Carbon dioxide gas, CO_2(g), by near-ambient pressure XPS

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Carbon dioxide gas, CO_2(g), by near-ambient pressure XPS

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Near-ambient pressure x-ray photoelectron spectroscopy (NAP-XPS) is a less traditional form of XPS that allows samples to be analyzed at relatively high pressures, i.e., at greater than 2500 Pa. With NAP-XPS, XPS can probe moderately volatile liquids, biological samples, porous materials, and/or polymeric materials that outgas significantly. In this submission, we show the survey, O 1*s*, C 1*s*, valence band, O *KLL* Auger, and C *KLL* Auger NAP-XPS spectra of gaseous carbon dioxide, CO_2, a material that would be difficult to analyze by conventional XPS. A small N 1*s* signal from N_2(g) is also observed in the survey spectrum. The C 1*s* and O 1*s* signals in the narrow scans are fit to Gaussian–Lorentzian sum and asymmetric Lorentzian (LA) functions. Better fits are obtained with the LA synthetic line shape. Since it is likely that CO_2(g) will be present in other NAP-XPS analyses, these data should serve as a useful reference for other researchers. *Published by the AVS.*
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Keywords: *near-ambient pressure X-ray photoelectron spectroscopy, NAP-XPS, XPS, carbon dioxide, CO_2(g)*

Accession #: 01486
Technique: XPS, XAES
Host Material: Carbon dioxide, CO_2(g)
Instrument: SPECS EnviroESCA
Major Elements in Spectra: O, C
Minor Elements in Spectra: N
Published Spectra: 6
Spectra in Electronic Record: 6
Spectral Category: Comparison

INTRODUCTION

Carbon dioxide, CO_2, is a colorless, odorless gas that is present in the earth's atmosphere at trace levels. It is produced by combustion (oxidation) of carbon-containing materials, e.g., the oxidation of methanol (Refs. 1 and 2), fermentation, and animal respiration. CO_2 is a major greenhouse gas because of its ability to absorb radiant energy. CO_2 conversation into fuels in the presence of metal catalysts is important for the reduction of environmental pollution (Ref. 3), and near-ambient pressure x-ray photoelectron spectroscopy (NAP-XPS) is well suited for understanding surface reactions of metallic catalysts during CO_2 hydrogenation (Refs. 4 and 5). CO_2 has previously been characterized in the solid state, as a pure ultrathin film (Refs. 6 and 7), and in combination with water and methanol by conventional XPS (Ref. 8). In this submission, we present the NAP-XPS characterization of carbon dioxide, CO_2. Because CO_2 has both theoretical and industrial importance, it is likely that its spectrum will end up superimposed on that of other materials in NAP-XPS analyses—we expect the spectra reported here to be useful references. Data were collected with the SPECS EnviroESCA instrument (Refs. 9–12). This document is part of a series of submissions on NAP-XPS that is being submitted to Surface Science Spectra. This set of articles and the NAP-XPS technique have previously been introduced in this journal (Ref. 13).

This submission contains the survey, O 1*s*, C 1*s*, valence band, O *KLL* Auger, and C *KLL* Auger NAP-XPS spectra of gas phase CO_2. A small N 1*s* signal from N_2(g) is also present in the survey spectrum. The O 1*s* narrow scan shows a main peak at a binding energy of ca. 537 eV from CO_2. The other two small peaks/groups of peaks at binding energies of ca. 550 and 554 eV are shake-up peaks (the C 1*s* narrow scan that is described below shows similar shake-up signals) (Refs. 1 and 14). The C Auger signal in the survey spectrum is barely discernible. This may be a combination of the fact that this signal is generally much smaller than C 1*s* signal and also that there may be greater attenuation of the signal at higher binding energy (lower kinetic energy where the C Auger signal appears) than at lower binding energy (higher kinetic energy where the C 1*s* signal appears). The C 1*s* narrow scan primarily shows one signal, which is attributed to carbon in CO_2(g). This signal appears at relatively high binding energy because the carbon in CO_2 is chemically shifted to a rather high oxidation state through four carbon-oxygen bonds (Ref. 15), and also because gas phase photoelectron signals generally appear at higher binding energies than those from condensed phases. The valence band of CO_2(g) is also presented. It has previously been shown and discussed in the literature (Refs. 14 and 16–18). No energy correction was applied to the spectra presented here, which are referenced to the Fermi level of the instrument. The work function of the spectrometer used in this study was 4.4463 eV.

