Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Coincident measurement of photo-ion circular dichroism and photo-electron circular dichroism

Carl Stefan Lehmann and Karl-Michael Weitzel *[a]

[a] Fachbereich Chemie, Philipps-Universität Marburg, 35032 Marburg, Germany.

Email: weitzel@chemie.uni-marburg.de

Electronic Supplementary Information

- **Raw PICD data**

In this section the raw (unsymmetrized) PICD data of Methyloxirane (MeOx) after multiphoton ionization at 396.0 nm are presented. The PICD as a function of mass to charge ratio is shown in Fig. S1 and listed in listed in Table S1. For all ions a negative PICD value was measured for R-MeOx, whilst for S-MeOx the PICD value is positive for all ions. The absolute PICD value for R-MeOx was larger than for S-MeOx, therefore the enantiomers can be clearly distinguished by their PICD value. In the main manuscript the PICD value was symmetrized around zero for each mass to charge ratio separately, i.e. the data was translated along the y-axis. The symmetrized PICD value is given in the last column of Table S1. The shift due to the symmetrisation is different for the smallest fragment ions (m/z up to 27)

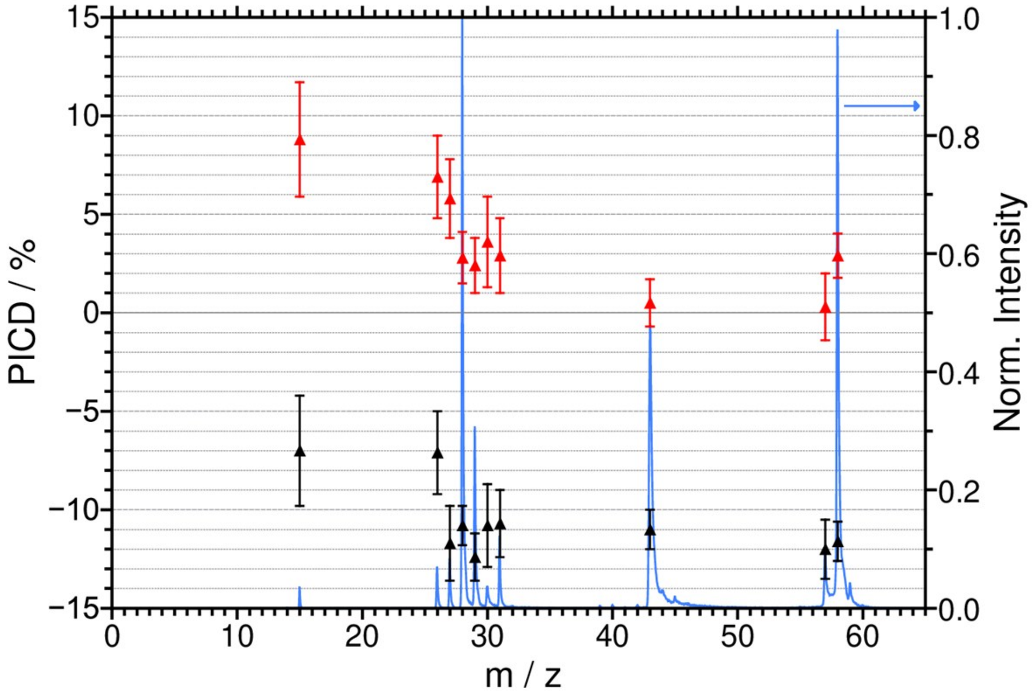

Fig. S1: PICD values, measured in coincidence, for R-Methyloxirane (black triangles) and S-Methyloxirane (red triangles) and the mass spectrum (blue line) for the multiphoton excitation at 396.0 nm. The PICD values are listed in the 2^{nh} and 3^{th} column of Table S1. For each ion fragment the measured PICD value of R-Methyloxirane is negative and positive for S-Methyloxirane. The difference between the two Enantiomers is plotted in Fig 3 in the main manuscript. The error corresponds to the standard error.

compared to parent ion and larger fragment ions. This might be connected to the difference in the number of photons involved. However, this requires further investigation.

