The Synthesis of [2-²H₁]Thiirane-1-oxide and [2,2-²H₂]Thiirane-1-oxide and the Diastereoselective Infrared Laser Chemistry of [2-²H₁]Thiirane-1-oxide

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Dedicated to Vladimir Prelog on the occasion of his 90th birthday

Abstract: We report the synthesis of the title compounds CH_2CHDSO and CH_2CD_2SO and their characterization by infrared spectroscopy. The monodeuterated species occurs in two isotopically diastereomeric forms with the D atom either *cis* or *trans* oriented to the O atom. The SO infrared chromophore in these diastereomers has a strong absorption centered near 1114 and 1116 cm^{-1}, respectively, with an integrated band strength $G = 2.8$ pm^2, which renders it very suitable for infrared multiphoton excitation with a CO_2 laser, leading to the laser chemical dissociation of the reactants into deuterated ethylene and $SO(^3\Sigma^-)$. We have established the first successful laser chemical separation of such a diastereomer pair, with a small but significant separation factor based on the small frequency difference of the ν_4 (SO stretching) fundamental mentioned above; the analysis used high-resolution FTIR spectroscopy in the region of the Q branches of ν_4. Our results are discussed in relation to various aspects of stereochemical reaction dynamics in chiral and achiral sulfoxides.

Keywords: IR spectroscopy · laser chemistry · multiphoton excitation · sulfoxides

Introduction

We have recently shown that organic sulfoxides are ideal candidates for IR-laser chemistry, because of the large band strength of the SO infrared chromophore with absorption in the emission range of the CO_2 laser.[1–3] This opens up a number of interesting potential applications of the infrared laser chemistry of these compounds. We may mention here the laser chemical generation of sulfoxide radicals and intermediates, which may be important in atmospheric chemistry.[4, 5] Also, one may consider laser chemical sulfur and oxygen isotope separation using these compounds.[6] Furthermore, because of the interesting stereochemistry of sulfoxides, one can envisage mechanistic studies by IR-laser chemistry of appropriately substituted sulfoxides. Of particular interest are chiral sulfoxides.[7–9] Indeed, laser spectroscopy and chemistry of small chiral sulfoxides may be one of the most promising routes towards the measurements of effects from the parity-violating weak nuclear force in chiral molecules.[10] We have therefore undertaken a more detailed study of the chiral thiirane-1-oxides CH_2CHDSO and

CH_2CD_2SO shown in Figure 1. While ordinary thiirane-1-oxide was well characterized some time ago[11, 12] and *cis* and *trans* isotopomers of CHDCHDSO have been synthesized and used for mechanistic studies on the stereochemistry of the reaction by Aalbersberg and Vollhard,[9] the title compounds of the present investigation (Figure 1) have not been prepared and investigated before. We report here their synthesis and spectroscopic characterization. For the diastereomeric pair, we have been able to provide the first selective, laser chemical dissociation and resulting enrichment. While isotope enrichment of ordinary isotopomers by infrared laser chemistry has now been known for two decades,[13, 14] the process of isotopomeric diastereomer selection has not been established before, to our knowledge. Further re-
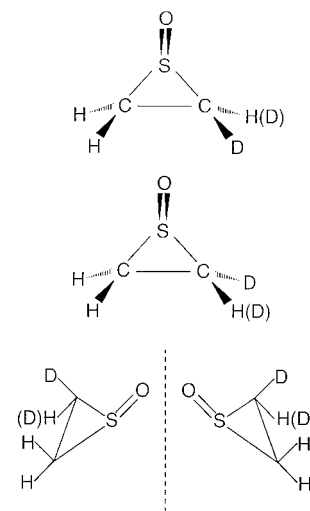

Figure 1. The various thiiran-1-oxides investigated. The diastereomers of CH_2CHDSO are distinguishable by the position of the D and O atom relative to the CCS ring: one diastereomer has both atoms on the same side of the CCS plane and the other form has both atoms on opposite sides of this plane. In the lower part one pair of enantiomers is shown.

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sults on the high-resolution analysis of infrared and microwave spectra of several isotopomeric thiirane-1-oxides will be presented elsewhere.[15]

Results

Synthesis: The preparation of sulfoxides from substituted ethylenes usually follows one of the two routes shown in Schemes 1 and 2. The first approach involves an oxirane as intermediate[9, 16] (Scheme 1), the other passes via the analo-
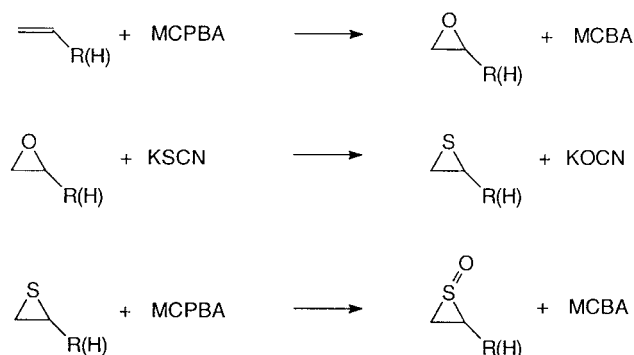
Scheme 1. Syntheses for substituted thiirane-1-oxides according to Aalbersberg.[9, 16] MCPBA = 3-chloroperbenzoic acid, MCBA = benzoic acid, KSCN = potassium thiocyanate, KOCN = potassium cyanate.
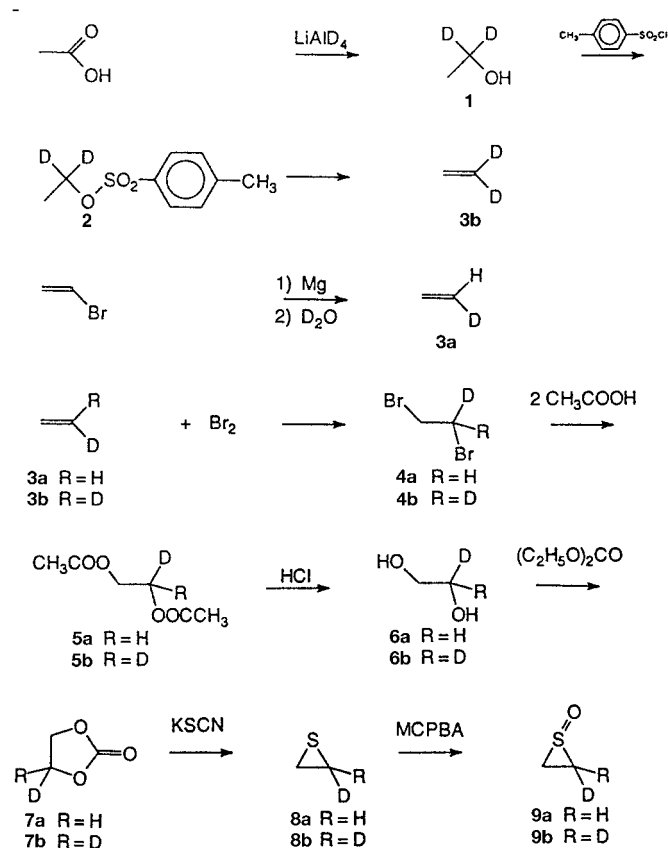
Scheme 2. Diagram of the syntheses for ethylenecarbonates according to Daub,[17] for thiiranes according to Searles,[18,19] and the final oxidation according to Kondo.[11]

