Upper limits for the circular dichroism for the C 1s and O 1s core excitation of methyl oxirane

G. Prümper, T. Lischke, H. Fukuzawa, K. Ueda

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

A. Reinköster

FHI der MPG, Berlin, Germany

Abstract

The circular dichroism in the total and partial ion yields of methyl-oxirane C_3H_6O was measured at the C 1s and O 1s edges. The difference of the response of the chiral molecule to circularly polarized light with opposite handedness was found to be less than 0.2% for the total ion yield and less than 0.5% for the partial ion yield. Additionally we tried to find a dipole allowed molecular orientation CD effect by analyzing the fragmentation in the forward and backward direction. For this effect we found an upper limit of 1-2% for all abundant ionic fragments.

Key words:

1 Introduction

Chirality, i.e. the existence of two different mirror image forms of molecules without symmetry, is the basis of stereo chemistry. The two enantiomers of the same molecule typically react very differently with a particular partner molecule of a given shape. Virtually all large biomolecules do not have any symmetry and are therefore chiral. Natural circular dichroism describes the different response of a randomly oriented sample of chiral molecules when irradiated by circularly polarized light with positive and negative helicities. The absorption of a photon with sufficient energy will lead to the fragmentation of the molecule, so CD has been suggested to selectively destroy molecules of a given handedness and thus to transform a racemic sample into one with

enantiomeric excess. For small molecules in solution or gas phase this stereo selective mechanism is very inefficient. To achieve an enantiomeric excess of a few percent most of the initially racemic sample has to be destroyed [1]. Therefore more than 150 years after the discovery of CD [2] and more than 50 years after the proof of principle of the enantiomeric enrichment by using CD [3], no practical application of this method for synthesis exists. Nevertheless it has been speculated that the process is indirectly responsible for the homochirality of amino acids and sugars in biology by providing a small enantiomeric excess in prebiotic evolution. [4–8]. Therefore there is a strong aim to find more efficient enantio-selective mechanisms than the natural CD of randomly oriented isolated molecules in the optical regime. In all experiments the strength of the CD for a given enantiomer of a chiral substance is the asymmetry of the absorption cross sections σ^+ and σ^- for left and right handed light.

$$\text{asymmetry} = \frac{\sigma^+ - \sigma^-}{\sigma^+ + \sigma^-} \ . \tag{1}$$

In our experiment not the absorption of the radiation but the ion yield is measured as a function of the light helicity. Please not that the asymmetry is half of the Kuhn anisotropy factor. Its range is from -1 to 1 or from -100% to +100%. For small molecules the CD asymmetry is typically 0.1% but values up to a few percent are possible in the optical region. Much higher values can not be expected because higher order terms beyond the dipole approximation are necessary for the description. Typical values for the CD asymmetry in the x-ray regime are even smaller as the relevant molecular orbitals are much smaller than the wavelength of the light. The search for large CD effects has been extended not only towards much shorter wavelengths using soft x-rays [9] (0.1-0.5%) but also towards nonlinear CD using high intensity ns lasers [10] (1.6%). The highest degree of CD (5%) was found using light of 193.4 nm wavelength, for much larger targets than single molecules : nano meter sized aerosol particles containing chiral molecules [11]. This effect was explained by exiton-coupling between neighboring molecules [12]. On the other hand, when comparing CD of molecules in the gas phase and molecules inside or on the surface of a larger particle another aspect is important: the molecules that are actually irradiated by the light can be oriented with respect to the light propagation direction [13] and therefore CD of fixed in space molecules or CD in the molecular ion orientation distribution (CDM) [14] can become important. Unlike natural CD this effect is dipole allowed. One way to study the effect of molecular orientation on CD is to consider oriented molecules in the gas phase by the fixed-in-space method, i.e to use an emission direction of one characteristic ionic fragment to estimate the orientation of one molecular axis in the moment of ionization. In this situation CDM causes a forward-backward asymmetry of the emission direction of characteristic fragments with respect to the light propagation direction.

Methyl-oxirane (MO) is a very common target for studies of CD as it is easy to handle, has a high vapor pressure and exists in only one conformation. It is also small enough to measure and discuss the absorption and fragmentation processes in detail and to calculate the corresponding transitions [15].

