Calibration of oxygen 1s ionization energies. Accurate energies for CO_2, H_2O, CO, and O_2

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ABSTRACT

Access to accurate reference data is a prerequisite in order to translate chemical shifts to an absolute scale for inner-shell ionization energies. Calibration standards for oxygen 1s (O 1s) ionization energies are less well established than, for instance, for carbon 1s. To improve upon this situation, adiabatic and vertical O 1s ionization energies for gaseous carbon dioxide (CO_2) are critically reviewed and used to establish the most accurate values currently available: 541.085(17) and 541.253(17) eV, respectively. Combining these with new precise measurements of shifts in O 1s ionization energies for H_2O, CO, and O_2 allows us to establish equally accurate absolute ionization energies for these molecules as for CO_2. The resulting adiabatic and vertical energies are 539.728(17) and 539.827(17) eV for H_2O, 542.439(17) and 542.495(17) eV for CO, 543.285(17) and 543.294 (17) eV for O_2 ($^4\Sigma$ final state), and 544.338(17) and 544.423(17) eV for O_2 ($^2\Sigma$ final state). It is proposed that O 1s in CO_2 be adopted as a standard of higher precedence, and that H_2O, CO, and O_2 be used also. The O 1s ionization energies in these molecules occur in the range 540–543 eV. These proposed standards should provide optimal internal calibration for a wide range of oxygen-containing compounds.

1. Introduction

Core-ionization energies are a powerful source of insight to electronic driving forces responsible for common chemical properties. [1,2] Although this information is mostly accessed through chemical shifts, *i. e.*, differences between core-ionization energies involving the same element in different chemical environments, it is preferable to report absolute ionization energies. This facilitates the comparison of energies between disjoint sets of compounds and thus consistent compilations of core-level ionization energies for wide classes of compounds.

High-precision measurements of core-level energies are carried out at synchrotron radiation (SR) facilities, where the high photon flux allows for precise photon energies and, in combination with accurate electron analyzers, high-resolution photoelectron spectra. Depending on the energy range, spectral fine structure including vibrational structure may be partly or fully resolved, allowing for determination of both adiabatic and vertical energy shifts accurate in the several-millivolt range within the recorded spectrum. In turn, this opens for a way around one of the limitations of SR, that the photon energy is not

accurately known: by recording spectra for a mixture of a conveniently-chosen reference compound and the compound of interest. Since the reference and compound peaks should be well separated yet close in energy, this approach presupposes the existence of well-calibrated core ionization energies for a set of convenient reference compounds. At least one calibration point must be obtained outside this set, typically by combining characteristic X-ray radiation of accurately known energy, with data on atomic (*i.e.*, vibration-free) calibration gases such as Ne or Ar.

For use in carbon 1s (C 1s) photoelectron spectroscopy, Myrseth et al. [3] determined accurate C 1s ionization energies for nine representative small molecules including CO_2, CH_4, and CF_4, using the well-established energy of Ar $2p_{3/2}$ in combination with accurately measured shifts in C 1s photoelectron spectra. Their work facilitated the compilation of C 1s energies covering a wide range of carbon-containing molecules, including linear and cyclic alkanes and alkenes, linear alkynes, and methyl- or fluoro-substituted benzenes. [2,4,5]

In the course of an ongoing study of alcohols, we became aware that calibration standards are less well established for oxygen 1s (O 1s)

ionization energies, complicating comparisons to energies reported in the literature and making chemical shifts computed from reported ionization energies to be much less accurate than what the underlying data would allow for.

Common calibrants used for O 1s spectroscopy are H_2O, CO_2, CO, and O_2 listed in the order of increasing O 1s ionization energy. Carbon dioxide is a particularly attractive alternative since it may be used for energy calibration of both C 1s and O 1s spectra. Unfortunately, two values for the vertical O 1s ionization energy of CO_2 are actively being used for calibration purposes, namely 541.28(12) and 541.32(5) eV by Johansson et al. [6] and Thomas & Shaw [7], respectively. While the two values agree with one another within the stated error bars, computing a chemical shift across these two reference values introduces an error of 0.04 eV or ten times the minimum uncertainty attainable for an accurately measured chemical shift today. These considerations motivate a closer look at the vertical and adiabatic O 1s ionization energies reported for the four compounds listed above. In particular, the understanding of recoil-induced internal excitation in core-level photoelectron spectra has undergone significant progress during the past decade with possible consequence for best reference energies.