gous ethylene carbonate,[17–19] from which the sulfide is prepared. Both approaches were tested in our laboratory. The first one seemed to be rather simple, involving only three steps after preparing the deuterated ethylene to realize deuterated thiirane-1-oxides, but we found it impossible to obtain yields as high as those reported in refs. [9, 16] (and references therein) in spite of several attempts to optimize the reaction conditions. The second approach, which was described in detail in refs. [17, 19] was tested and optimized by us step by step with undeuterated substances before we started the synthesis with isotopes. The yields obtained in our work were comparable to or higher than those given in the literature.

Small amounts of each intermediate were highly purified when necessary to analyse the intermediates by IR spectroscopy, ^{1}H NMR, ^{13}C NMR, and mass spectroscopy. Purity was checked by gas chromatography. As we were interested mostly in the final products we made more accurate measurements only on [2-^{2}H$_1$]thiirane-1-oxide and [2,2-^{2}H$_2$]thiirane-1-oxide to determine the IR frequencies of all fundamentals.

Survey of infrared spectra and analysis: The analysis of the rotational fine structure in the high-resolution infrared spectra of the various thiirane-1-oxides presents a considerable challenge, and details of such investigations will be reported elsewhere.[15] On the other hand, a low-resolution investigation of the infrared spectra of the undeuterated compound was reported quite some time ago[20] and we have already presented a preliminary analysis of somewhat improved data from our work on C$_2$H$_4$SO and C$_2$H$_3$DSO.[3] In the present paper we shall provide a survey of data at modest resolution and summarize their analysis for all three isotopomers. Until high-resolution analyses are available for all bands, a project that will need quite some time to complete, if it can be completed at all within the current state of the art, the assignments must remain preliminary, but should nevertheless provide good initial insights. Table 1 provides a summary of the vibrational data for all isotopomers investigated here, compared with ab initio calculations for CH$_2$CD$_2$SO (see also ref. [3] for related calculations of C$_2$H$_4$SO and C$_2$H$_3$DSO). The experimental fundamental wavenumbers ν give rough band positions from overall band shape, except for those cases where in ref. [15] high-resolution analyses have been reported.

Figure 2 shows the survey of the far infrared range covering the two SO bending fundamentals ν_{10} and ν_{18} for the H$_4$, H$_3$D, and H$_2$D$_2$ isotopomers in comparison. This band system should, in principle, be particularly attractive for a high-resolution analysis, because of minimal Doppler broadening and the absence of overtones or combination tones from other fundamentals. Nevertheless, the two overlapping and interacting fundamentals already lead to some complexity in the analysis.

Figure 3 shows the range 350 to 1100 cm^{-1}, which has particularly rich vibrational structures, dominated in the low-frequency part by the two strong, overlapping CS stretching fundamentals around 550 cm^{-1}. In this frequency range, the assignments in Table 1 are particularly uncertain, because the skeletal modes do not have such a well-defined character. We

Table 1. Summary of vibrational data of CH_2CD_2SO compared with CH_2CHDSO and C_2H_4SO. The harmonic wavenumbers (ω_e) are calculated ab initio (MP2) with a 6-311G** basis set (GAUSSIAN 92). $\tilde{\nu}_i$ are measured fundamental wavenumbers, G are integrated band strengths,[28] calculated ab initio (MP2) for CH_2CD_2SO or from experiment[3] for C_2H_4SO.

| | CH_2CD_2SO | | | CH_2CHDSO | C_2H_4SO | | Description |
	ω_e /cm⁻¹	G /pm² (this work)	$\tilde{\nu}$/cm⁻¹	$\tilde{\nu}$ /cm⁻¹ trans/cis[3,15]	$\tilde{\nu}$ /cm⁻¹ [3,15]	G /pm²	(approx.) for C_2H_4SO
ν_1	3289	0.036	3097.6	3095	3104	0.004	asym. CH stretching
ν_2	3180	0.033	2997.7	3015	3016	0.020	sym. CH stretching
ν_3	1476	0.048	1408	1408	1418	0.020	CH₂ scissoring
ν_4	1147	2.182	1114.370[a,e]	1116/1114	1120	2.40	SO stretching
ν_5	1108	0.154	968	1042	1061.697[e]	0.20	CC stretching
ν_6	1068.4	0.181	990	–	987	0.40	CH₂ twisting
ν_7	920	0.092	881	870	919.647[e]	0.060	CH₂ wagging
ν_8	675.0	0.033	639	685/675	769	0.030	CH₂ rocking
ν_9	567.0	0.454	527	550		[b]	CS stretching
ν_{10}	319.4	0.489	316.1	319	330	0.40	SO bending
ν_{11}	2453.4	0.058	2339.3	3050	3090	0.005	asym. CH stretching
ν_{12}	2307.3	0.007	2222.2	2270	[c]		sym. CH stretching
ν_{13}	1186.4	0.288	1140.258[e]	1288/1285	1399.399[e]	0.050	CH₂ scissoring
ν_{14}	1133.2	0.397	1043.758[e]	1130			CH₂ twisting
ν_{15}	835.9	0.127	772	927.6/952.793[e]	994	0.40	CH₂ wagging
ν_{16}	703.5	0.202	679	732/705	824.779[e]	0.050	CH₂ rocking
ν_{17}	603.3	0.432	555	527/570	572	0.50	CS stretching
ν_{18}	295.6	0.374	284.8	300/290	321	[d]	SO bending

