  $v_7$ .  $d_{rms}$  represents the root mean square of the deviation between calculated and experimental frequencies ( $N_{data}$ ). See ref. [20] for the definition of the parameters and for the numerical procedure.



Figure 4. Structural parameters of the fluorooxiranes. The bond lengths [pm] and angles [°] are obtained by fitting the coordinates of he heavy atoms to the experimental rotational constants. The deviations  $(r_{\rm fit} - r_{\rm a})$  between the fitted and the pure ab initio structure are given in parentheses. An estimation of the errors of the fitted structure can be made by a sensitivity analysis of the fitted coordinates. The uncertainty in the bond distances is of the order of 2 pm; for the bond angles it is about 2°. Additional bond angles in degrees:  $H^2C^1H^3 = 117.6 (\pm 0)$ ,  $H^1C^2F = 110.8 (\pm 0.3)$ ,  $FC^2O = 114.6 (-0.9)$ ,  $C^1C^2F = 118.7 (+0.2)$ ,  $C^1C^2H^1 = 117.7 (\pm 0)$ ,  $C^2C^1H^2 = 120.8 (\pm 0)$ ,  $C^2C^1H^3 = 124.5 (\pm 0)$ ,  $H^2C^1O = 114.9 (+0.1)$ . The angle between the CCO and the  $H^2C^1H^3$  planes is 90.9  $(\pm 0)^\circ$  with respect to  $H^2$ . The angle between the cCO and the  $H^1C^2F$  planes is 88.8  $(+0.5)^\circ$  with respect to F. H<sup>3</sup> is oriented *trans* to F.

absorption of about n = 27 photons ( $\tilde{v} = 952.9 \text{ cm}^{-1}$ ) to give ketene and hydrogen fluoride (Scheme 2). The position of the exciting laser line with respect to the band center is rather similar for both the deuterated (excitation: 1083.5 cm<sup>-1</sup>, m = 24 photons; band center: 1100 cm<sup>-1</sup>) and the nondeuterated compound (excitation: 952.3 cm<sup>-1</sup>, band center: 968 cm<sup>-1</sup>).

$$H_2C \xrightarrow{nh\nu} CHF \xrightarrow{nh\nu} H_2C=C=O + HF$$
2
Scheme 2.

Because of the higher band strength G of the excited vibration, the process of excitation is more efficient for the deuterated isotopomer (Figure 1, Table 1) than for the nondeuterated compound. This results in higher yields for the laser chemical reaction in the case of the 2,2- $[^{2}H_{2}]$ -fluoroxirane. The infrared spectra of the product mixture shows clearly the strong absorption at 2130 cm<sup>-1</sup>, which is characteristic for ketene, <sup>[25]</sup> and can be represented by the superposition of the spectra of the ketene, which we prepared separately by published methods, <sup>[26]</sup> and the reactant. The reaction product hydrogen fluoride reacts with the walls of the glass cells used in the experiments. The very large isotope shifts in the infrared spectrum would offer excellent H/D isotopomer selectivities, although for large-scale hydrogen isotope separation simpler compounds are known to be useful.<sup>[18]</sup> The monodeuterated fluorooxirane HDCOCHF is present as a *cis-trans* diastereoisomer pair, which should be also separable quite easily by laser chemistry.<sup>[27]</sup> Chiral selection by infrared laser chemistry with circularly polarized light should be possible in principle, but has not yet been reported. However, mode selectivity, which could be tested for by irradiating  $D_2$ COCHF near 980 cm<sup>-1</sup> and near 1080 cm<sup>-1</sup>, is not expected under our experimental conditions.<sup>[18]</sup>

As the reaction products of an  $\alpha\alpha$  (HF + [<sup>2</sup>H<sub>2</sub>]-ketene) and an  $\alpha\beta$  (DF + [<sup>2</sup>H<sub>1</sub>]-ketene) elimination are different (Scheme 3),

Scheme 3.

the laser chemistry of the 2,2- $[{}^{2}H_{2}]$ -fluorooxirane gives insight into the mechanism of hydrogen fluoride elimination. Because of a lack of information about the rovibrational parameters of the 2130 cm<sup>-1</sup> absorption of ketene, the high resolution IR spectrum gives only a hint that both the deuterated and the doubly deuterated ketene are present in the reaction mixture. The mass spectrometric analyses yield a ratio of 2.7 to 1 for the molecular ions of  $[{}^{2}H_{2}]$ -ketene and  $[{}^{2}H_{1}]$ -ketene, whereas their fragment ions CD<sub>2</sub> and CHD show a shifted ratio of 1.3 to 1, due to isotope effects. From these results we conclude that at least two different mechanisms for the elimination of hydrogen fluoride from the fluorooxirane operate, and that the one leading to HF and the doubly deuterated ketene is clearly favored. This preference is in agreement with our expectations from the structure-reactivity relationship discussed at the beginning.