A small CD of 0.15% in the total ion yield (TIY) of MO was found near the top of the C 1s resonance [16]. The experimental method is based on comparing the shape of the two TIY curves for the two helicities of the light. Therefore this method is limited to resonant CD effects. The aim of our experiment was three-fold: first we wanted to confirm the small CD in the TIY and if possible to trace the fragmentation channel that shows the largest asymmetry, second to look for non-resonant CD effects and third to search for larger enantio-selective effects using fixed-in-space molecules.
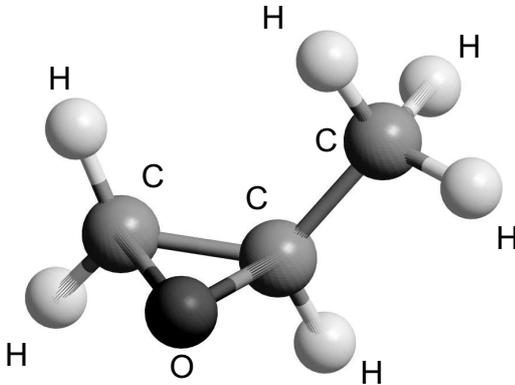

Fig. 1. The methyloxirane = propylene oxiyde molecule C_3H_6O.

2 Experiment

As the experiment deals with very small effects one has to be extremely careful about systematic experimental errors. A convenient experimental method for recording partial ion yields is to use an ion time of flight (TOF) spectrometer with static electric fields. The starting pulse for the TOF measurement can either come from the light source or an electron detector mounted opposite to the ion detector. Both methods have serious disadvantages. Typically the repetition rate of a synchrotron light source is very high leaving only a few hundreds of ns as a time window between subsequent light pulses. This puts severe design restrictions on the ion spectrometer, so that reasonable mass $> 1/50$ and momentum resolution $> 1/10$ cannot be achieved at the same

time. The use of an electron as a start signal introduces a large systematic error because the angular distribution of electrons is known to change dramatically when changing the light helicity or the enantiomer [17–20]. As the detection efficiency is not constant over the electron detector, the resulting systematic errors for the ion count rate can easily be a few percent, i.e. larger than typical CD effects. This error can not be accounted for by changing the enantiomers of the molecule and/or the helicity of the light.

In the experiment described here, a dedicated ion TOF spectrometer using a pulsed voltage at one electrode was used. See figure 2.

pusher pulsed +360V, starts 50 ns before ligth pulse duration 700ns, rep. rate ca. 15 kHz

gas inlet needle +278V

extractor +196V

acceleration electrodes

drift tube -1722V entrance grid

lens -1300V

A

B

✳ light pulses every 800 ns

distances:
pusher - extractor 8 mm
extractor - DT entrance grid 96 mm
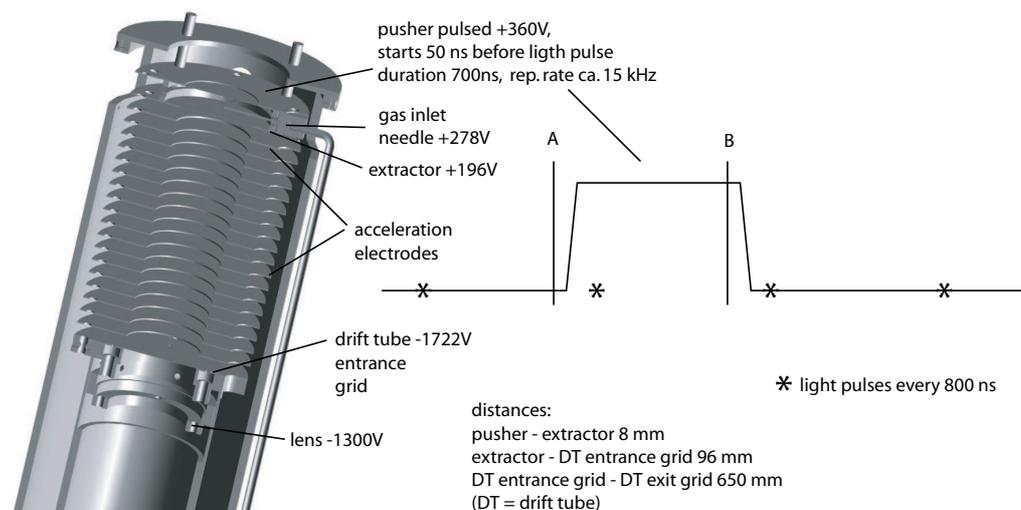DT entrance grid - DT exit grid 650 mm
(DT = drift tube)

Fig. 2. Schematic of the upper part of the ion TOF spectrometer.