The O 1*s* and C 1*s* signals here are fit to Gaussian–Lorentzian sum (GLS) (Ref. 19) and asymmetric Lorentzian (LA) (Ref. 20) functions above flat, linear baselines. These baselines are typical for NAP-XPS spectra because of a lack of inelastically scattered electrons from gas phase materials. These peaks are better fit with LA synthetic line shapes, which suggest that they have a significant amount of Lorentzian character. For the O 1*s* fit, the GLS had a Lorentzian contribution of 20%, while the LA function had α, β, and m values of 1.7, 2.7, and 0, respectively. The α and β parameters in the LA function are exponents that determine the degree of asymmetry on the lower and higher binding energy sides of the synthetic peak, respectively. The parameter m is a measure of the Gaussian contribution to the LA function vis-à-vis the convolution of a Gaussian with the asymmetric Lorentzian portion of the LA function, i.e., the LA function allows an asymmetric Voigt function to be created. For the C 1*s* fit, the GLS had a Lorentzian contribution of 20%, while the LA function had α, β, and m values of 1.5, 2.2, and 0, respectively.

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SPECIMEN DESCRIPTION (ACCESSION #01486)

Host Material: Carbon dioxide, CO_2(g)

CAS Registry #: 7732-18-5

Host Material Characteristics: Homogeneous; gas; amorphous; inorganic compound; other

Chemical Name: Carbon dioxide, CO_2(g)

Source: Messer Griesheim GmbH

Host Composition: Carbon dioxide, CO_2(g)

Form: Gas

Structure: CO_2, O═C═O

History and Significance: CO_2 is an important product of the combustion (oxidation) of organic materials and an important greenhouse gas.

As Received Condition: Compressed gas cylinder

Analyzed Region: Carbon dioxide gas molecules encountered by the X-ray beam.

***Ex Situ* Preparation/Mounting:** N/A

***In Situ* Preparation:** N/A

Charge Control: 200 Pa CO_2

Temp. During Analysis: 300 K

Pressure During Analysis: 200 Pa

Preanalysis Beam Exposure: 30 s

INSTRUMENT DESCRIPTION

Manufacturer and Model: SPECS EnviroESCA

Analyzer Type: Spherical sector

Detector: Other 1D delay line detector (1D-DLD)

Number of Detector Elements: 25

INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA

Spectrometer

Analyzer Mode: Constant pass energy

Throughput ($T = E^N$): N = 0

Excitation Source Window: Silicon nitride

Excitation Source: Al K_α monochromatic

Source Energy: 1486.6 eV

Source Strength: 42 W

Source Beam Size: $250 \times 250\ \mu m^2$

Signal Mode: Multichannel direct

Geometry

Incident Angle: 55°

Source-to-Analyzer Angle: 55°

Emission Angle: 0°

Specimen Azimuthal Angle: 0°

Acceptance Angle from Analyzer Axis: 22°

Analyzer Angular Acceptance Width: 44°

DATA ANALYSIS METHOD

Energy Scale Correction: No correction

Recommended Energy Scale Shift: 0

Peak Shape and Background Method: GLS and also asymmetric Lorentzian (LA) functions were used for peak fitting on top of linear backgrounds. All peak fitting was with CASAXPS (Casa Software Ltd., Version 2.3.18PR1.0).

Quantitation Method: Elemental compositions were calculated using the standard SPECS software.