The aim of this work is thus to establish accurate absolute adiabatic and vertical O 1s ionization energies for CO_2, and, secondly, to obtain the most accurate adiabatic and vertical O 1s energies for H_2O, CO, and O_2 while using CO_2 as a standard of higher priority.

2. Experimental

Gas phase oxygen 1s spectra were measured at beamline I411 at MAX-lab [8,9] using a photon energy of ≈580 eV. Photoelectrons were analyzed with a Scienta 2000 hemispherical electron analyzer. The kinetic energy scale was calibrated using the xenon $N_{4,5}OO$ Auger spectrum [10]. Relative calibration of the ionization energy scale was achieved by recording data for a mixture of carbon dioxide and a second gaseous compound; H_2O, CO, or O_2. Assuming a Gaussian shape for the instrumental broadening function, the full width at half maximum (fwhm) was determined from fits to the experimental data (see next section) and found to be in the range 150–160 meV.

Oxygen (99.99%) and carbon dioxide (99.7%) were obtained from the AGA company, and carbon monoxide (99.94%) was supplied by Air Liquide. Ultrapure water was obtained using the Milli-Q Integral Purification System with air removed by several freeze-pump-thaw cycles. Each sample was mixed with carbon dioxide in a manifold and introduced into the gas cell via a gas-inlet system. The gas pressure in the vacuum chamber was maintained at around 5×10^{-6} mbar.

2.1. Fitting models

In order to determine accurate adiabatic energies, line-shape profiles representing the contribution from each molecule in the mixture were fit to the measured spectra. These profiles combine vibrational structure through Franck-Condon distributions and various contributions to line broadening. The vibrational profiles were adopted from previous studies [11–14] and kept fixed in the fitting process. The vibrational line-shape was convoluted with a Gaussian function representing experimental broadening and the asymmetric function of van der Straten et al. [15] representing the combined effects of lifetime broadening and post-collision interaction between the Auger electron and the photoelectron.

Life-time widths (fwhm) were obtained from the literature as follows: H_2O 160 meV [12], CO 167 meV [13], O_2 140 meV [14], and for CO_2 166 meV calculated from refs [11,16,17] as a weighted average with reciprocal squared uncertainties as weights.

The appropriate fwhm value of the Gaussian distribution is obtained by adding (in squares) the molecule-specific Doppler contribution [18] and the contribution from instrumental broadening. It turns out that the Gaussian fwhm values pertaining to each sample differ from that of CO_2

by 1 meV or less, which is negligible in the present context.

Evidence for trace amounts of water was found in the CO/CO_2 spectrum. The H_2O signal is well separated from the CO spectrum. Although the water signal was very weak, *viz.*, less than 1 % of the CO_2 intensity, it may possibly affect the CO_2 background. To account for this, we included a model of the water spectrum in the analysis, with the position of the water model fixed by the O 1s energy shift between water and carbon dioxide.

The fitting parameters for each spectrum were the position and intensity of the adiabatic peak for each molecular line shape and a constant background. These were determined in least-squares fits to the observed spectra by means of the SPANCF fitting package [19,20]. Adiabatic ionization energies were defined from the position of the 0-0′ vibrational line in each case, while the corresponding vertical ionization energy is formed from the adiabatic energy by adding the average vibrational energy as computed from the adopted Franck-Condon profile.

2.2. Chemical shifts and their uncertainties

Adopting a fixed vibrational model, the difference between the adiabatic and vertical ionization energies, *i.e.*, the mean vibrational excitation energy, becomes a predefined property of the fitting model. The accuracy of the vibrational lineshape models and the implied mean vibrational energy affects the accuracy of our energy shift data through $\Delta E_{vert} = \Delta E_{adiab} + E_{vib}(X) - E_{vib}(CO_2)$ with X = H_2O, CO, or O_2. Taking a practical approach to error analysis, we systematically explored the robustness of the fitting models and resulting energy shifts by investigating the effect of allowing the intensities of the vibrational profiles to vary in the fits. Constraints on the vibrational models were released in three steps for each experimental spectrum, first those for CO_2, then for the sample molecule, and finally for both molecules at the same time. Uncertainty estimates were obtained from the spread of the resulting adiabatic and vertical ionization energies for the sample molecule, cf. Table 1. We find that shifts relative to CO_2 are determined with a precision of only a few meV. These shifts have been combined with absolute values of the adiabatic and vertical energies of CO_2 to determine absolute values of adiabatic and vertical energies of H_2O, CO, and O_2, as shown below.