It was used at the synchrotron radiation facility BESSY II in Berlin Germany at the UE56/2 Beamline. The MO gas was introduced as an effusive beam through a needle. The needle was mounted between two parallel plates called pusher and extractor. They have circular holes covered with high transmission (>80%) copper grids. The ionizing radiation passes the gap between the pusher and extractor electrodes and crosses the effusive gas beam perpendicularly. This results in a relatively large source region for the ions of about 20 mm length. In the single bunch operation mode the time between two consecutive light pulses is the revolution time of the electrons in the ring is about 800ns. The ion spectrometer was operated in a pseudo DC mode: a constant voltage of +196 V was applied to the extractor electrode. A pulsed voltage of +360 V was applied to the pusher electrode. As long as no pulse is applied, all ions created are pushed towards the - inappropriately named - pusher electrode and escape from the ion spectrometer without being detected. We confirmed in an earlier test experiment that at the photon energies concerned here the yield of ions with a mass larger than 45 amu is negligible. The time for such an ion to reach the pusher electrode was estimated as 600 ns, depicted as the

4

vertical line labeled A in figure 2.

The storage ring provides an electronic signal that resembles the electron revolution in the ring. Using an appropriate delay and a frequency divider of 1:83 this signal can be used to trigger the +360 V pulse with a repetition rate of about 15kHz. The 15kHz are chosen because of limitations of the HV pulse generator and the data acquisition system. Ultimately the trigger rate is determined by the time of flight of the heaviest ion to be detected. E.g. for 10us the maximum possible trigger rate would be 100kHz. If the delay of the HV trigger signal is properly chosen, the pulse will be applied about 50 ns before the next light pulse arrives. This time is long enough to ensure that the voltage is stable. Then between the two electrodes there will be a homogeneous field of 196 V/8 mm. The gas inlet needle does not disturb the field as it is held at a voltage of +278 V. The ions created by the light pulse will be accelerated towards the extractor electrode. Again the maximum time for ions to pass the grid in the extractor electrode is 600 ns, depicted as the vertical line labeled A in figure 2. The +360 V pulse is switched off after 700 ns, so that the ions created by the next light pulse will not be accelerated towards the extractor electrode. Behind the extractor electrode follows a stack of ring electrodes providing a homogeneous field of the same field strength like the 196 V/8 mm between the pusher and extractor during the ion extraction. The purpose of the grid at the extractor electrode is to prevent field penetration into this region after the +360 V pulse has gone to 0 V. The ions will then be accelerated towards a long drift tube held at -1722 V. After entering the drift tube, the ions fly almost field free to the detector. The length of the drift tube of 650 mm is necessary for a good mass resolution and a broad illumination of the ion detector. The disadvantage of this experimental technique is that 82 out of 83 light pulses are not used for the experiment. This reduces the ion count rate substantially, but because of the 4π acceptance angle of the ion spectrometer and the simultaneous measurement of all ions irrespective of their mass an ion count rate of typically 100 Hz to 1 KHz was obtained. This was sufficient to perform the experiment.

In order to distinguish ions being emitted in the forward and backward direction with respect to the light propagation direction, a position-sensitive delay-line type ion detector with an active-diameter of 70 mm was used. The basic idea being that the hit position reflects the two components of the momentum perpendicular to the detector surface. The resolution is limited by the large length (about 20 mm) of the source volume of the ions because the needle was 10 mm away from the ionizing beam to avoid the detection of ions created by the collision of electrons or photons with the MO covered surface of the needle. The momentum of the fragment ions was relatively small (typically 1 eV kinetic energy) and therefore the momentum resolution using perfectly homogeneous fields would not be sufficient because the source volume is projected 1:1 onto the detector. Therefore at the entrance of the drift tube a ring