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SPECTRAL FEATURES TABLE

Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV counts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
01486-01	Valence band	0–50	…	…	…	…	CO_2(g)
01486-01	C 1*s*	293.7	…	…	…	…	CO_2(g)
01486-01	N 1*s*	405.8	…	…	…	…	N_2(g)
01486-01	O 1*s*	537.3	…	…	…	…	CO_2(g)
01486-01	O *KLL*[a]	494.1	…	…	…	…	CO_2(g)
01486-01	C *KLL*[a]	251.7	…	…	…	…	CO_2(g)
01486-02	O 1*s*	537.2	0.64	2805	2.48	67.5	CO_2(g)
01486-03	C 1*s*	293.6	0.55	545.0	1.00	32.5	CO_2(g)
01486-04	O *KLL*[a]	494.1	…	…	…	…	CO_2(g)
01486-05	C *KLL*[a]	247.2	…	…	…	…	CO_2(g)
01486-06	$1\pi_g$	9.6	…	…	…	…	CO_2(g)
01486-06	$1\pi_u$	13.9	…	…	…	…	CO_2(g)
01486-06	$3\sigma_u$	14.1	…	…	…	…	CO_2(g)
01486-06	$4\sigma_g$	15.2	…	…	…	…	CO_2(g)

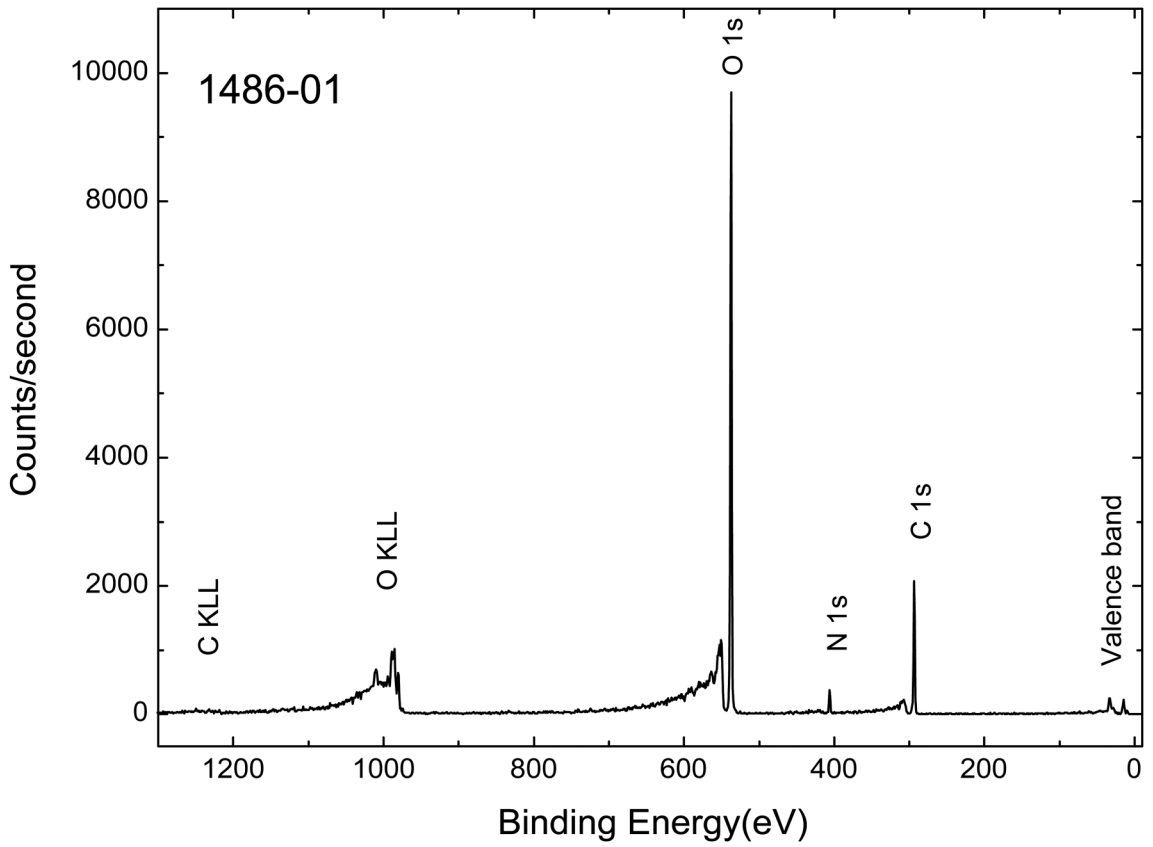
[a]Peak energy value indicated as kinetic energy.