3. Results and discussion

3.1. A critical review of O 1s ionization energies in CO_2

The O 1s ionization energy of CO_2 has been subject to a number of investigations [6,7,21–23]. Johansson et al. published a vertical O 1s ionization energy of E_{vert} = 541.28 (12) eV for CO_2 in their calibration paper from 1973 [6]. This energy agrees within experimental uncertainties with the more accurate value of 541.32 (5) eV obtained by Thomas & Shaw in 1974 [7]. The calibration procedures were similar for the two investigations and involved measurements of Ne 1s and 2s

Table 1
Measured adiabatic and vertical ionization energy shifts relative to CO_2, and mean vibrational excitation energies (eV).

Molecule	Shift in ionization energy		Mean vibrational excitation energy	Ref.[a]
	Adiabatic ΔE_{adiab}	Vertical ΔE_{vert}	E_{vib}	
CO_2	0.000	0.000	0.168 (2)	[11]
H_2O	−1.357 (2)	−1.426 (4)	0.099 (3)	[12]
CO	1.354 (3)	1.242 (4)	0.056 (2)	[13]
$O_2 {}^4\Sigma$	2.200 (3)	2.041 (4)	0.008 (1)	[14]
$O_2 {}^2\Sigma$	3.253 (2)	3.170 (4)	0.084 (3)	[14]

[a] Reference to the applied model for vibrational fine structure.

ionization energies. Since then, the Ne 1s energy has been determined more accurately. [24] Correcting for the change in Ne 1s reference energy (−0.023 eV) would reduce the Thomas-Shaw value to $E_{vert} = 541.30$ (5) eV. The Thomas-Shaw experiment was repeated by Carroll et al. in 1988 [23] using improved experimental conditions and updated reference energies. [24] The improved value for the vertical O 1s ionization energy in CO_2 is 541.28 (2) eV, [23] in agreement with the Johansson value [6] albeit with significantly lower uncertainty.

These earlier measurements were made with either aluminum or magnesium Kα X-rays as the source of ionizing radiation. As pointed out by Thomas et al. [25] the vertical ionization energies must be corrected for the effect of recoil-induced internal excitation – vibrational and rotational.[1] In the case of CO_2 ionized by Al Kα X-rays, recoil excitation amounts to 0.021 eV. Accounting for this in the Carroll et al. experiment [23] leads to the most accurate value presently available for the <u>vertical</u> O 1s ionization energy in CO_2, at $E_{vert} = 541.26$ (2) eV.

Turning to the adiabatic O1s ionization energy of CO_2, accurate values are available from high-resolution X-ray emission spectroscopy. Pettersson et al. reported an adiabatic energy of $E_{adiab} = 541.08$ (5) eV [21], in close agreement with the value $E_{adiab} = 541.07$ (3) eV obtained by Nordgren et al. [22].

A rather different adiabatic ionization energy of 541.254 eV was derived from Rydberg excitation energies by Prince et al. [26]. The authors stated that the monochromator was calibrated using the known value of the O 1s → π* resonance in O_2, quoted as 530.800 eV. This latter value may be traced back to Wight & Brion, stating it as 530.8 ± 0.2 eV. [27] When Coreno et al. in a later paper [28] relied on the 530.8 eV value, they assigned a smaller absolute error of 0.1 eV to it, without further justification. Returning to CO_2 and the oxygen spectra in Ref. [26], the authors introduced an energy shift of 0.2 eV in order to align with the π* resonance at 535.4 ± 0.2 eV, as obtained from previous EELS measurements. [29] This raises the question whether the adiabatic O 1s ionization energy reported in Ref. [26] may be affected by a similar error. No uncertainty estimate was provided in that work.

Rydberg excitation energies in the O 1s region were also reported by Okada et al. [30]. Angle-resolved measurements and extrapolation of well-resolved Σ and Π channel 1s–to–Rydberg transitions resulted in an adiabatic threshold energy of 541.20 eV, which is similar to the value of 541.254 eV obtained by Prince et al. [26]. No uncertainty estimate was provided, but the authors refer to Prince et al. for their calibration of the photon-energy scale. From the discussion above we tentatively assign an uncertainty of ±0.1 eV for both of these results used in Fig. 2.

Adiabatic and vertical ionization energies are related through the vibrational energy, *i.e.*, $E_{vert} = E_{adiab} + E_{vib}$, where E_{vib} is the average vibrational excitation energy. High-resolution measurements of CO_2 using synchrotron radiation provide highly reliable vibrational excitation energies and intensities [11,17]. The O 1s spectrum recorded by Hatamoto et al. allows unambiguous assignment of individual vibrational peaks [11]. From their reported peak energies and intensities, we compute the mean vibrational excitation energy to be 0.168 (2) eV. Adding this value to the adiabatic ionization energy obtained by Nordgren et al. [22], 541.07 (3) eV, gives a vertical energy of $E_{vert} = 541.238$ (30) eV, consistent with and very close to the recoil-corrected value of Carroll et al. [23].