Table S1: PICD values and their corresponding standard error as a function of ion mass for the multiphoton excitation of Methyloxirane at 396.0 nm for each enantiomer. The last column contains the symmetrized PICD values which are listed in Table 3 in the main manuscript.

	PICD value / %		Symm. PICD value / %
m/z	R	S	(R-S)/2
15	-7.0 ± 2.8	8.8 ± 2.9	-7.9 ± 2.9
26	-7.1 ± 2.1	6.9 ± 2.1	-7.0 ± 2.1
27	-11.7 ± 1.9	5.8 ± 2.0	-8.8 ± 2.0
28	-11.4 ± 1.0	0.7 ± 1.3	-6.1 ± 1.2
29	-12.6 ± 1.3	2.7 ± 1.5	-7.7 ± 1.4
30	-10.8 ± 2.1	3.6 ± 2.3	-7.2 ± 2.2
31	-10.7 ± 1.9	2.5 ± 2.1	-6.6 ± 2.0
43	-13.0 ± 1.2	-0.4 ± 1.3	-6.3 ± 1.3
57	-12.0 ± 1.5	0.3 ± 1.7	-6.2 ± 1.6
58	-11.6 ± 1.0	2.9 ± 1.2	-7.3 ± 1.1

- **Raw PECD data**

In this section we present the raw (unsymmetrized) PECD data of Methyloxirane (MeOx) after multiphoton ionization at 396.0 nm. Unlike the PICD, the PECD can be obtained from each single measurement of an enantiomer (R or S) at a given circular polarization (LCP or RCP) using the following equation:

$$PECD = 4 \cdot \left(\frac{Y_{LCP,f} - Y_{LCP,b}}{Y_{LCP}} \right) = -4 \cdot \left(\frac{Y_{RCP,f} - Y_{RCP,b}}{Y_{RCP}} \right)$$

These PECD values with their corresponding standard errors are listed in Table S2. Table S3 lists the PECD values per enantiomer (LCP – RCP) and per circular polarized light (R – S). The former are also shown in Fig. S2. A negative PECD value of around -10% was measured for R-MeOx, whilst for most ions of S-MeOx the PECD value was closer to zero. The absolute PECD value for R-MeOx was larger than for S-MeOx and therefore the enantiomers could be distinguished without a doubt by their symmetrized PECD value (last column of Table S3). The shift due to the symmetrisation is, within the error margins, basically independent of the mass of the species considered.