ANALYZER CALIBRATION TABLE

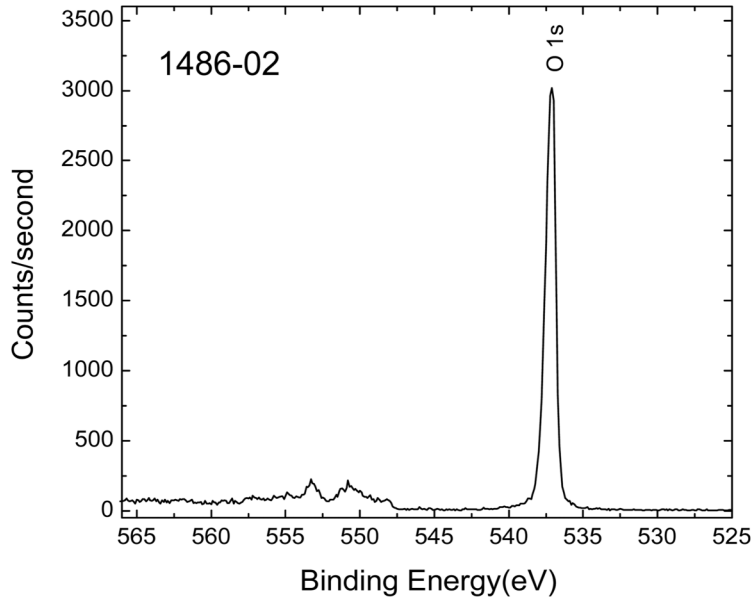
Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV counts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
…	Au 4*f*	83.9	0.67	8 940.7	…	…	…
…	Ag 3*d*	368.1	0.60	13 854.9	…	…	…
…	Ge 2*p*	1217.5	1.15	8 064.6	…	…	…