[a] The experimental integrated band strength in the range 1070–1170 cm⁻¹ is $G = 1.9$ pm². [b] Together with ν_{17}. [c] Together with ν_2. [d] Together with ν_{10}. [e] From an accurate analysis of the rotational fine structure.[15]
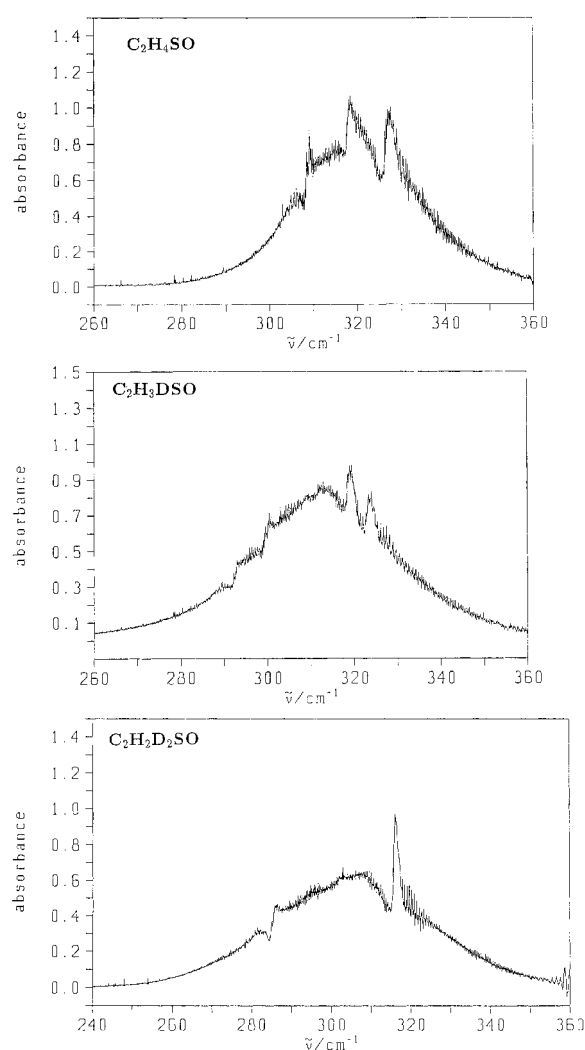
have based our assignment upon a combination of frequency ordering and intensity predictions from ab initio calculations.

Figures 4 and 5 show the range of the higher frequency fundamentals 1200–3300 cm⁻¹. The differences between the spectra arise mostly from the CH/D stretching and bending motions. One must note the high band strength of the overtone of the SO stretching vibration near 2200 cm⁻¹, which is close in both frequency and intensity to the CD stretching fundamentals. For the undeuterated compound, the total integrated band strength in the SO stretching overtone range is about $G = 0.02$ pm², which is in fact larger than the CD stretching intensity in C_2H_3DSO. Our high-resolution analyses of the intense fundamentals in the range 800–1400 cm⁻¹ will be reported.[15]

Enrichment of one diastereomer of C_2H_3DSO by selective infrared laser chemistry: The pronounced differences in the vibrational fundamentals of the two isotopic diastereomers of C_2H_3DSO offer an opportunity to try a laser chemical enrichment of one diastereomer from the mixture that resulted from the synthesis. Figure 6 shows the infrared spectrum in the emission range of the CO₂ laser. From the point of view of high selectivity, the best choice for irradiation would be the ν_{15} CHD wagging fundamental near 952 cm⁻¹ for the *cis* isomer, which is nearly unperturbed[15] and predicted to have a large isotopomer shift $\nu_{cis} - \nu_{trans} > 30$ cm⁻¹, although it is not yet definitely assigned for the *trans* isomer. The band is weakly visible in Figure 6. From studies of isotope separation, we know that with such a high-frequency separation an almost