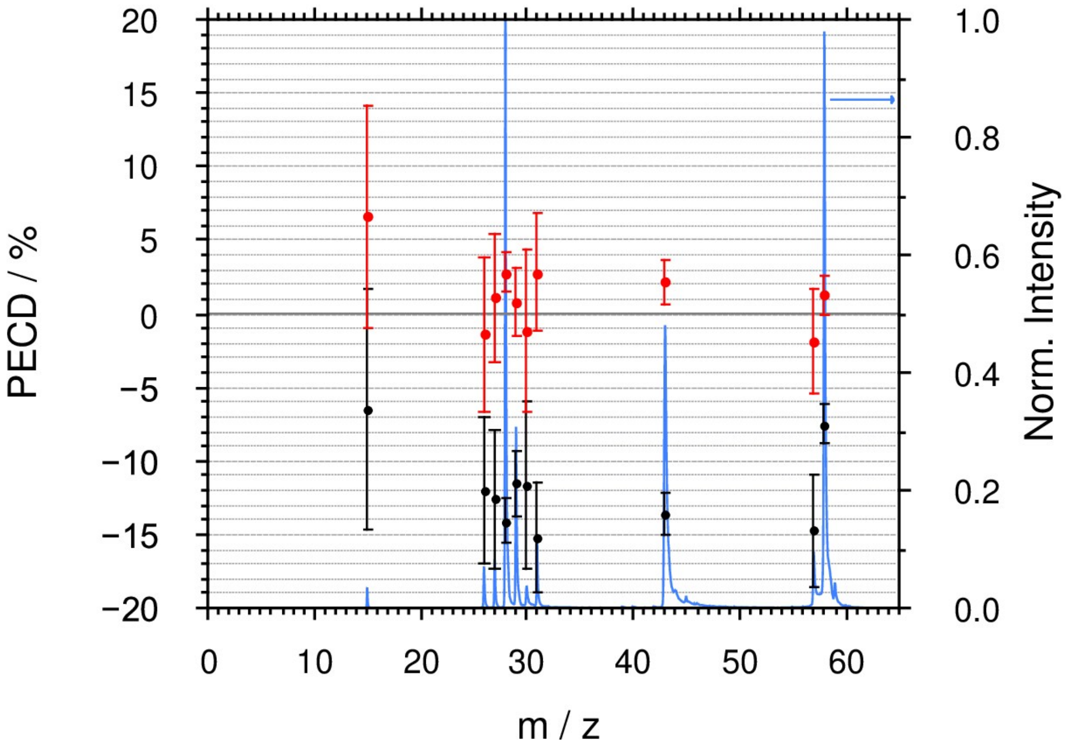

Fig. S2: PECD values, measured in coincidence, for R-Methyloxirane (black circles) and S-Methyloxirane (red circles) and the mass spectrum (blue line) for the multiphoton excitation at 396.0 nm. The PECD values are listed in the 2nd and 3th column of Table S3. For each ion fragment the measured PECD value of R-Methyloxirane is more negative than that of S-Methyloxirane. The error corresponds to the standard error.

Table S2: The raw PECD values and their corresponding standard error measured for each enantiomer (R or S) and circular polarization (LCP or RCP) for the multiphoton excitation of Methyloxirane at 396 nm. The PECD values are calculated with the last two equations of Eq. 3 in the main manuscript.

	Raw PECD values / %			
m/z	R_{LCP}	R_{RCP}	S_{LCP}	S_{RCP}
15	-7.8 ± 8.4	5.2 ± 7.9	12.3 ± 7.5	-0.8 ± 7.7
26	-12.7 ± 5.2	11.3 ± 4.7	-0.8 ± 4.9	2.0 ± 4.8
27	-13.9 ± 4.5	11.3 ± 4.9	3.0 ± 4.5	0.8 ± 4.2
28	-16.6 ± 1.9	15.9 ± 1.8	1.2 ± 1.6	-4.5 ± 1.7
29	-18.7 ± 2.9	9.2 ± 2.7	1.8 ± 2.7	-1.8 ± 2.7
30	-8.6 ± 5.9	14.6 ± 5.5	-2.1 ± 5.2	0.3 ± 5.7
31	-8.0 ± 4.6	26.1 ± 4.2	9.8 ± 4.7	2.4 ± 4.8
43	-23.0 ± 2.6	18.3 ± 2.5	4.9 ± 2.5	-7.0 ± 2.7
57	-15.1 ± 3.9	14.2 ± 3.7	-0.7 ± 3.5	3.1 ± 3.6
58	-8.9 ± 1.3	6.1 ± 1.3	1.4 ± 1.3	-1.2 ± 1.3

Table S3: PECD values and their corresponding standard error as a function of ion mass for the multiphoton excitation of Methyloxirane at 396.0 nm. The columns headed ‘PECD value per enantiomer and per CPL’ contain the difference of the raw PECD values (Table S2) for each enantiomer and circular polarized light (CPL). The last column contains the symmetrized PECD values which are listed in Table 3 in the main manuscript.