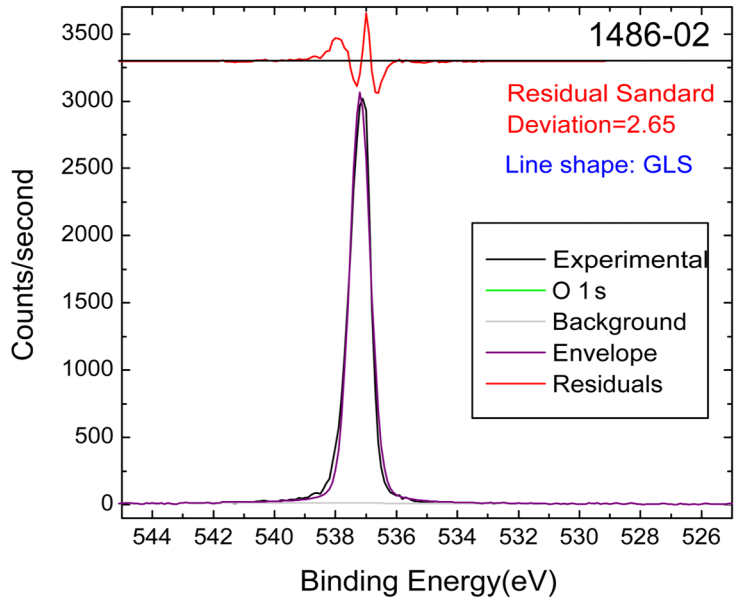
GUIDE TO FIGURES

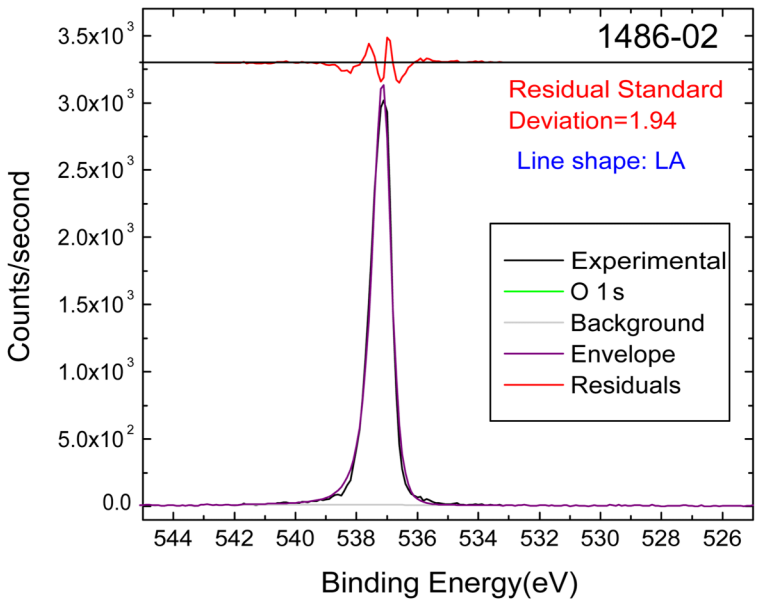
Spectrum (Accession) #	Spectral Region	Voltage Shift	Multiplier	Baseline	Comment #
01486-01	Survey	0	1	0	From CO_2 (g)
01486-02	O 1*s*	0	1	0	From CO_2 (g)
01486-03	C 1*s*	0	1	0	From CO_2 (g)
01486-04	O *KLL*	0	1	0	From CO_2 (g)
01486-05	C *KLL*	0	1	0	From CO_2 (g)
01486-06	Valence band	0	1	0	From CO_2 (g)



Accession #	01486-01
Host Material:	Carbon dioxide, CO_2(g)
Technique:	XPS
Spectral Region:	Survey
Instrument:	SPECS EnviroESCA
Excitation Source:	Al K_α monochromatic
Source Energy:	1486.6 eV
Source Strength:	42 W
Source Size:	0.250×0.250 mm^2
Analyzer Type:	Spherical sector analyzer
Incident Angle:	54.7°
Emission Angle:	0°
Analyzer Pass Energy:	100 eV
Analyzer Resolution:	1.7 eV
Total Signal Accumulation Time:	270 s
Total Elapsed Time:	145 s
Number of Scans:	2
Effective Detector Width:	25 eV