Figure 2. Survey of the far infrared range covering the two SO bending fundamentals ν_{10} and ν_{18} for the H₄ (upper part), H₃D (middle), and H₂D₂ (lower part) isotopomers in comparison. The absorption length l is 14 m, the instrumental bandwidth is 0.1 cm⁻¹. A CuGe detector and a 3 μ Mylar beam splitter were used and the substance pressure p was 0.7 mbar.
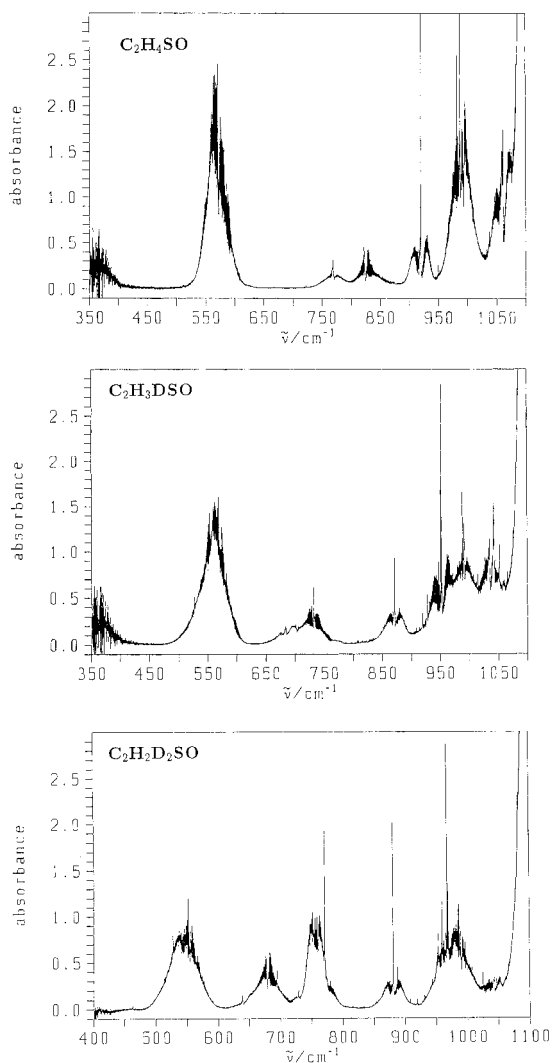
Figure 3. IR spectra as absorbance $\ln(I_0/I)$ of the three sulfoxides in the range 400 to 1100 cm^{-1}. The absorption length l is 14 m, the instrumental bandwidth is 0.1 cm^{-1}. A CuGe detector and a KBr beam splitter were used and the substance pressure p was 0.7 mbar.

Figure 4. IR spectrum in the region of the higher frequency fundamentals (1200 – 3700 cm^{-1}) of the undeuterated and the monodeuterated molecule. The absorption length l is 14 m, the instrumental bandwidth is 0.1 cm^{-1}. A HgCdTe detector and a KBr beam splitter were used and the substance pressure p was 0.7 mbar.
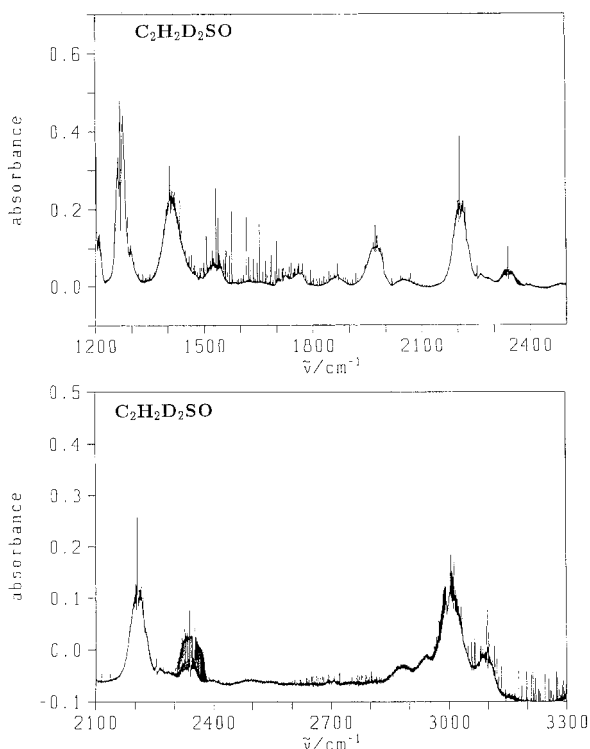
Figure 5. IR spectrum in the region 1200 – 2400 cm^{-1} (top) and 2100 – 3300 cm^{-1} (bottom) of the higher frequency fundamentals of CH$_2$CD$_2$SO. The absorption length l is 14 m, the instrumental bandwidth is 0.1 cm^{-1}. A HgCdTe detector and a KBr beam splitter were used and the substance pressure p was 0.7 mbar.

complete separation in a one-step laser chemical process should be possible.[6, 21] However, with a band strength $G \approx$ 0.26 pm^2, these fundamentals are predicted[6] to give very low laser chemical yield, particularly since the thiirane oxides are known[1–3] to fall in the range of the nonlinear case C of multiphoton excitation.[22] This prediction of low yields was indeed confirmed in test experiments by means of excitation with the 10 P 12 line of the CO$_2$ laser at 951.19 cm^{-1} with pulses of a maximal fluence of 8 J cm^{-2}. No useful yield of the product C$_2$H$_3$D could be detected by IR spectroscopy under these conditions.

We thus tried selective dissociation by multiphoton excitation of the ν_4 SO stretching fundamental, which gives high laser chemical yields owing to its large band strength $G =$ 2.8 pm^2 (transition moment 0.26 D). The fundamentals are $\nu_4 = 1114$ cm^{-1} for the *cis* and $\nu_4 = 1116$ cm^{-1} for the *trans* isomer, which are visible as two close-lying but well-separated Q branches in Figure 6. Because of the small wavenumber separation of the two bands, we have chosen two laser lines on
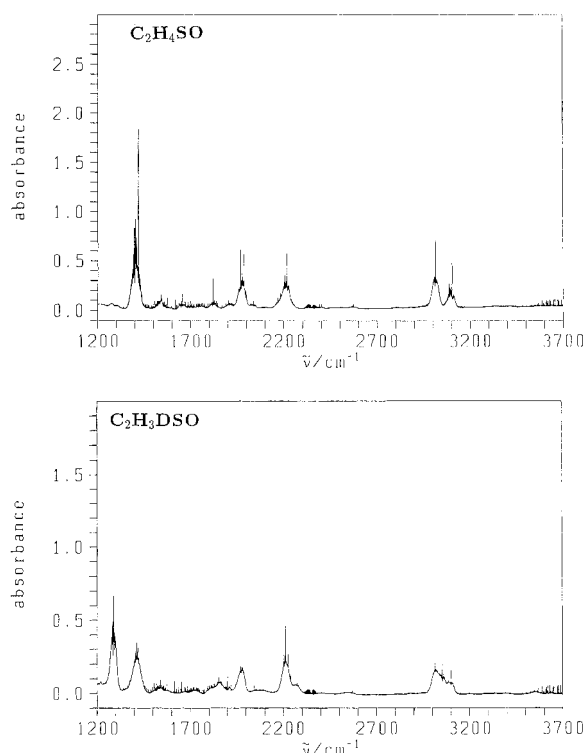
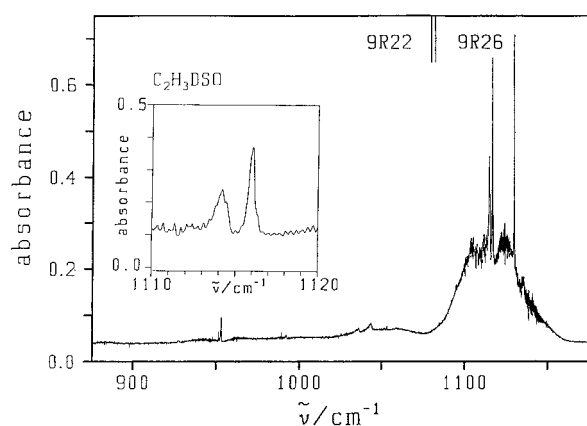Figure 6. Survey of the IR spectrum in the emission range of the CO_2 laser (875–1175 cm⁻¹) of CH₂CHDSO. The position of the two laser lines 9 R 22 and 9 R 26 is also shown. The insert shows the Q branches of the ν_4 (SO stretching) of both diastereomers (absorption length $l = 0.18$ m, instrumental bandwidth res $= 0.1$ cm⁻¹, FWHM, and substance pressure $p = 0.7$ mbar).