	PECD values per Enantiomer and per CPL / %					Symm PECD / %
m/z	$R_{(LCP-RCP)/2}$	$S_{(LCP-RCP)/2}$	$LCP_{(R-S)/2}$	$RCP_{(R-S)/2}$		(R-S)/2
15	-6.5 ± 8.2	6.6 ± 7.6	-10.1 ± 8.0	3.0 ± 7.8		-6.5 ± 7.9
26	-12.0 ± 5.0	-1.4 ± 4.9	-6.0 ± 5.1	4.7 ± 4.8		-5.3 ± 4.9
27	-12.6 ± 4.7	1.1 ± 4.4	-8.5 ± 4.5	5.3 ± 4.6		-6.9 ± 4.5
28	-16.3 ± 1.9	2.9 ± 1.7	-8.9 ± 1.8	10.2 ± 1.8		-9.6 ± 1.8
29	-14.0 ± 2.8	1.8 ± 2.7	-10.3 ± 2.8	5.5 ± 2.7		-7.9 ± 2.8
30	-11.6 ± 5.7	-1.2 ± 5.5	-3.3 ± 5.6	7.2 ± 5.6		-5.2 ± 5.6
31	-17.1 ± 4.4	3.7 ± 4.8	-8.9 ± 4.7	11.9 ± 4.5		-10.4 ± 4.6
43	-20.7 ± 2.6	6.0 ± 2.6	-14.0 ± 2.6	12.7 ± 2.6		-13.3 ± 2.6
57	-14.7 ± 3.8	-1.9 ± 3.6	-7.2 ± 3.7	5.6 ± 3.7		-6.4 ± 3.7
58	-7.5 ± 1.3	1.3 ± 1.3	-5.2 ± 1.3	3.7 ± 1.3		-4.4 ± 1.3

- **PICD and PECD as a function of photoelectron kinetic energy release (PEKE)**

The PICD and PECD as a function of the PEKE for the three main ions (m/z = 28, 43 and 58) are shown in Fig. S3 and Fig. S4, respectively. Electrons measured in coincidence with the parent ion have a higher kinetic energy than those associated with the fragment ions. The maximum of the kinetic energy distribution is at 1.7 eV for the parent ions, for the $C_2H_3O^+$ (m/z = 43) ions the distribution peaks around 1 eV. Whilst the electrons measured in coincidence with fragment ions corresponding to m/z = 28 have the lowest kinetic energy, with the distribution peaking around 0.8 eV.

For all 3 ions, the observed PICD value does not change significantly as a function of photoelectron kinetic energy. On the other hand, the observed PECD of the parent ion increases from -4.4 ± 1.3% to -7.7% ± 2.0% when selecting electrons with higher kinetic energy (electrons inside the blue lines in Fig. S4). For the $C_2H_3O^+$ (m/z = 43) fragment ion, the PECD increases from -7.9 ± 1.9% to -13.6 ± 2.6% for electrons with a kinetic energy in the range of 1.3 to 2.3 eV.

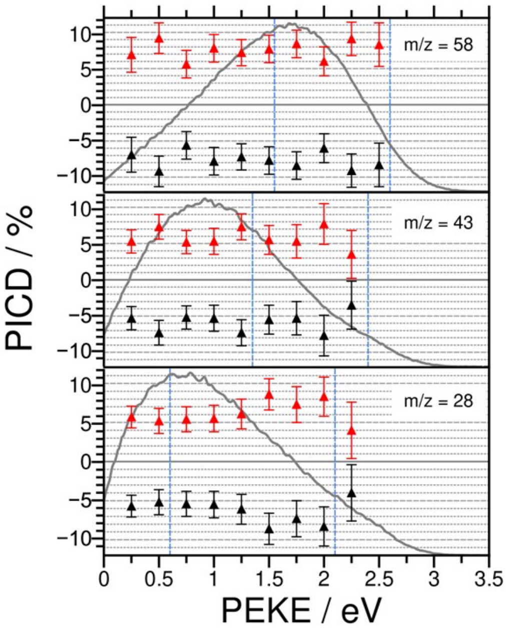

Fig. S3: PICD of R- (black triangles) and S-Methyloxirane (red triangles) as a function of photoelectron kinetic energy (PEKE) distributions for different fragment ions measured after multiphoton ionization at 396.0 nm. The grey line shows the photoelectron spectrum of the given data. The error corresponds to the standard error. The blue dashed line represent selected PEKE regions for which the PICD and PECD values are discussed in the main manuscript.