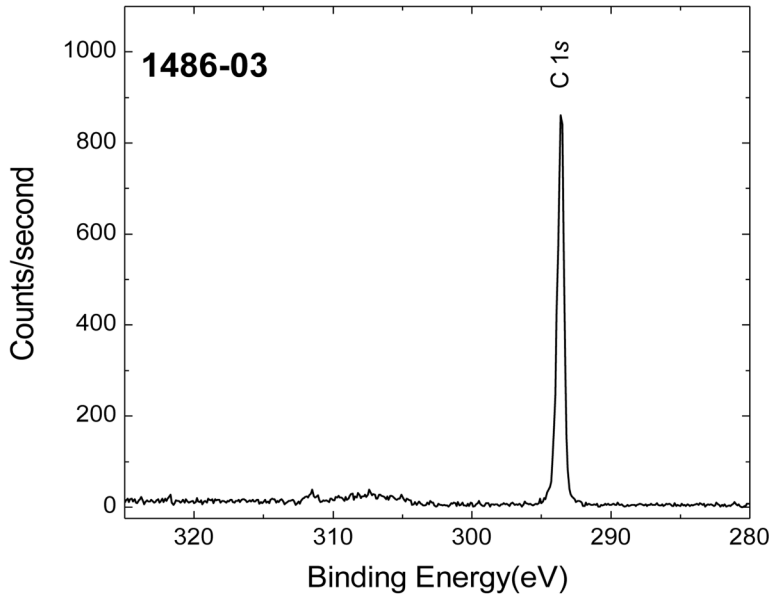


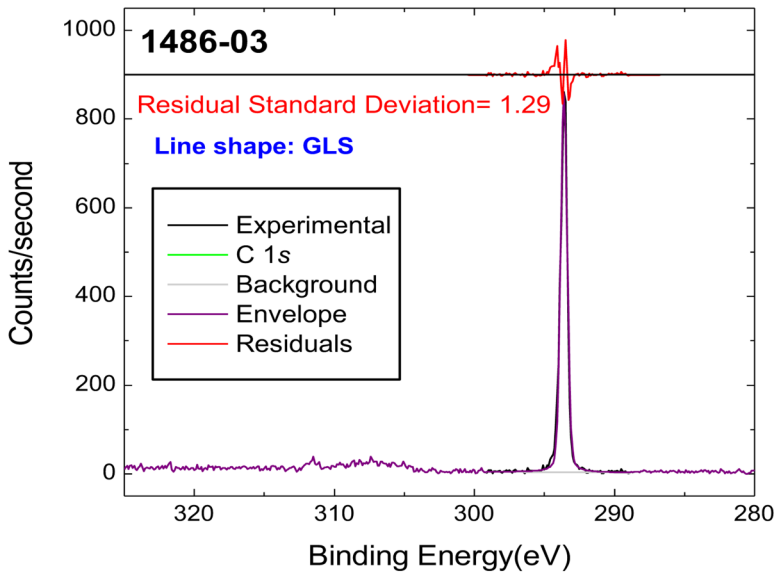


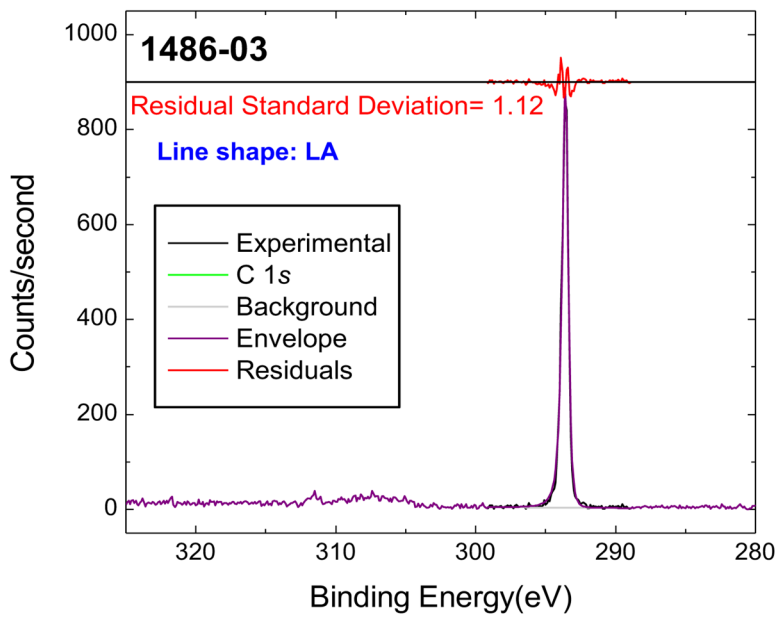


- **Accession #:** 01486-02
- **Host Material:** Carbon dioxide, CO_2(g)
- **Technique:** XPS
- **Spectral Region:** O 1*s*

Instrument: SPECS EnviroESCA
Excitation Source: Al K_α monochromatic
Source Energy: 1486.6 eV
Source Strength: 42 W
Source Size: 0.250 × 0.250 mm^2
Analyzer Type: Spherical sector
Incident Angle: 54.7°
Emission Angle: 0°
Analyzer Pass Energy: 20 eV
Analyzer Resolution: 0.60 eV
Total Signal Accumulation Time: 300 s
Total Elapsed Time: 334 s
Number of Scans: 3
Effective Detector Width: 2.5 eV

