Core Electron Transitions as a Probe for Molecular Chirality: Natural Circular Dichroism at the Carbon K-edge of Methyloxirane

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Circular dichroism (CD) of electronic and vibrational transitions has been widely used as a probe of molecular chirality. The extension of CD to core transitions is now possible at third-generation synchrotrons equipped with insertion devices which produce radiation with a high rate of circular polarization. The first CD measurements in the X-ray region were reported for core to valence state transitions of metal complexes in oriented crystalline chiral molecules[1,2] and for bulk crystalline samples.[3] Here we report the first CD measurements on a randomly oriented system: the carbon K-edge absorption spectrum of methyloxirane in the vapor phase. The signs and the intensity of the dichroism agree with previous calculations[4,5] indicating that a considerable hybridization occurs between the core 1s and the valence molecular states.

Core electron excitations give rise to highly localized transitions which enable a very precise description of the ground and excited states of a molecule, and thus help provide a geometrical description of the coordination and short-range ordering around an absorbing atom[6,7] as well as the assignment of excited-state symmetries and insights into dynamic photochemical processes. The reported experimental and theoretical results[8] in oriented systems at the L- and K-edges of Nd, I, and Co provide new information about the edge and near-edge structure of those compounds. It was shown that the CD in these oriented systems is dominated by the interference of electric dipole and electric quadrupole excitation channels (the E1−E2 mechanism).

Except for a problematic[9] ORD experiment at the cobalt K-edge,[10] no CD spectra have been reported for molecules in random orientation. In this experiment the leading term contributing to circular dichroism is the interference of the electric and magnetic dipole transition amplitudes[11] (the E1−M1 mechanism) which, expressed as the rotational strength in the Rosenfeld−Condon equation, is given by the pseudoscalar product of the electric and magnetic dipole transition moments

$$R_{if} = \text{Im}\langle i|\mu|f\rangle \cdot \langle f|\mathbf{m}|i\rangle$$

This expression carries information about the chiral scattering paths of the photoelectron which is complementary to the information obtained from standard X-ray absorption spectroscopy. For K-edge excitations the magnetic dipole transition element is, to a first approximation, zero because magnetic dipole transitions arising from s orbitals are forbidden. Thus, the only possible source of magnetic dipole intensity involves 1s−np (particularly 1s−2p) mixing. Two calculations[4,5] have suggested that this mixing is sufficient to produce observable CD for simple organic molecules. In this contribution we present the carbon K-edge CD of methyl-

oxirane, which contains three chemically distinct saturated carbon atoms whose core electronic excitations are partially resolved at the edge of the absorption spectrum.

The differential absorption experiments were all performed during a beamtime allocation of one week at the "POLAR" beamline, which operates downstream from the Electromagnetic Elliptical Wiggler (EEW),[12] inserted in the 4.2 straight section of the ELETTRA synchrotron in Trieste. The EEW produces alternate right- and left-handed circularly polarized radiation at a frequency of 0.1 Hz when operating in the wiggler mode. To invert the beam polarization ellipses, alternating currents are applied to the horizontal EEW coils. In this way the inversion of polarization handedness is produced dynamically every five seconds. The polarization handedness convention is that of the viewer looking at the incoming light rotation. A suitable reference status voltage level from the EEW power supply controls timing of the measured signals to that of the polarization state. The magnitude of the Stokes parameter S_3 of the beam in the close vicinity of the carbon K-edge, at 276 eV, has been measured and computed to be ±0.83. The resolution of the monochromator was 200 meV at 300 eV with a flux of 2×10^{10} photon/s at the sample.

A double Samson-type ionization cell,[13] separated from the line UHV by a Si_3N_4 window 100-nm thick, was adopted to measure the absorption coefficients. Special care was devoted to ensure that the molecular species under test were inert and stable, not undergoing any significant chemical reaction or decomposition in the experimental chamber. We ascertained the above by performing time-of-flight MS experiments and verifying that the valence and core XPS and absorption spectra at the carbon and oxygen edges were stable over long time periods. Time-of-flight-MS results showed that the parent ion of mass peak at $m/e = 58$ was always present at several energies across the whole carbon K-edge. The fragmentation pattern was slightly different with respect to that reported for valence excitations,[14] notably for the larger abundances of ions m/e 26 and 14. No clusters or parent ions larger than $m/e = 58$ were ever observed at any energy tested. As a consequence, it can be stated that no chemical recombination takes place inside the gas cell, and therefore the absorption spectra are attributable only to the pure optical isomers under examination.