shaped lens is mounted. We applied a voltage of -1300V to this lens element and reduced the image of the source on the detector to a small spot of about 5 mm diameter. This is significantly smaller than the detector illumination by the fast ionic fragments. Figure 3 shows the detector illumination for CH_2^+ ions from the fragmentation of MO.
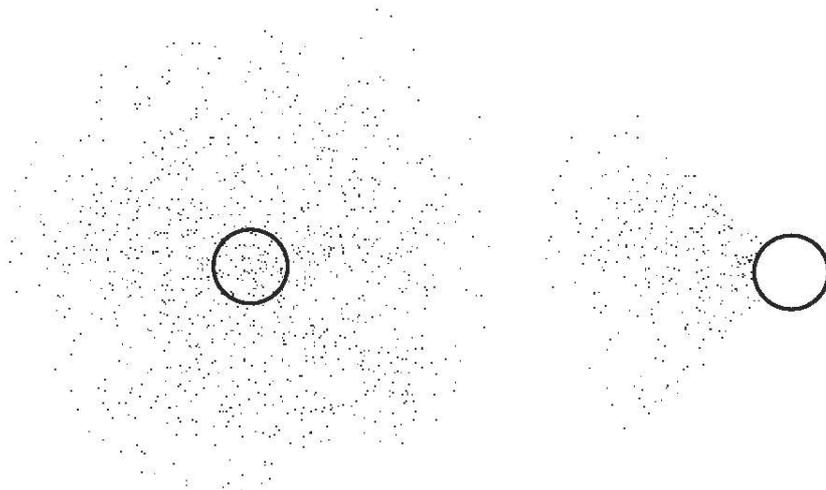

Fig. 3. Images of the detector illumination. The circle represents the approximate size of the source image, determined from the image of CO_2 parent ions in a reference measurement. The left image shows the illumination by the CH_2^+ ions from the fragmentation of MO. The right image shows the detector area used for defining the forward direction of the fragmentation. In this coordinate frame the light is propagating from the right to the left.

S and D MO with a purity of 99 percent was bought at ALDRICH. It was used without further purification. The air was removed by the pump and freeze technique. The sample was held at room temperature. It was introduced into the experimental chamber through a needle valve. It took several hours to stabilize the pressure of the MO in the experimental chamber. The typical partial pressure of the MO was $1 \cdot 10^{-4}$ pa. The variation of the MO pressure during the experiment was less than 10 percent per hour. For calibration purposes neon with a similar partial pressure was introduced at the same time through the same gas inlet. Its partial pressure was adjusted using a second needle valve. In order to get similar ion counts rates for neon and MO fragments, the neon partial pressures was increased for the measurements at the c 1s edge, because of the strong resonant amplification of the MO ion signal. Neon was chosen because it is non-chiral, has a large ionization cross section and its ion mass spectrum does not overlap with the one of MO.

For the measurement of the CD one has to measure the ion count rates C^+ and C^- for two opposite helicities of the light at the same experimental conditions,

i.e. with the same gas pressure and light intensity. The asymmetry can be calculated from C^+ and C^-

$$\text{asymmetry} = \frac{\sigma^+ - \sigma^-}{\sigma^+ + \sigma^-} = \frac{C^+ - C^-}{C^+ + C^-} \ . \tag{2}$$

If the light intensity varies when the helicity is switched from I^+ to I^- the asymmetry has to be calculated as

$$\text{asymmetry} = \frac{\frac{C^+}{I^+} - \frac{C^-}{I^-}}{\frac{C^+}{I^+} + \frac{C^-}{I^-}} \ . \tag{3}$$

In our experiment we use the Ne^+ count rate as a measure of the light intensity. As we do not have an very accurate (better than 10^{-3}) measure of the partial pressures of Ne and MO we have to make sure that the pressure variation can be neglected. Therefore we used the fast switching of the helicity of the light available at beamline UE56/2. This beamline offers a two beam mode. Two beams are coming from an upstream and downstream undulator. We will refer to this as UU-beam and DU-beam. They enter the beamline along two different paths if a device called chicane between the two undulators is used. A mechanical chopper is used to interrupt one or the other beam, depending on the chopper position UU or DU. The chopper stands still at position UU for 5 s. Then it moves to position DU. This motion takes about 1 s. Then it stands still again for 5 s in position DU. Then it moves back to position UU. An electronic signal representing the chopper position was fed into the data acquisition system. The interval used for the data evaluation was 3 s long. It started about 0.5 s after the change of the chopper position. During 10 minutes of switching two ion mass spectra for the two beams were recorded almost simultaneously. For the resonant CD measurements great care was taken to minimize the difference in the photon energy between the two beams. It was measured by comparing the total ion yield curves recorded for the two different beams at the O 1s and C 1s edge. For this measurement no neon was introduced into the chamber. The most convenient method is to tilt the exit slit of the beamline to minimize the energetic shift. Using this method we reduced the energetic shift at the oxygen edge from 300 meV to less than 50 meV. The possible systematic error of the CD due to the remaining small energetic shift was eliminated by exchanging the helicity of the two beams, as will be described below. The intensity difference was between the UU-beam and the DU-beam was typically about 10 percent at the oxygen edge and about 50 percent at the carbon edge, because one beam suffered more than the other from the contamination of the optical elements. During the experiment the resolution of the beamline was set to about 230 meV at the oxygen edge and about 125xxx meV at the carbon edge. For all measurements we calculated the measured asymmetry asymmetry_m from the numbers of counts of MO and

UU	DU	MO	sf
+	-	D	1
-	+	D	-1
+	-	S	-1
-	+	S	1

Table 1

The sign factor for the TIY and PIY CD measurements.