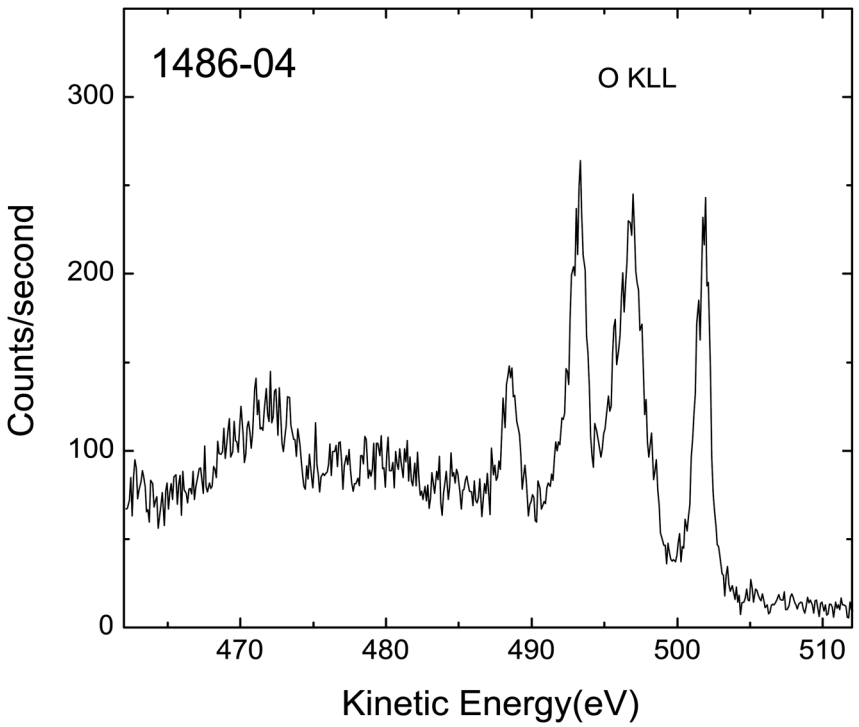






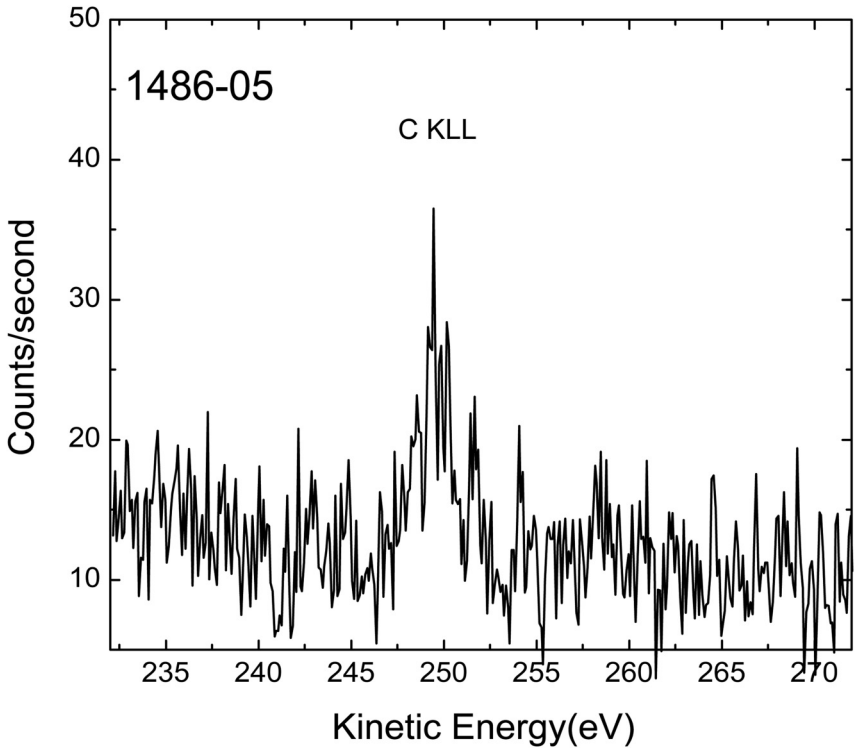
- **Accession #:** 01486-03
- **Host Material:** Carbon dioxide, CO_2(g)
- **Technique:** XPS
- **Spectral Region:** C 1*s*

Instrument: SPECS EnviroESCA
Excitation Source: Al K_α monochromatic
Source Energy: 1486.6 eV
Source Strength: 42 W
Source Size: 0.250 × 0.250 mm^2
Analyzer Type: Spherical sector
Incident Angle: 54.7°
Emission Angle: 0°
Analyzer Pass Energy: 20 eV
Analyzer Resolution: 0.60 eV
Total Signal Accumulation Time: 270 s
Total Elapsed Time: 303 s
Number of Scans: 3
Effective Detector Width: 2.5 eV