the low wavenumber side of the laser chemical yield spectrum,[3] where the yield starts to drop steeply to low values (line 9 R 22 at 1079.85 cm⁻¹ and line 9 R 26 at 1082.30 cm⁻¹). This should maximize the separation factor T, which we have determined by measuring the integrated absorbances X of the ν_4 Q branches before (′) and after (″) infrared laser photolysis [Eq. (1)].

$$T = \frac{X''_{trans}}{X'_{trans}} \times \left(\frac{X''_{cis}}{X'_{cis}}\right)^{-1} \tag{1}$$

$$X = \int_{Q\ branch} \ln(I_0/I) d\tilde{\nu} \tag{2}$$

The experimental set-up for these experiments is shown in Figure 7. We used the far field to obtain well-defined beam profiles; for other details see ref. [1]. The total number of laser shots in the experiments was typically 200, which gives about 30 % apparent primary yield under our conditions. In
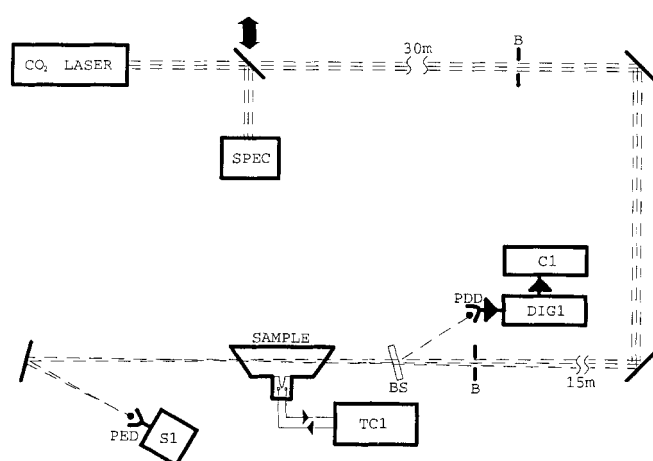
these experiments, we used glass cells without reservoirs, but filled these with 0.7 mbar reactant and waited for a sufficiently long time that wall adsorption had essentially reached saturation. We know from our spectroscopic experiments that wall adsorption is appreciable. Therefore the exchange of adsorbed reactants at the walls with reactants in the vapor phase will *decrease* the apparent separation factor, compared to the primary separation factor. We used an inert gas (N_2) pressure of 9.3 mbar in order to reduce exchange of excitation energy between the diastereomers by collisions and secondary dissociation.

The results for T are summarized in Table 2. Although the separation efficiency is small, it is significant at the 95 % confidence level (from 4 independent experiments) for both excitation lines, which establishes for the first time an infrared laser chemical isotopic diastereomer enrichment. Much great-

Table 2. Results of the diastereoselective IR-laser chemical multiphoton dissociation of 2-[²H₁]thiirane-1-oxide with CO_2 laser pulses of a fluence around 3 J cm⁻² and a substance pressure of $p = 0.7$ mbar (total pressure with inert gas $N_2 = 10$ mbar). The uncertainty is given as a Student t-interval with 95 % confidence. The number of experiments is 3 for the excitation on the 9 R 22 laser line and 4 on the 9 R 26 laser line.

Laser line	$\tilde{\nu}$ /cm⁻¹	$T \pm \Delta T$
9 R 22	1079.85	0.9577 ± 0.0118
9 R 26	1082.30	0.9412 ± 0.0407

er separation factors could no doubt be achieved with molecular systems specifically designed for such a separation. This would not be such a difficult task. A much more challenging problem would be to use infrared circular dichroism with circularly polarized light in order to achieve enantiomer enrichment by infrared laser chemistry. Such experiments are underway in our laboratory.

Discussion and Conclusions

The syntheses of deuterium-labeled thiirane-1-oxides used and optimized in our work provide easy access to relatively large amounts of these compounds, which are useful for spectroscopic, laser chemical, and thermochemical investigations.[1–3] Even at modest resolution, a complete survey of the infrared spectra of C₂H₄SO, C₂H₄DSO, and CH₂CD₂SO has allowed us to assign a large portion of the vibrational fundamentals by comparison with extended ab initio calculations of the harmonic frequencies. This will be useful in the further spectroscopic characterization of these compounds as well as for infrared laser chemistry. Indeed, the particularly high band strength $G > 2$ pm² of the SO infrared chromophore associated with the SO stretching fundamental transition in these molecules, with a frequency covered by CO_2 laser emission, renders them particularly suitable for infrared multiphoton excitation with pulsed CO_2 lasers and laser chemistry. We have already shown that this process is a useful source for essentially pure SO(³Σ⁻).