A primary goal of the present investigation is to establish the most accurate value for the vertical ionization value for O 1s in CO_2 based on the available literature, along with a reliable uncertainty estimate. To avoid the complication of correlated errors, we choose to make use of only the most accurate value reported from each instrument and

laboratory. Computing an average with reciprocal squared uncertainties as weights, from the recoil-energy-corrected value of Carroll et al. of 541.26 (2) eV, and the vertical energy obtained from Nordgren et al. and Hatamoto et al. of 541.238 (30) eV, we arrive at a recommended value of 541.253 (17) eV for E_{vert} of CO_2. The corresponding adiabatic ionization energy of O 1s in CO_2 may be obtained as 541.085 (17) eV by subtraction of the mean vibrational energy from $E_{vert} = 541.253$ (17) eV.

The CO_2 spectrum with the recommended vertical and adiabatic energies just given, is used as an internal reference for calibration of the O 1s spectra for H_2O, CO, and O_2 to be presented below. The CO_2 lineshape used in the analysis of the subsequent spectra makes use of the vibrational parameters from Hatamoto et al. [11].

3.2. H_2O

Fig. 1 (top) shows the O 1s photoelectron spectrum of H_2O in its gaseous state, measured simultaneously with that of carbon dioxide. The H_2O spectrum appears at lower energies and well separated from the CO_2 peak. In the analysis of the spectrum, we adopted the empirical vibrational model from Sankari et al. [12] for the fine structure in the water spectrum. Sankari et al. obtained the model by fitting to a high-resolution spectrum recorded at a photon energy of 590 eV, *i.e.*, comparable to the energy used in our experiment, and the model implies a mean vibrational energy of 0.099(3) eV.

Using the vibrational models reported by Hatamoto et al. for CO_2 [11] and by Sankari et al. for H_2O [12] in a fit to our experimental spectrum of the H_2O+CO_2 mixture, we are able to extract adiabatic and vertical shifts in ionization energy of water relative to those of carbon
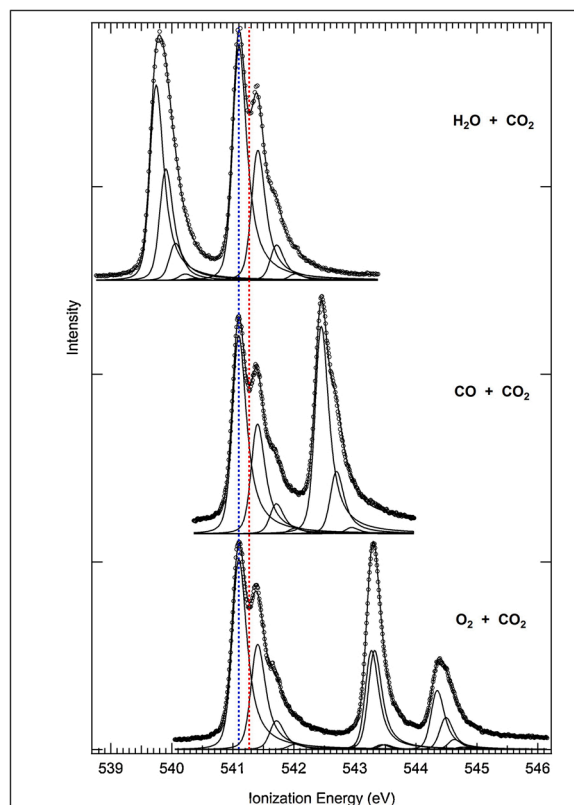

Fig. 1. Oxygen 1s photoelectron spectra of CO_2 along with those of H_2O, CO, and O_2. The circles are experimental data, and solid lines are the results from fitting. The adiabatic and vertical ionization energies of CO_2 are represented by blue and red dotted lines. Vibrational profiles of CO_2, CO, H_2O, and O_2 are obtained from the work of Hatamoto [11], Matsumoto [13], Sankari [12], and Sorensen [14], respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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[1] The correction for recoil-induced internal excitation is equal to $ke * m_e(1/m_a - 1/M)$, where ke is the electron kinetic energy, m_e is the mass of the electron, m_a is the mass of the ionized atom and M is the mass of the molecule in amu. [25] For the molecules considered here the corrections range from 3 to 21 meV.

dioxide, of −1.357(2) and −1.426(4) eV, respectively. Invoking the recommended vertical ionization energy of our preferred calibration gas, CO_2, gives O 1s adiabatic and vertical ionization energies for water, as 539.728(17) and 539.872(17) eV, respectively, *cf.* Tables 1 and 2 .