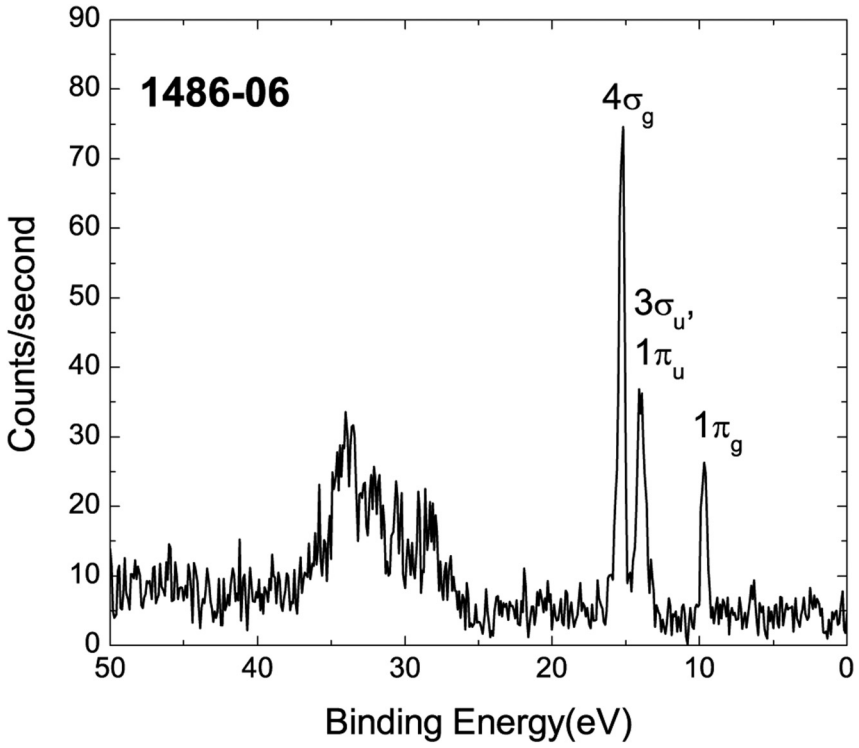
- **Accession #:** 01486-04
- **Host Material:** Carbon dioxide, CO_2(g)
- **Technique:** XAES
- **Spectral Region:** O *KLL*

Instrument: SPECS EnviroESCA
Excitation Source: Al K_α monochromatic
Source Energy: 1486.6 eV
Source Strength: 42 W
Source Size: 0.250 × 0.250 mm^2
Analyzer Type: Spherical sector
Incident Angle: 54.7°
Emission Angle: 0°
Analyzer Pass Energy: 20 eV
Analyzer Resolution: 0.60 eV
Total Signal Accumulation Time: 400 s
Total Elapsed Time: 445 s
Number of Scans: 4
Effective Detector Width: 2.5 eV



- **Accession #:** 01486-05
- **Host Material:** Carbon dioxide, CO_2(g)
- **Technique:** XAES
- **Spectral Region:** C *KLL*

Instrument: SPECS EnviroESCA
Excitation Source: Al K_α monochromatic
Source Energy: 1486.6 eV
Source Strength: 42 W
Source Size: 0.250 × 0.250 mm^2
Analyzer Type: Spherical sector
Incident Angle: 54.7°
Emission Angle: 0°
Analyzer Pass Energy: 20 eV
Analyzer Resolution: 0.60 eV
Total Signal Accumulation Time: 320 s
Total Elapsed Time: 363 s
Number of Scans: 4
Effective Detector Width: 2.5 eV



- **Accession #:** 01486-06
- **Host Material:** Carbon dioxide, CO_2(g)
- **Technique:** XPS
- **Spectral Region:** O 2*s* and Valence band

Instrument: SPECS EnviroESCA
Excitation Source: Al K_α monochromatic
Source Energy: 1486.6 eV
Source Strength: 42 W
Source Size: 0.250 × 0.250 mm^2
Analyzer Type: Spherical sector
Incident Angle: 54.7°
Emission Angle: 0°
Analyzer Pass Energy: 20 eV
Analyzer Resolution: 0.60 eV
Total Signal Accumulation Time: 416 s
Total Elapsed Time: 461 s
Number of Scans: 4
Effective Detector Width: 2.5 eV