Figure 7. Experimental setup for the CO_2 laser chemical diastereomer selective multiphoton excitation and dissociation. SPEC: spectrum analyzer, B: aperture, C1: computer, DIG1: digitizer, PDD: photon-drag detector, BS: beam splitter, SAMPLE: sample cell, TC1: temperature control, PED: pyroelectric detector, S1: oscilloscope).

A particularly interesting result of the present work is the laser chemical enrichment of one isotopic diastereomer in C_2H_3DSO. While the enrichment factors are insufficient to be used on a preparative scale, more favorable cases will generally exist, which would allow for such preparative enrichment, similar to isotope separation.[6] The novel laser chemical techniques, which also include theoretical proposals for selective stereomutation,[23] open up many new possibilities beyond the established methods of stereochemistry.[24]

An interesting extension of our work would be the inclusion of pure *cis* and *trans* dideutero isotopomers of thiirane-1-oxide, which have been investigated by Aalbersberg and Vollhardt[9] in view of the stereochemistry and electronic nature of the thiirane-1-oxide decomposition. While their work has already shown high stereoselectivity of the process with 95% retention in the product ethylene isotopomers formed,[9] our direct kinetic investigations under collision-free conditions with ns resolution have proven beyond doubt that the primary products of infrared laser chemical decomposition are $SO(^3\Sigma^-)$ and ethylene ($^1A'$); this corresponds to the spin-forbidden product channel.[1] This result answers, in a sense, the question raised by Aalbersberg and Vollhardt. It is the result expected both from the calculated avoided crossing of the triplet excited and singlet ground-state potential functions,[25] with a large singlet–triplet coupling for the moderately heavy S atom involved here, and from a possible biradical intermediate $S\dot{O}CH_2-\dot{C}H_2$. Because infrared laser photolysis leads to a reaction in the *electronic ground-state potential*, rather similar to thermolysis, a further confirmation of the stereochemical results of Aalbersberg and Vollhardt by infrared laser chemical techniques might be of interest. In this case, one might like to return to the synthesis route chosen in their work.[9] Another challenging problem for the future concerns both the synthesis of pure enantiomers, for instance of CH_2CD_2SO, or their enrichment by laser chemistry from the racemic mixture and investigations of parity-violating energy differences.[10] Once pure enantiomers are available, one may also investigate the problem of laser-induced or thermal stereomutation. Somewhat less radical questions concern the analysis of high-resolution microwave and infrared spectra of the isotopomers with the aim of generating accurate structures of the thiirane-1-oxides. This latter work is, in fact, essentially complete and will be reported separately.[15]

Experimental Section

General and spectroscopy: D_2O with a deuterium content of more than 99.5% purity was obtained from Paul Scherrer Institut (Villigen, Switzerland). MCPBA (3-chloroperbenzoic acid, Fluka, 85%) was washed with a phosphate buffer and dried in an exsiccator (>99% purity).[26] This was necessary to optimize the final oxidation reaction of the sulfide. Lithium aluminum deuteride (LAD, Fluka, >99% D), ethyldicyclohexylamine (Fluka, pract. 97%), diethyleneglycol monomethyl ether (Fluka, purum), and all other chemicals purchased from Fluka were used without further purification. Tetrahydrofuran (THF, Fluka, puriss.) was dried over $LiAlH_4$ and 2-(tetrahydrofurfuroxy)tetrahydropyran (THFTHP) was synthesized from dihydropyran and distilled from sodium.[27] All other solvents (Fluka, puriss.) were used without further purification.

The purity of reactants and products was determined by gas chromatography (Hewlett Packard HP-5880, 50 m WCOT column, 0.2 mm diameter, 0.25 mm OV-101, carrier gas He, FID detector) and with mass spectroscopy (VG, Tribrid, EI, 70 eV) including the degree of deuteration. Configuration analysis was carried out by ^1H and ^{13}C NMR (Bruker AC-200-F, 200 MHz, [D_6]acetone, 27 °C, TMS; ^{13}C spectra with and without proton decoupling were acquired with NOE-presaturation for signal enhancement) and by low-resolution (0.5 cm^{-1}) IR spectroscopy (Perkin Elmer G938 wavenumber accuracy $\pm$ cm^{-1}, liquid or film, and solids as KBr wafers). For the final deuterated sulfoxides high-resolution IR spectroscopy was performed using our BOMEM DA002-Spectrometer system (0.1 cm^{-1} to 0.0024 cm^{-1} instrumental bandwidth, FWHM as described in ref. [28], wavenumber accuracy equal to or better than band width). All boiling and melting points are uncorrected (uncertainty about ± 2 K).

Preparation of [2-$^2H_1$]thiirane-1-oxide (9a)

($\pm$)-1,2-Dibromo[$^2H_1$]ethane (4a):[17] Vinyl bromide (90 g, 0.84 mol) was dissolved in THF (700 mL), placed in an ice-cooled flask, equipped with an intensive condenser, and cooled to −20 °C. This solution was reacted with an equimolar amount of magnesium turnings in THF (about 50 mL) and afterwards heated to 50 °C for half an hour. The cooled Grignard compound was hydrolyzed with an excess of D_2O, and the resulting [$^2H_1$]ethene (3a) passed through an ice-cooled solution of bromine in CCl_4. The excess bromine was destroyed by an aqueous solution of sodium thiosulfite. After removal of the solvent by distillation the crude product 4a was redistilled through a Spaltrohr column to obtain 4a (131.9 g, 0.69 mol, 99% purity, b.p. 131 °C) with a yield of 82% referred to vinyl bromide. The degree of deuteration was more than 98% as determined by mass spectroscopy. MS: $M^+ = 188.9$, fragments: 159.9, 116.9, 108.0, 80.9, 28.1; IR: $\tilde{v} = 2971, 2222, 1437, 1200, 1135, 577$ cm^{-1}; ^1H NMR: $\delta = 3.78$ (s); ^{13}C NMR: $\delta = 31.27$ (st, $^1J(C,H) = 156$ Hz, $^2J(C,H) = 4.4$ Hz); 31.16 (td, $^1J(C,D) = 24$ Hz, $^1J(C,H) = 156$ Hz, $^2J(C,H) = 4.0$ Hz).