It is important to note that energy shifts that are calculated from a single spectrum can be determined to meV accuracy. But the accuracy of absolute values of ionization energies depend on absolute calibrations and are naturally much lower. Thus, the uncertainties given in Table 1 are on the order of meV while those in Table 2 are on the order of a few hundredths of an eV.

The adiabatic ionization energy of H_2O was reported by Sankari et al. as 539.79 ± 0.02 eV [12]. Their estimated uncertainty is probably too optimistic since the photon-energy and ionization-energy scales were calibrated using the CO_2 excitation energy from Prince et al. [26] and the O 1s ionization energy in O_2 from Sorensen et al. [14], respectively. Each of these probably carries uncertainties of 0.1 eV or more.

Similar reservations apply to the adiabatic energy obtained by Okada et al. [31], of 539.82 eV. This value is reported without uncertainty, but their photon energy scale was calibrated by using energies of the O 1s-to-Rydberg transitions in CO_2 given by Prince et al. [26], which, according to our discussion for CO_2, carries an uncertainty of 0.1 eV or more. A value of ±0.1 eV is used in Fig. 2.

Two old literature values for vertical ionization energies of H_2O are published as shifts in vertical ionization energies, one relative to the $^4\Sigma$ peak in the O_2 spectrum, by Mills et al. [32], and one relative to CO_2 by Davis et al. [33]. In Table 2, these are corrected for recoil-indiced excitation and turned into absolute energies by adding the reference values for O_2 and CO_2 as recommended here. They both agree well with our results.

3.3. CO

The O 1s photoelectron spectrum of carbon monoxide mixed with carbon dioxide is shown in the middle of Fig. 1. The CO spectrum has been analyzed previously by several groups; Kempgens et al. [34], Kugeler et al. [35], and Matsumoto et al. [13].

An important aspect of the O 1s spectrum of CO is that the vibrational structure displays a significant dependency on the photon energy up to about 80 eV above threshold. In more detail, the intensity ratio I(1)/I(0)

drops from 0.35 to 0.25 between 10 and 50 eV above threshold. [13] Since our way of extracting energy parameters involves fitting vibrational line-shape models to the experimental spectrum, the CO case offers stronger coupling between derived energy positions and the line-shape model adopted, than what is usually the case. On the other hand, the CO spectrum is strongly dominated by the adiabatic peak, and thus, a reasonable but not necessarily accurate vibrational model will still serve to determine the adiabatic ionization energy well.

The vertical ionization energy may be obtained by combining the adiabatic energy with the average vibrational energy determined (computed or measured) at high kinetic energies. The Kempgens vibrational model [34] is obtained by fitting to an experimental spectrum recorded at a photon energy of 581.8 eV and may possibly be used for fitting to our CO spectrum as we use a very similar photon energy. It is, however, not permissible for computing the mean vibrational energy since the photon energy is too low in order to estimate the vertical ionization energy from the adiabatic value.

A more accurate vibrational model is obtained by Kugeler et al. [35], but this investigation seems to be limited to spectra up to about 20 eV above threshold. [13] It was therefore decided to adopt the result obtained by Matsumoto et al. as determined from an average of several spectra between 80 and 160 eV above threshold. [13] The mean vibrational energy calculated from their published Franck-Condon profile is 0.056(2) eV. Implementing this energy in the fitting routine, gives 1.354(3) and 1.242(4) eV for the respective adiabatic and vertical shifts relative to CO_2, cf. Table 1. In turn, this leads to absolute energies of E_{adiab} = 542.439(17) and E_{vert} = 542.495(17), as reproduced in Table 2.