Ne for the UU and DU-beam :

$$\text{asymmetry}_m = \frac{\frac{MO_{UU}}{Ne_{UU}} - \frac{MO_{DU}}{Ne_{DU}}}{\frac{MO_{UU}}{Ne_{UU}} + \frac{MO_{DU}}{Ne_{DU}}} \ . \tag{4}$$

The sign of this quantity does of course depend on the setting of the helicity of the two undulators. For checking the accuracy of the normalization of the MO to the Ne-signal we performed a measurement using the same helicity in both beams UU and DU. If the two undulators are set to the same helicity asymmetry_m is expected to be zero. For the O edge the measured asymmetry was very close to zero, for the C edge a systematic error of about 1.5 percent remained, probably due to different relative contributions of higher order light in beam UU and DU or dead time effects due to the very different count rates of the two beams. Therefore for the CD measurement we did not only use the setting UU-beam at positive helicity and DU-beam at negative helicity but also the opposite. The corresponding data treatment will be described below. The procedure of the CD measurement was as follows: one CD measurement took 10 min. Then we exchanged the helicities of the undulators and restarted the measurement. In total we took 10 to 15 of these CD measurements for each of the two enantiomers and each photon energy. As the data acquisition system does not record the helicity of beam UU and DU, we determine the measured asymmetry defined by equation 4. Depending on the effect studied MO_{UU} and MO_{DU} refer to the TIY of MO or the partial ion yield PIY of a particular MO fragment or to the ion yields in the forward (backward) direction. The error of asymmetry_m was calculated by error propagation from the statistical errors of the numbers of events $MO_{UU}, MO_{DU}, Ne_{UU}$ and Ne_{DU}. The sign of asymmetry_m depends on the setting of the undulators and the MO enantiomer used. Therefore we define the asymmetry with reference to the sign-factor sf whose values are given in tables 1 and 2.

$$\text{assymetry} = \text{asymmetry}_m \cdot sf \tag{5}$$

The error of the asymmetry is of course the error of asymmetry_m. The asymmetries given in this work are determined as the weighted average of all measured values of the asymmetry and the corresponding errors. The scatter of

UU	DU	MO	direction	sf
+	-	D	F	1
-	+	D	F	-1
+	-	S	F	-1
-	+	S	F	1
+	-	D	B	-1
-	+	D	B	1
+	-	S	B	1
-	+	S	B	-1

Table 2
The sign factor for the molecular orientation CD using ions in the forward (F) or backward (B) direction only.

the individual measurements belonging to one line in tables 1 and 2 around their mean was consistent with the calculated errors of each of the 10 min measurements.

3 Experimental results

The mass spectra for various resonant photon energies are shown in figures 4 and 5. Here the resolution of the beamline was set to about 230 meV for all shown mass spectra. These spectra were recorded using the UU beam only. They show many fragments that belong to a C-C-O ring opening reaction, consistent with the high resolution Auger spectra measured earlier [21]. These ion mass spectra also show, that the variations of the pattern of fragmentation across the C 1s and O 1s resonances are small. In total 2x96 spectra of similar quality were recorded for the CD measurement. They will not be presented. We only summarize the results for the average asymmetry based on the areas of the individual peaks. The results summarized in table 3 are based on measurements using both enantiomers and both helicity combinations of the undulator for 530.85 eV and 535.11 eV. The results given for 289.36 eV are based on measurements using D-MO only but both combinations of the undulator helicities. The results summarized in table 4 are based on measurements using both enanitiomers and both helicity combinations of the undulator and the forward and backward emission direction for 530.85 eV and 535.11 eV. The results given for 289.36 eV are based on measurements using D-MO only but both combinations of the undulator helicities and the forward and backward emission direction.