($\pm$)-1,2-Diacetoxy[$^2H_1$]ethane (5a):[17] 1,2-Dibromo[$^2H_1$]ethane (4a; 68.7 g, 0.36 mol, 99% purity) was added to freshly fused potassium acetate (70.5 g, 0.72 mol) and acetic acid (21.5 g, 0.36 mol), refluxed under exclusion of moisture for 2 h and then distilled at a pressure of 15 mbar. The distillate (containing 69% of the product) was again mixed with freshly fused potassium acetate (86.0 g, 0.88 mol) and 4a (64.9 g, 0.34 mol, 99% purity), refluxed for 2 h, and distilled. The distillate (b.p. 78 °C, 20 mbar, 89% purity) was diluted with ether, then washed with water, a saturated aqueous solution of $NaHCO_3$, and finally again with water, and dried over sodium sulfate. After stripping off the solvent we obtained 5a (88.7 g, 0.6 mol, 99% purity, 85% yield) as a pale yellow liquid. IR: $\tilde{v} = 1737$, 1375 cm^{-1}; ^1H NMR: $\delta = 4.23$ (s, 3H), 2.01 (s, 6H); ^{13}C NMR: $\delta = 170.9$ (s), 62.74 (st, $^1J(C,H) = 147$ Hz, $^2J(C,H) = 1.5$ Hz); 62.51 (td, $^1J(C,D) = 12$ Hz, $^1J(C,H) = 147$ Hz); 20.63 (sq, $^1J(C,H) = 128$ Hz).

($\pm$)-[$^2H_1$]1,2-Ethanediol (6a):[17] 1,2-Diacetoxy[$^2H_1$]ethane (5a; 69.5 g, 0.47 mol, 99% purity) was dissolved in a solution of gaseous hydrogen chloride (4 g, 0.11 mol) in methanol (86 mL) and refluxed for 3 h. After distillation of the solvent, the crude 6a was purified by vacuum distillation, yielding a colorless liquid (9.2 g, 0.30 mol, 99.8% purity, yield: 64%, b.p. 91–95 °C, 28 mbar). The degree of deuteration was 92.1% as determined by mass spectroscopy. MS: $M^+ = 63.0$, fragments: 46.0, 44.0, 34.1; IR: $\tilde{v} = 3350, 2924, 2145$ cm^{-1}.

($\pm$)-[$^2H_1$]-1,3-Dioxolane-2-one (7a):[29] Sodium (0.16 g, 7 mmol) was dissolved in [$^2H_1$]-1,2-ethanediol (19.2 g, 0.30 mol, 99.8% purity) by heating to 90 °C in a flask equipped with a condenser. Then diethylenecarbonate (39.6 g, 0.34 mol) was added to the chilled solution and the reflux condenser was exchanged for a Liebig condenser. The reaction mixture was heated slowly and the theoretical amount of ethanol from the reaction was distilled at a bath temperature of 125–135 °C. After cooling, the sodium ethylate was neutralized by addition of an equal amount of concentrated hydrochloric acid. Finally the reaction product was heated again to 135 °C under 40 mbar pressure in order to remove all volatile impurities. After cooling we obtained [$^2H_1$]-1,3-dioxolane-2-one (27.6 g, 0.27 mol, purity: 88.3%, yield 88%) as colorless crystals; this was used without further purification in the next step. Only a small fraction was purified by recrystallization for a spectroscopic characterization. IR: $\tilde{v} = 3631, 3461, 2959, 2473, 2202, 1747, 1435, 1373, 1216, 1048, 967, 605$ cm^{-1}; ^{13}C NMR: $\delta = 155.7$ (s), 63.83 (st, $^1J(C,H) = 139$ Hz, $^2J(C,H) = 1.8$ Hz), 63.53 (td, $^1J(C,D) = 21$ Hz, $^1J(C,H) = 139$ Hz).

(±)-[²H₁]Thiirane (8a):[29,19] Potassium thiocyanate (40 g, 0.41 mol) was placed in a flask connected to a vacuum line. The system was evacuated and the salt was heated under permanent pumping until it was molten. After 0.5 h heating and pumping were stopped and the flask was cooled slowly to room temperature, then [²H₁]-1,3-dioxolane-2-one (27.3 g, 0.27 mol, 88% purity) was added. Under atmospheric pressure and moisture exclusion a distillation was started. Reaction occurred when the system reached 100 °C. The receiver for the distilled thiirane was cooled in a dry ice/acetone bath. We obtained [²H₁]thiirane (9.2 g, 0.15 mol) as a colorless liquid (purity: 99.2%, degree of deuteration: 92%), corresponding to a yield of 55%. The product is stable for several months stored at $-25\,°C$. MS: $M^+ = 61.0$, fragments: 45.0, 28.1.

***cis-, trans-*[²H₁]Thiirane-1-oxide (9a)**:[11,12] [²H₁]Thiirane (8 g, 0.13 mol, purity 99.2%) was dissolved in CH_2Cl_2 (300 mL) cooled to about $-15\,°C$ and a solution of equimolar MCPBA in CH_2Cl_2 (0.5 molar) was added. Afterwards gaseous ammonia was passed over the still cold ($-15\,°C$) solution. The complex formed by the sulfoxide with MCBA was thereby destroyed through precipitation of ammonium benzoate. Excess of ammonia was removed by a stream of nitrogen. After filtration the solvent was removed on a rotary evaporator and the residue was vacuum distilled. We obtained [²H₁]thiirane-1-oxide as a colorless liquid (9.4 g, 0.115 mol, 94% purity), corresponding to a yield of 88%. The purity was checked only by IR spectroscopy because of thermal decomposition of the product in the gas chromatograph. The substance is stable for several months stored at $-25\,°C$. Analysis: MS: $M^+ = 77.0$, fragments: 64.0, 60.0, 32.0, 29.0; IR: $\tilde{v} = 1114$ (*cis* form), 1116 cm^{-1} (*trans* form).