Figure 1 shows the isotropic absorption spectrum of methyloxirane. The absorption profile is composed of two steps, followed by the white line and a shoulder; a vibrational progression is also visible. Few organic molecules have had their core electron absorption spectra measured, and a photoemission experiment at the carbon 1s core level was required to help understand the absorption spectrum manifold of methyloxirane. Three states (see pointing arrows in Figure 1) of 291.2, 292.2, and at 292.6 eV binding energies were found in good agreement with the computed ionization potentials.[5]

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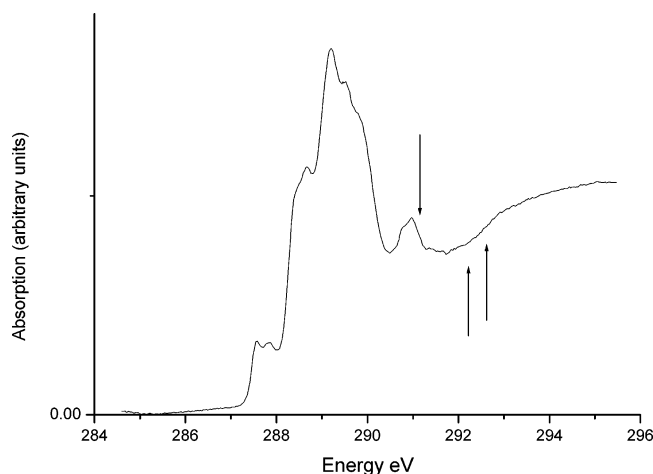
Figure 1. Carbon K-edge absorption spectrum of methyloxirane with 60 meV resolution and at 6×10^{-1} mbar vapor pressure. The ionization potentials of the three kinds of carbon atoms are indicated with vertical arrows.

Thus, the absorption spectrum at the carbon K-edge can be attributed to core level excitations originating from the three distinct carbon atoms. Although a clear-cut assignment of the transitions can come only from spectra in oriented systems, some empirical considerations, based on ground states SCF energies, field effects, oxidation state, and atomic partial charge calculations, indicate that the absorption spectrum will show the transitions localized at the two oxygen-bound carbon atoms, i.e., methylene and methine, at higher energies than that localized on the more protonated methyl group.

The CD spectra of the enantiomers and that of the racemate are shown in Figure 2a. All the spectra have a nonlinear sloping background, and to remove this, the spectra of the two enantiomers were halved and algebraically subtracted (see Figure 2b) leaving a monosignate signal. Subtraction of the spectrum of the racemate gave essentially the same results as can be anticipated by noticing the close resemblance between the "half-sum" spectrum and that of the racemate. The ratio of the differential absorption intensities to that of the absorption is of the order of 10^{-3}. Calculations, at frozen and relaxed core approximation,[4,5] suggest that transitions from all three carbons are optically active. The methyl transitions are calculated to be a near conservative couplet with a small energy separation at 1.6 eV to lower energy of a multiplet attributed to transitions arising from the methylene and methyne carbons. We assign the experimental dichroism to this multiplet which is not fully resolved due to the energy resolution of the experiment. The overall sign and magnitude of the dichroism agree with both theoretical predictions. We suggest that the methyl carbon dichroism essentially cancels to zero because of the small energy splitting and the resolution of the experiment. Due to the magnetic dipole selection rule on transitions originating from s orbitals, it had been unclear as to whether CD could be measured in randomly oriented systems. Our experiments show that it can be measured and that the magnitude of the dichroism is of the same order as that of valence transitions. We believe the main reason the CD is so large is the close proximity of the 1s and 2p orbitals in first row atoms, thus allowing the efficient mixing required to overcome the magnetic dipole selection rules. In addition we have shown that the experiment, even at low spectral resolution, can single out particular carbon atoms, thus allowing the possibility of "tuning in" to a specific chiral carbon atom in a large molecule.
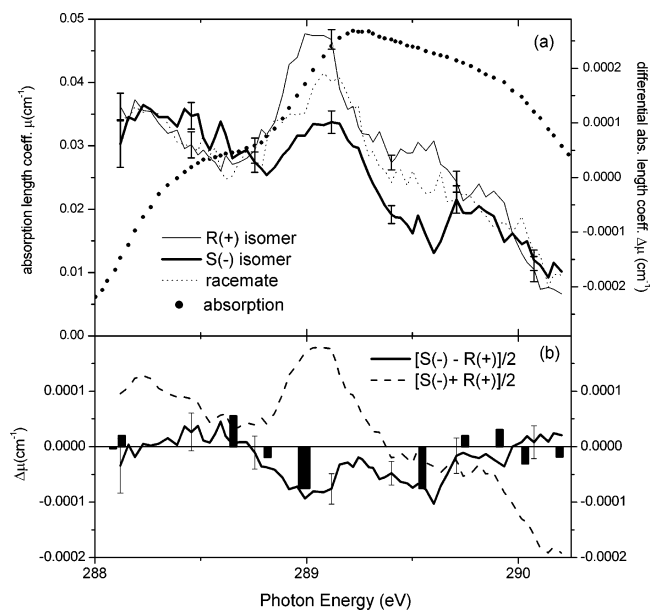
Figure 2. (a) Absorption and CD spectra of R-$(+)$- and S-$(-)$-methyloxirane at 6×10^{-1} mbar vapor pressure, (b) "composite" CD spectrum of S-$(-)$-methyloxirane and that of the racemate as obtained by the "half-difference" and the "half-sum" of the spectra of the enantiomers. The histograms are the rotational strength for the S-$(-)$-enantiomer as calculated in ref 5 "relaxed core" and aligned in energy to the experimental CD maxima. The monochromator slits were set at 50 μm with an energy resolution of 200 meV.

Supporting Information Available: [S-$(-)$-racemate] and the "half-difference" spectra, ion yield graphs, XPS, and TOF spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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