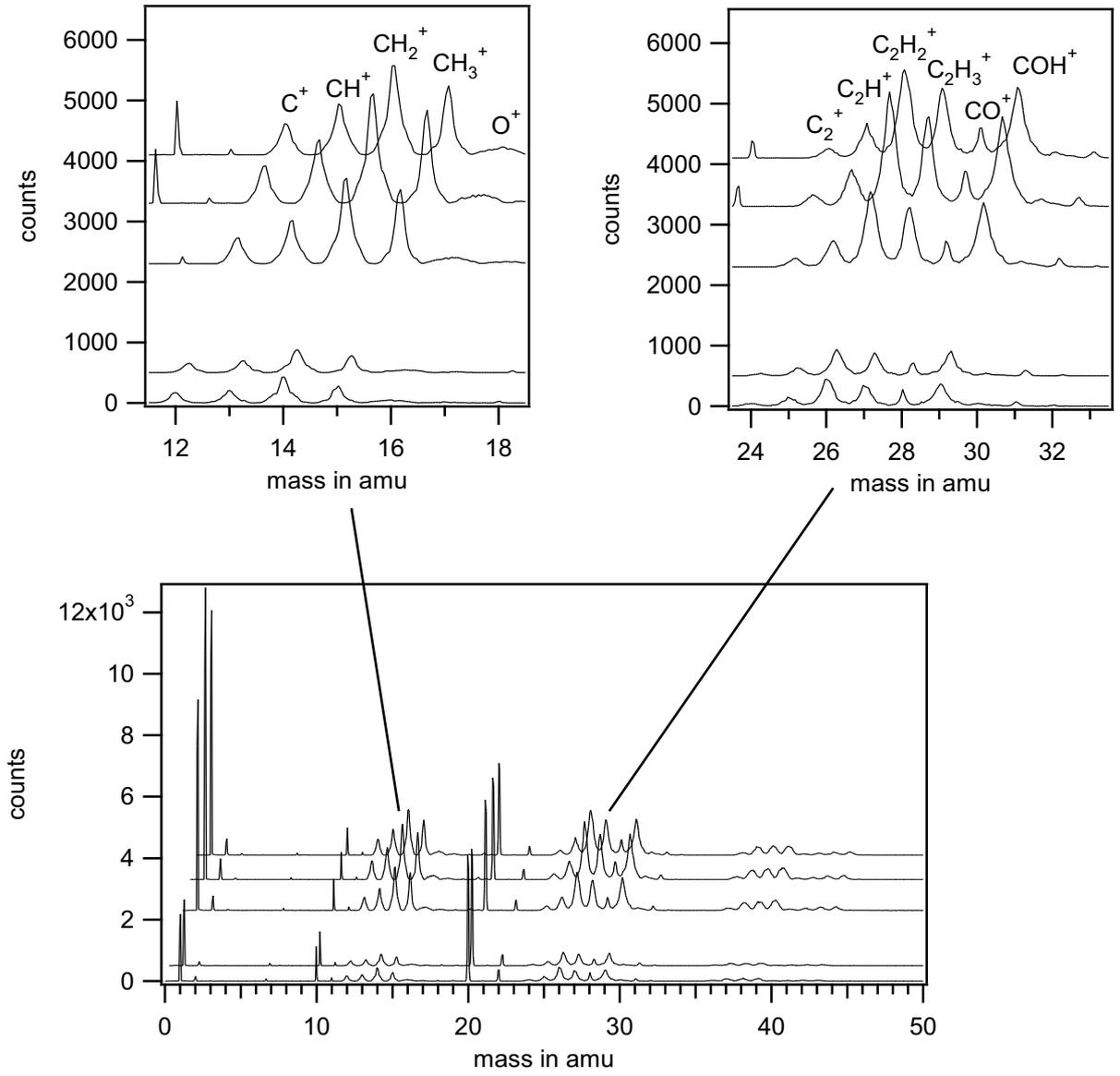Going though the values of the asymmetry summarized in the two tables,

Fig. 4. Mass spectra as a function of photon energy close to the C1s edge. The photon energies are from bottom to top: 287.48, 287.73, 288.63, 289.13, 289.53 eV.