Preparation of [2,2-²H₂]Thiirane-1-oxide (9b)

[1,1-²H₂]Ethanol (1):[30,31] [1,1-²H₂]Ethanol was synthesized by a modification of the method of Cox and Warne.[30,31] A solution of acetic acid (20.0 g, 0.33 mol) dissolved in THFTHP (200 mL) was added slowly to LAD (14.0 g, 0.33 mol) suspended in THFTHP (400 mL) under a nitrogen atmosphere. When no more gas was produced the reaction mixture was heated to 70 °C for 20 min. The reflux condenser was replaced by a Liebig condenser and a following trap cooled with liquid nitrogen. Under a moderate stream of nitrogen, **1** was liberated by the slow addition of 500 mL diethylene glycol monomethyl ether. The temperature was raised to 200 °C simultaneously. After addition of the glycol, slow distillation of the product continued for several hours. After combining distillate and condensate from the trap we obtained crude **1** (16.8 g) with a content of 86%. Distillation by means of a Spaltrohr column gave **1** (13.1 g, 0.27 mol, yield 82%, purity 99%, b.p. 78 °C). MS: $M^+ = 48$, fragments: 49, 46, 33, 32, 31, 30, 29, 28. The deuterium content cannot be determined from the mass spectra, because of the different decay patterns of the parent ions.

[1,1-²H₂]Ethyl-4-toluenesulfonate (2)[32] was synthesized by a modification of the method of Edgell and Parts. 4-Toluenesulfonyl chloride (110.5 g, 0.58 mol) was placed in a flask and a solution of **1** (13.1 g, 0.27 mol, purity 99%) in dichloromethane (400 mL) was added. Pyridine (97 g, 1.27 mol) was added to the ice-cooled solution in such a way that the temperature never exceeded $+6\,°C$. A few minutes after the addition was completed a white precipitate was formed. The reaction mixture was stirred for a further 6 h at 4 °C, then overnight at room temperature. Afterwards it was hydrolyzed by the addition of 400 mL ice water. The lower organic layer was separated and the aqueous phase was extracted three times with ether. The combined organic phases were washed with 20% hydrochloric acid, water, a saturated aqueous solution of sodium carbonate, and finally with water. After drying over sodium sulfate and removing the solvents by distillation, the colorless, viscous liquid residue consists of **2** (51.4 g, 0.25 mol, 94% yield). The product was used in the following step without further purification.

[1,1-²H₂]1,2-Dibromoethane (4b):[33,34,17] Toluenesulfonate **2** (51.4 g, 0.25 mol) was placed in a flask and gradually heated to 210 °C. [1,1-²H₂]Ethene (**3b**) was formed and passed directly through a condenser into an ice-cooled solution of bromine (34.3 g, 0.43 mol) in CCl_4. The further procedures were performed as described above for the synthesis of (±)-1,2-dibromo[²H₁]ethane (**4a**). We obtained **4b** (25.2 g, 0.13 mol, 99% purity, b.p. 131 °C) with a yield of 51% related to the tosylate. MS: $M^+ = 188, 190, 192$, fragments: 158, 160, 162, 111, 109, 95.

1,2-Diacetoxy[1,1-²H₂]ethane (5b):[17] 1,2-Diacetoxy[1,1-²H₂]ethane was synthesized in the same way as **5a**. From **4b** (65.5 g, 0.34 mol, 99% purity) we obtained **5b** (43.2 g, 0.29 mol, 99% purity, 85% yield) as a pale yellow

liquid. The degree of deuteration was over 99% (determined by mass spectroscopy). MS: $M^+ = 149$, fragments: 118, 116, 104, 103, 88, 87, 86, 75, 73, 43; ¹H NMR: $\delta = 4.23$ (s, 2 H), 2.02 (s, 6 H); ¹³C NMR: $\delta = 170.9$ (s), 62.7 (st, $^1J(C,H) = 147$ Hz), 20.6 (sq, $^1J(C,H) = 129$ Hz).

[1,2-²H₂]Ethanediol (6b):[17] Compound **6b** was synthesized in the same way as **6a**. From **5b** (42.9 g, 0.29 mol, 99% purity) we obtained compound **6b** (13.2 g, 0.20 mol, 98% purity, 70% yield, b.p. 105 °C, 36 mbar) as a colorless liquid. The degree of deuteration cannot be determined by mass spectroscopy, because of the somewhat complex decomposition pattern of the parent ions. MS: $M^+ = 64$, fragments: 47, 46, 45, 44, 43, 35, 34, 33, 32, 31, 30, 29, 28.

[4,4-²H₂]-1,3-Dioxolane-2-one (7b):[29] Compound **7b** was synthesized in the same manner as **7a**. From **6b** (13.2 g, 0.20 mol, 98% purity) we obtained **7b** (16.3 g, 0.17 mol, 94% purity, 84% yield) as a colorless crystalline substance.

[2,2-²H₂]Thiirane (8b):[29,18,19] Compound **8b** was synthesized in the same manner as **8a**. From **7b** (15.5 g, 0.17 mol, 94% purity) we obtained **8b** (5.7 g, 90 mmol, 98% purity, 55% yield) as a colorless, viscous liquid.

[2,2-²H₂]Thiirane-1-oxide (9b):[11,12] Compound **9b** was prepared according to the method used for **9a**. From **8b** (5.15 g, 82 mmol, 98% purity) we obtained **9b** (5.2 g, 63 mmol, 95% purity, 77% yield) after removing the solvent on a rotary evaporator and vacuum distillation of the residues.

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