The most accurate adiabatic literature value for O 1s in CO is obtained by Pettersson et al. from high-resolution X-ray emission spectroscopy, to 542.43(1) eV. [36] Note that this value comes with an uncertainty of only half of that of ours, but is nevertheless very close to our value. This gives credibility to the energy obtained here.
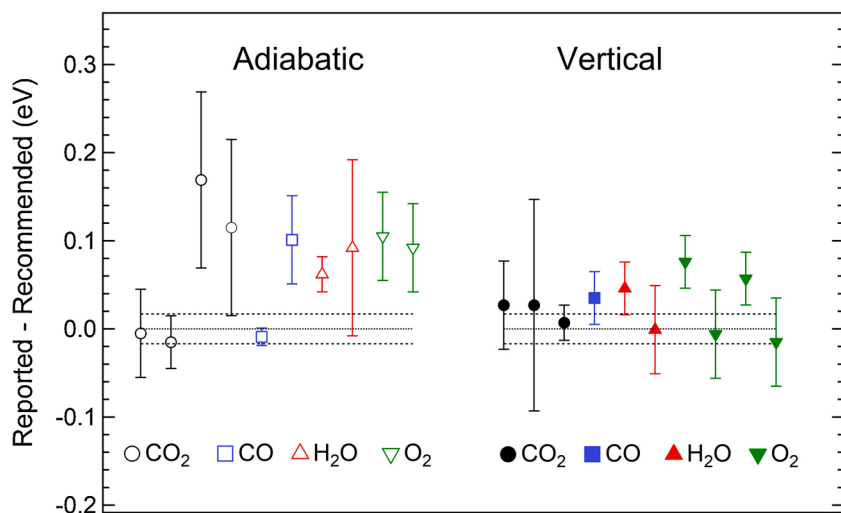
An adiabatic energy for CO was also obtained by Püttner et al. from analysis of Rydberg transitions [37], to 542.543 ± 0.05 eV. The spectra were calibrated from the value of the O $1s^{-1}3\sigma$ Rydberg state for NO as given by Remmers et al. [38], where the photon energy in turn was calibrated using the N $1s^{-1}\pi^*$, $v' = 0$ state of N_2 at $h\nu = 400.88 \pm 0.02$ eV. [39] The authors estimate absolute errors to be ±50 meV at $h\nu \approx 530$ eV, *i.e.*, the same value as reported by Püttner et al. The value 542.54(5) eV is about 0.10 eV higher and thus significantly different from the result obtained in the present work.

Two values for the vertical energy of O 1s in CO have been reported by Smith & Thomas; 542.59 eV and 542.56 eV [40]. The first of these is based on CO_2 calibration, while the second one is based on Ne calibration. The uncertainty of the average value, 542.57 eV was estimated to 0.03 eV. From the present knowledge of recoil-induced internal excitation as well as improved experimental reference values, we are now in the position to evaluate these results.

Focusing first on the energy based on CO_2 calibration, we note that the O 1s shift of CO relative to CO_2 is 1.27 eV. Correcting this for recoil-induced internal excitation gives a shift of 1.28 eV, and combining this shift with the recoil-corrected value for CO_2 from Carroll et al. [23], we obtain E_{vert} = 542.54 eV. For the energy based on Ne 1s calibration, new experimental reference values (−0.023 eV) and correction for CO rotational recoil (−0.014 eV) lowers the value of E_{vert} to 542.52 eV. Averaging the two corrected values from Smith & Thomas gives 542.53 ± 0.03 eV, which is the value we have indicated in Table 2.

3.4. O_2

Fig. 1 (bottom) shows the O 1s photoelectron spectrum recorded for a gas mixture of molecular oxygen ($^3\Sigma_u$) and carbon dioxide, with the two strong peaks that appear at high energy representing the quartet ($^4\Sigma$) and doublet ($^2\Sigma$) states of core-ionized molecular oxygen, respectively.

Table 2
Absolute adiabatic and vertical oxygen 1s ionization energies (eV).

Molecule	E_{adiab}		E_{vert}	
	This work	Literature	This work	Literature
CO_2	541.085 (17)	541.07 (3) [22]	541.253 (17)	541.26 (2)[a] [23]
		541.08 (5) [21]		541.28 (5)[b] [7]
		541.254[c] [26]		541.28 (12) [6]
		541.20[c] [30]		
H_2O	539.728 (17)	539.79 (2) [12]	539.827 (17)	539.87 (3)[d] [32]
		539.82[c] [31]		539.83 (5)[e] [33]
CO	542.439 (17)	542.43 (1) [36]	542.495 (17)	542.53 (3)[b] [40]
		542.54 (5) [37]		
$O_2(^4\Sigma)$	543.285 (17)	543.39 (5) [14]	543.294 (17)	543.37 (3)[f] [41]
				543.29 (5)[g] [33]
$O_2(^2\Sigma)$	544.338 (17)	544.43 (5) [14]	544.423 (17)	544.48 (3)[f] [41]
				544.41 (5)[g] [33]

[a] Corrected for recoil-induced internal excitation, see text.

[b] Corrected for new reference values and for recoil-induced internal excitation, see text.

[c] No uncertainty reported.