Ab initio calculations<sup>[28]</sup> on the transition states, products, and reaction pathways of the fluorooxirane show a manifold of possible reactions like the thermodynamically favored dissociation to CO and CH<sub>3</sub>F, the rearrangement to fluoroacetaldehyde or acetyl fluoride followed by HF elimination, as well as the concerted  $\alpha\beta$  and the  $\alpha\alpha$  elimination of HF. The latter reaction is followed by ring opening of oxiranylidene to yield ketene. The experimental facts suggest that the last two mechanisms are reasonable, because no additional product beyond ketene and hydrogen fluoride is observed in the experiments. For a quantitatively correct description, the reaction threshold of the  $\alpha\alpha$ elimination is fitted to the experimental branching ratio. The experimental laser-chemical yields  $P_{app}$ , which correspond approximately to the fraction of molecules dissociated in one laser shot in the effectively irradiated volume (for exact definition see Ref.<sup>[29]</sup>) are analyzed quantitatively by means of a complete simulation of the reaction (Figure 5) in terms of the non-



Figure 5. Reaction yield  $P_{app}$  (defined according to Ref. [29]) of the laser-chemical reaction of 3 as a function of laser fluence on excitation with the laser line 9 R 28 (1083.5 cm<sup>-1</sup>). The solid curve represents the calculated reaction yield. A rate constant of  $k(st) = 2.8 \times 10^7 \text{ s}^{-1}$  at a laser intensity of 100 MWcm<sup>-2</sup> is determined by fitting the coupling width  $DV = 160 \text{ cm}^{-1}$  to the experimental data. The reaction threshold of the  $\alpha\beta$  channel is calculated ab initio to be 304.0 kJmol<sup>-1</sup>, including zero point corrections. The threshold of the  $\alpha\alpha\beta$  existing from the ab initio value until the experimental branching ratio of  $\alpha\alpha:\alpha\beta\approx 2:1$  was reached (final value also 304.0 kJmol<sup>-1</sup>). This turned out to be only slightly fluence (*F*) dependent ( $F = \{Idt$  with laser intensity *I*).

linear case B/C master equation with respect to the spatial and temporal beam profile in the reaction cell and statistical specific rate constants.<sup>[30]</sup> A laser chemical rate constant for the decomposition of  $k(st) = 2.8 \times 10^7 \text{ s}^{-1}$  at a laser intensity of 100 MWcm<sup>-2</sup>, where the intensity proportional region is almost reached, is derived. The calculated branching ratio depends only slightly on the laser fluence ( $\alpha \alpha / \alpha \beta = 2 \pm 0.3$ ). Thus we have opened the route to the laser chemistry of the fluoro-oxiranes qualitatively and quantitatively for the first time.

#### Experimental section

Chlorotrifluoroethylene is obtained from Aldrich (29,516-7). 2-chloro, 2-fluoroethanol (5g) is heated to 80 °C, and 4 KOH pellets are added. The apparatus is closed, and the produced gas is trapped at -78 °C. The trap is warmed to room temperature, and the evolving gas condensed in a glass finger on a vacuum line. The yield of 2 or 3 is 15%. The vapor pressure is more than 250 mbar at 20 °C. The compounds can be stored in liquid nitrogen for several days and are stable under gas-phase conditions. MS(C<sub>2</sub>H<sub>3</sub>FO. 70 eV): m/z 62, 44, 42, 33, 32, 31, 29 (100%), 28, 18, 17, 16, 15; MS (C<sub>2</sub>D<sub>2</sub>HFO, 70 eV): m/z 64, 45, 33, 31, 30 (100%), 29, 17, 16. The mass spectra have been recorded on a Alkaid quadrupole spectrometer, the FTIR spectra with our BOMEM DA002 spectrometer (see Ref. [31] and references therein for experimental details). The product analysis has been carried out on a Perkin-Elmer 983 G grating spectrometer. For the laser chemistry, a Lumonics TEA 103-2 CO<sub>2</sub> Laser with multimode pulses of 100 ns duration [32] was available. The pressure in these experiments was 1 mbar fluoroxirane and 10 mbar nitrogen.

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#### Ene Reactions of Alkynes for the Stereoselective Synthesis of Allylamines\*\*

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Dedicated to Professor Rolf Gleiter on the occasion of his 60th birthday

Reactions of terminal acetylenes with formaldehyde and secondary amines yielding propargylamines through the intermediacy of iminium ions were first reported by Mannich in the 1930s (Scheme 1).<sup>[1]</sup> Later it was found that these reactions are often

$$R_2NH + HCHO + H-C \equiv C-R' \longrightarrow R_2N-CH_2-C \equiv C-R'$$

Scheme 1. Synthesis of a propargylamine from a secondary amine, formaldehyde, and a terminal acetylene.

promoted by the addition of copper salts.<sup>[2]</sup> Dialkyl-substituted acetylenes undergo intramolecular reactions with in situ generated iminium ions only with the assistance of external nucleophiles such as  $I^{-}$ .<sup>[3]</sup> Nucleophilic assistance is not needed for the aminomethylations of the more reactive propargylsilanes,

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