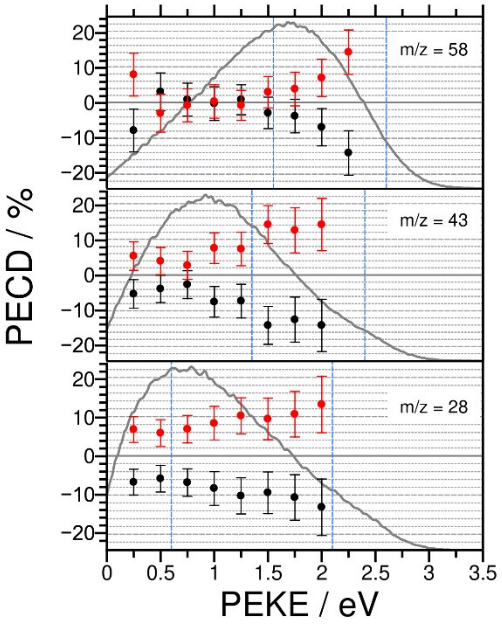

Fig. S4: Multiphoton PECD of R- (black circles) and S-Methyloxirane (red circles) as a function of photoelectron kinetic energy (PEKE) distributions for different fragment ions measured after ionization at 396.0 nm. The grey line shows the photoelectron spectrum of the given data. The error corresponds to the standard error. The blue dashed line represent selected PEKE regions for which the PICD and PECD values are discussed in the main manuscript.

- **Laser Spectrum**

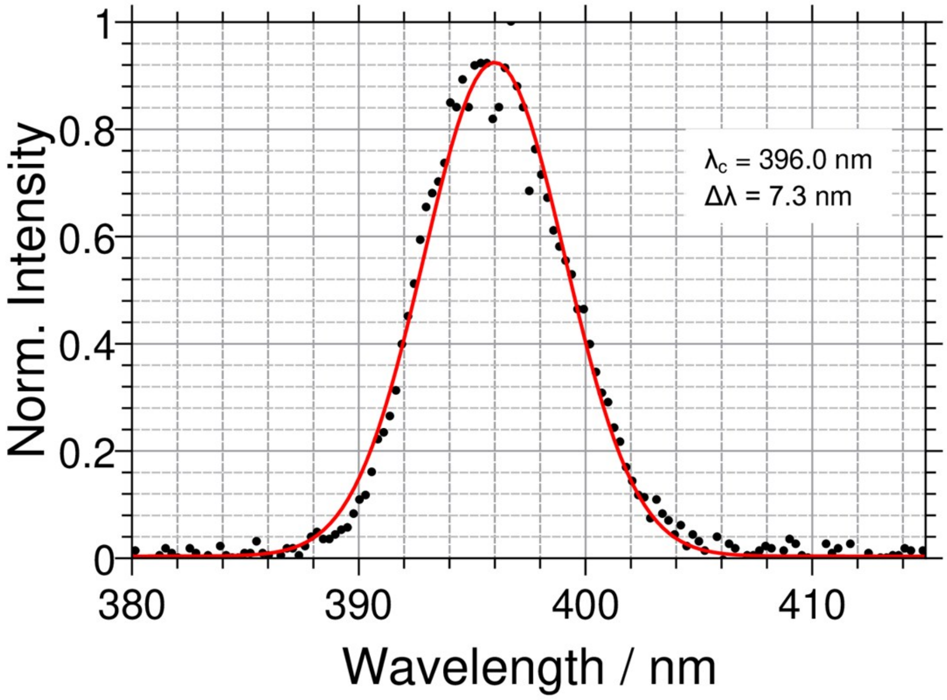

Fig. S5: The typical spectrum of the frequency double femtosecond laser pulse. The pulse had a central wavelength of 396.0 nm and a fitted (Gauss) FWHM of 7.3 nm.