[d] Obtained by combining the reported shift relative to O_2 $^4\Sigma$ corrected for recoil-induced excitation, with the absolute value for O_2 $^4\Sigma$ of this work.

[e] Obtained by combining the reported shift relative to CO_2 corrected for recoil-induced excitation, with the absolute value for CO_2 of this work.

[f] Uncertainty obtained from ref. [43].

[g] Obtained by combining the reported shift relative to H_2O corrected for recoil-induced excitation, with the absolute value for H_2O of this work.

Fig. 2. Differences between absolute ionization energies as reported in Table 2 and the values recommended in this paper. Open symbols (left), adiabatic energies from left to right, CO_2 [21,22,26,30]; CO [36,37]; H_2O [12,31]; O_2 ($^4\Sigma$, $^2\Sigma$) [14]; Filled symbols (right) vertical energies – CO_2 [7], [6], [23]; CO [40]; H_2O [32], [33]; O_2 ($^4\Sigma$, $^2\Sigma$) [41], [33]. The zero lines represent recommended energies. Departure from our value is plotted along with a vertical bar that indicates the uncertainty of the corresponding ionization energy, as stated in the original work or, in the absence of such, as estimated and discussed here.

The O_2 spectrum is fit using the *ab initio* Franck-Condon model developed by Sorensen et al. [14]. For the quartet state, this gives a vertical shift of $E_{vert}(O_2) – E_{vert}(CO_2) = 2.041$ (4) eV, while the corresponding number for the doublet state is 3.170 (4) eV, *cf*. Table 1. Focusing on the quartet state, we obtain $E_{vert}(O_2) = 543.294$ (17) eV and $E_{adiab}(O_2) = 543.285$ (17) eV. Thus, the vertical and adiabatic ionization energies are the same within error bars. The corresponding values for the doublet final state may be found in Table 2.

There are three independent measurements of the O 1s ionization energies reported in the literature. The most recent one by Sorensen et al. [14] reports the adiabatic value of the quartet state as 543.39 ± 0.05 eV. The discrepancy to our value is thus a tenth of an eV or about six times the estimated uncertainty of our energy. However, this deviation is consistent with the calibration scheme adopted by Sorenson et al. based on the O 1s $\rightarrow \pi^*$ excitation energy given by Coreno et al. [28]. As noted above, Coreno et al. estimates the uncertainty in their absolute calibration to ±0.1 eV. Thus, the uncertainty given by Sorensen et al. is probably too low.

The two older literature values for the O 1s ionization event that leads to the quartet final state, are given as vertical ionization energies and found to be 543.37 eV and 543.29(5) eV from Larsson et al. [41] and Davis et al. [33], respectively. The first of these deviates from our result by 0.08 eV and is thus significantly higher. The result is given without an error estimate in the original paper, but the spectrum was calibrated against the $^4\Sigma_u^-$ line in the valence region at 24.577(12) eV as adopted from Edqvist et al. [42] and the uncertainty was later estimated to about ±0.03 eV [43]. The second value is obtained from the measured shift relative to H_2O corrected for recoil-induced excitation and combined with the absolute value for H_2O as recommended here. The value is found to be in close agreement with our result.

As expected the literature values for the doublet final state follow closely those for the quartet state, the deviations being 0.09 eV for the adiabatic result [14] and 0.06 eV for the vertical [41], *cf*. Table 2. Again the vertical result obtained from the corrected shift measurement by Davis et al. [33] agrees fully with the present work.

4. Summary

Before comparing our absolute ionization energies with those of others, it is interesting to compare our shifts in vertical O 1s energies to those obtained using conventional XPS about 50 years ago. Davis et al. published a chemical-shift study that includes the compounds studied here. Apart from the data on CO, which were later shown to be flawed [40], they obtained shift values with a stated uncertainty of 0.05 eV relative to H_2O. Drawing also on the chemical shift between CO and CO_2

reported in 1976 by Smith & Thomas [40], we have made a comparison with shifts obtained in this work in Table 3. The shifts have been corrected for recoil-induced internal excitation. The differences between corrected and uncorrected shift and this work are comparable and well below the uncertainties in both cases.

The agreement between our series of synchrotron-based, low-photon-energy measurements and those obtained with Mg or Al $K\alpha$ radiation in the seventies is astounding. It shows that the pioneers in this field were able to determine chemical shift data with significantly higher accuracy than claimed and possibly down to within 0.02 eV.