no significant deviation from zero is found. The only number for the CD that shows some significant deviation from zero is the PIY of $C_3H_3^+$ at $h\nu$=530.85 eV in table 3. If we only measured this CD we would consider the result significant. However the chance that one number out of 96 PIY CD measurements accidentally shows a 2.6 sigma deviation from zero is almost 50%. So focusing on this value would be misleading.
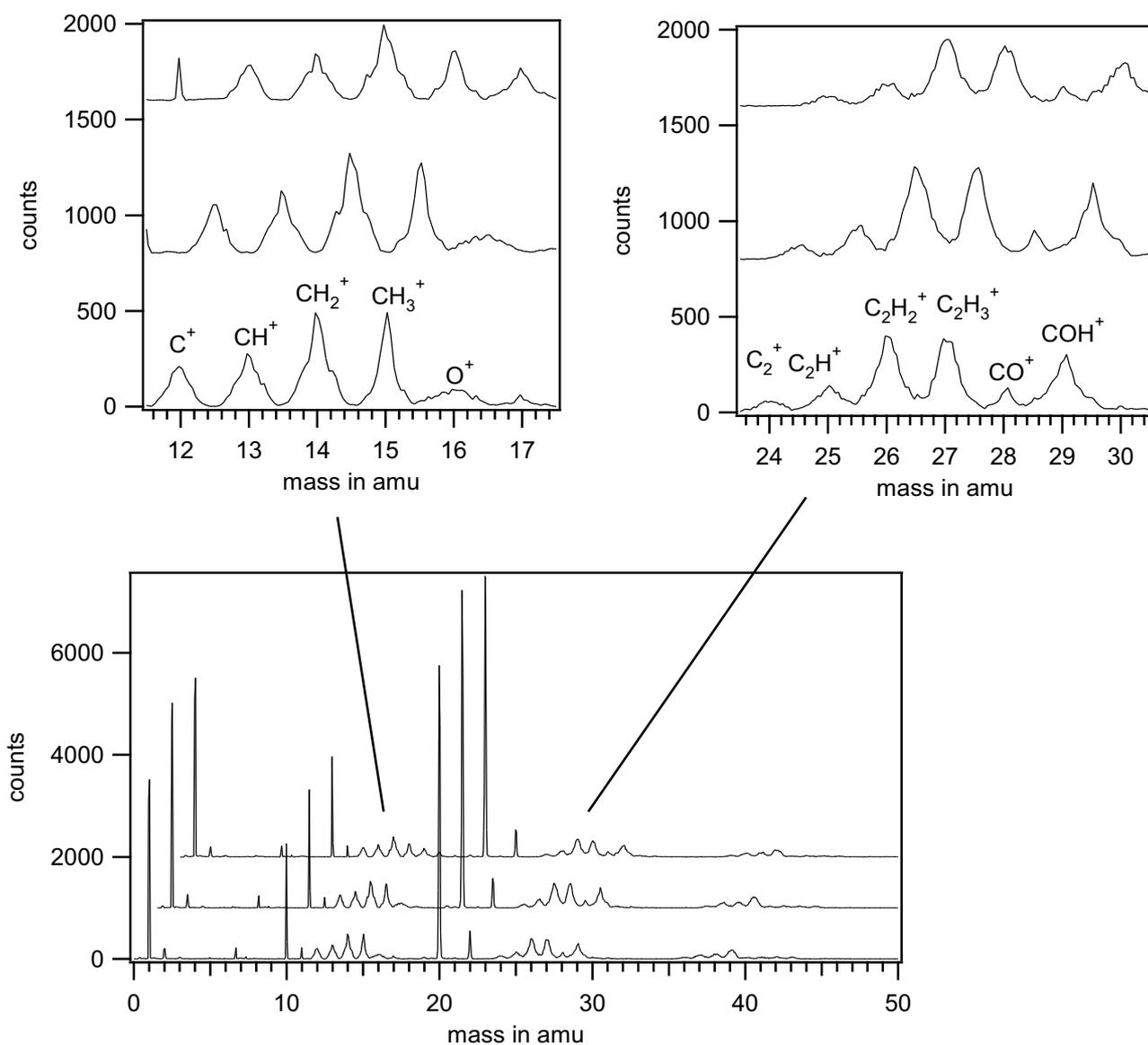
Fig. 5. Mass spectra as a function of photon energy close to the O1s edge. The photon energies are from bottom to top: 534.61, 535.11, 535.61 eV.