Now we look at the deviation between our and previously published absolute values of O 1s ionization energies, *cf*. Fig. 2. The dashed lines above and below the horizontal axes show the estimated uncertainties of our values. For each data point from the literature, the departure from our value is plotted along with a vertical bar that indicates the uncertainty of the corresponding ionization energy, as stated in the original works or, in the absence of such, as estimated and discussed here.

It is immediately clear that, with a few exceptions, the present ionization energies are given with unprecedented accuracy. For the adiabatic energies, there are three measurements that agree closely with our values, all of which were measured using X-ray emission spectroscopy. The remaining six adiabatic energies are displaced to higher energy by about 0.1 eV in average. Except for the CO result obtained by Püttner et al. [37], they were all estimated using the O 1s $\rightarrow \pi^*$

Table 3

Comparison of vertical chemical shifts (eV).

Chemical shift	Davis et al. [a]	This work	Difference
$CO_2 – H_2O$	1.43(5)	1.426(4)	0.00(5)
$O_2\,^4\Sigma – H_2O$	3.46(5)	3.467(6)	−0.01(5)
$O_2\,^2\Sigma – H_2O$	4.58(5)	4.596(6)	−0.02(5)
$O_2\,^4\Sigma – CO_2$.	2.03(7)[b]	2.041(4)	−0.01(7)
$O_2\,^2\Sigma – CO_2$	3.15(7)[c]	3.170 (4)	−0.02(7)
$CO – CO_2$	1.26(3)[d]	1.242(4)	0.02(2)
$CO – H_2O$	2.68(6)[e]	2.668(6)	0.01(6)
$O_2\,^4\Sigma – CO$	0.78(8)[f]	0.799(6)	−0.02(8)
$O_2\,^2\Sigma – CO$	1.90(8)[g]	1.928(6)	−0.03(8)

[a] Shifts from ref. [33] except for the CO – CO_2 shift. The shifts have been corrected for recoil-induced internal excitation, see text.
[b] Obtained by subtracting the (CO_2 – H_2O) shift from the ($O_2^4\Sigma$ – H_2O) shift.
[c] Obtained by subtracting the (CO_2 – H_2O) shift from the ($O_2^2\Sigma$ – H_2O) shift.
[d] Average shift obtained from Smith and Thomas.[40]
[e] Obtained by adding the (CO_2 – H_2O) and (CO – CO_2) shifts.
[f] Obtained by subtracting the (CO – H_2O) shift from the ($O_2^4\Sigma$ – H_2O) shift.
[g] Obtained by subtracting the (CO – H_2O) shift from the ($O_2^2\Sigma$ – H_2O) shift.

excitation energy of 530.8 eV for calibration [27,28,44]. As discussed in detail above, the absolute calibration error was estimated by Coreno et al. to ±0.1 eV [28]. With this in mind, we consider our adiabatic energies to be in substantial agreement with, and yet improve upon, all previously published values.

Turning to the vertical ionization energies, our values are in agreement with literature values within the stated uncertainties, except for those of O_2 ($^4\Sigma$, $^2\Sigma$) obtained by Larsson et al. [41]. In general, most existing energies are equal to ours within the uncertainties, meaning that the main result of our effort on the absolute vertical energies is to reduce the uncertainties.

5. Conclusions

Available adiabatic and vertical oxygen 1s ionization energies for gaseous carbon dioxide are critically reviewed and used to establish the most accurate values currently available: 541.085(17) and 541.253(17) eV, respectively. These values include corrections for recoil effects and reflect the recent progress in understanding on this matter.

High-resolution oxygen 1s photoelectron spectra of H_2O, CO, and O_2 have been recorded simultaneously with CO_2, which was used as an internal reference. The spectra were analysed using selected vibrational excitation energies and intensities adopted from the literature. From these measurements highly accurate adiabatic and vertical ionization energy shifts of H_2O, CO, and O_2 relative to CO_2 were obtained.

Combining the absolute energies of CO_2 with the corresponding shift values for H_2O, CO, and O_2 gives the corresponding adiabatic and vertical ionization energies with accuracy hitherto not available. The uncertainty of the ionization energies are all equal to those of CO_2, since uncertainties of energy shifts as well as for the mean vibrational energies are comparably unimportant.

A comparison with results from other experimental studies has been performed and deviations from the present work discussed. For the adiabatic values there are excellent agreement with results obtained from X-ray emission spectroscopy, whereas results derived from Rydberg excitations are found to be systematically too high, possibly due to calibration uncertainties. For vertical energies our values are generally in good agreement with previous results.

Conflict of interest

The authors declare no conflict of interest.

Declaration of Competing Interest

The authors report no declarations of interest.

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