4 Conclusion

The CD effects in the TIY were found to be less than 0.2%. In the PIY they were found to be less than 0.5%. These upper limits do not contradict the findings of[16]. The CD in the TIY was reported to be about 0.15%. However the smallness of both the TIY CD and the PIY CD gives some insight into the CD effect. The CD seems to be the same for all fragmentation channels. If the smallness of the CD in TIY was because of cancellation of CD effects with different sign for different ions fragments, table 3 would certainly show deviations from zero. Therefore we conclude that the stereo-selectivity is a

fragment	$h\nu$=530.85 eV	$h\nu$=535.11 eV	$h\nu$=289.36 eV
H^+	0.187 ± 0.376	-0.547 ± 0.328	0.141 ± 0.164
H_2^+	-0.156 ± 1.184	0.052 ± 0.919	0.456 ± 0.526
C^+	1.159 ± 0.735	-0.424 ± 0.595	-0.099 ± 0.330
CH^+	-0.260 ± 0.689	-0.733 ± 0.531	-0.472 ± 0.257
CH_2^+	-0.080 ± 0.552	-0.379 ± 0.412	0.108 ± 0.195
CH_3^+	-0.814 ± 0.773	-0.382 ± 0.489	0.243 ± 0.236
O^+	-0.845 ± 0.596	-0.645 ± 0.692	0.350 ± 0.426
C_2^+	1.117 ± 1.061	0.123 ± 0.853	0.708 ± 0.459
C_2H^+	-0.114 ± 0.812	0.198 ± 0.577	-0.053 ± 0.266
$C_2H_2^+$	-0.013 ± 0.573	0.278 ± 0.380	0.214 ± 0.166
$C_2H_3^+$	-1.314 ± 0.699	-0.756 ± 0.392	0.184 ± 0.189
CO^+	-1.399 ± 0.930	-0.063 ± 0.651	-0.019 ± 0.284
COH^+	-0.412 ± 0.598	-0.129 ± 0.439	0.009 ± 0.179
C_3H^+	1.143 ± 1.326	0.491 ± 0.675	-0.089 ± 0.313
$C_3H_2^+$	-1.695 ± 1.384	0.631 ± 0.636	0.159 ± 0.301
$C_3H_3^+$	4.077 ± 1.545	0.182 ± 0.492	0.130 ± 0.290
TIY	-0.071 ± 0.237	-0.267 ± 0.221	0.100 ± 0.090

Table 3
The observed CD in percent (asymmetry · 100) for all mayor MO fragments.

property of the photoabsorption process only. The fragmentation occurs in a second step independent from the helicity of the absorbed photon. Further the upper limit of 1-2% of the CD in the molecular ion orientation distribution (CDM) confirms the thesis that it is nor sufficient just to align the molecules on a surface or in a nano-particle but that the interaction between neighboring molecules is essential to generate large CD effects.

5 Acknowledgements

fragment	$h\nu$=530.85 eV	$h\nu$=535.11 eV	$h\nu$=289.36 eV
H^+	0.426 ± 0.512	-0.482 ± 0.408	0.102 ± 0.226
H_2^+	1.127 ± 1.735	1.104 ± 1.311	0.821 ± 0.768
C^+	-0.804 ± 1.081	-1.098 ± 0.859	-0.932 ± 0.498
CH^+	-1.627 ± 0.992	-0.344 ± 0.749	-0.436 ± 0.384
CH_2^+	1.388 ± 0.794	0.185 ± 0.566	-0.715 ± 0.286
CH_3^+	-0.722 ± 1.149	0.917 ± 0.711	-0.143 ± 0.363
O^+	-1.413 ± 0.811	0.092 ± 0.998	0.384 ± 0.636
C_2^+	-1.605 ± 1.584	1.105 ± 1.256	-0.52 ± 0.706
C_2H^+	0.420 ± 1.202	0.261 ± 0.842	-0.343 ± 0.405
$C_2H_2^+$	0.413 ± 0.838	0.378 ± 0.529	-0.594 ± 0.243
$C_2H_3^+$	-1.273 ± 1.045	1.147 ± 0.561	-0.544 ± 0.288
CO^+	-2.212 ± 1.397	0.553 ± 1.003	0.139 ± 0.472
COH^+	-0.630 ± 0.855	0.644 ± 0.634	-0.690 ± 0.266
C_3H^+	-0.238 ± 1.998	1.989 ± 1.025	-0.311 ± 0.494
$C_3H_2^+$	-2.240 ± 2.131	1.039 ± 0.978	0.559 ± 0.478
$C_3H_3^+$	0.629 ± 2.448	-0.447 ± 0.749	-0.034 ± 0.463
TIY	-0.256 ± 0.274	0.263 ± 0.220	-0.340 ± 0.101

Table 4

The observed CD in the molecular orientation (equivalent to forward/backward asymmetry of the ion yield) in percent (asymmetry · 100) for all mayor MO fragments.

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