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X-RAY PHOTOELECTRON SPECTROSCOPY OF CARBON MONOXIDE*

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ABSTRACT

The ionization potentials for all of the electrons on carbon monoxide have been measured by x-ray photoelectron spectroscopy. The values found (in eV) are 1σ (oxygen 1s) 542.3, 2σ (carbon 1s) 296.2, 3σ - 38.9, 4σ - 19.8, 1π - 17.2, and 5σ-14.0. The 1σ ionization potential is 1.2 eV less than the 1s ionization potential for molecular oxygen; the 2σ ionization potential is 5.4 eV greater than the 1s ionization potential in methane. These results indicate a positive charge on the carbon of carbon monoxide and a negative charge on the oxygen, in agreement with the relative electronegativities, but opposite to what might be expected from the dipole moment of carbon monoxide. The ionization potentials for the three least bound electrons are in agreement with those found by other techniques, provided

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That allowance is made for the fact that these values represent vertical (rather than adiabatic) ionization potentials. Although the relative intensities of the photoelectrons reflect the atomic photoelectric cross sections and the molecular orbital composition in a qualitative way, there is not quantitative agreement between the measured intensities and theoretical cross sections.

X-Ray Photoelectron Spectroscopy of Carbon Monoxide

I. INTRODUCTION

Photoelectron spectroscopy provides a convenient and accurate method for investigation of the ionization potentials for the electrons on a molecule and of the molecular orbitals from which these electrons are removed. Ultraviolet photoelectron spectroscopy gives rather detailed information on the outermost electrons. X-ray photoelectron spectroscopy gives less precise information on the inner electrons and provides data from which it may be possible to determine the atomic orbital composition of the molecular orbitals.

As has been shown in a variety of experiments,[1-7] the inner electron binding energies reflect the distribution of charge in the molecule. A transfer of valence electrons from one atom to another causes an increase in the inner-shell binding energies of the atom that has lost an electron and an increase for the atom that has gained an electron. The shifts in inner shell binding energies are a measure of the relative electronegativaties of the ligands. This effect has been amply demonstrated experimentally. X-ray photoelectron spectroscopy thus provides a tool for investigating the relative electronegativity of ligands and the redistribution of charge when a molecule is formed from atoms.

It has also been observed that the intensities of the photoelectrons containing molecules ejected from the outer orbitals of carbon by x rays depend strongly on the amount of 2s and 2p character in the orbitals.[8-9] The atomic photoelectric cross section for the 2s orbital in carbon is expected to be many times that for the 2p orbital;[10] the intensities from the molecular orbitals reflect these atomic cross sections. The combination of the measured intensities together with a reliable calculation of the photoelectric cross section should provide a test of molecular orbital calculations.

I report here the results of measurements of the ionization potentials of the electrons of carbon monoxide. In particular, I have investigated the shift of the carbon 1s binding energy(carbon monoxide 2σ) relative to that in methane and the shift of the oxygen 1s binding energy (carbon monoxide 1σ) relative to that of oxygen. For all of these molecules, there are good Hartree-Fock calculations. It is thus possible to make comparison between the experimental shifts and those predicted by the theoretical calculations. Carbon monoxide is also of interest because it has a small dipole moment of sign opposite to what our chemical intuition would lead us to believe and opposite to what the theoretical calculations predict. The information that can be obtained from x ray photoelectron spectroscopy on charge distribution in the molecule may give us a clearer understanding of the sources of this dipole moment.

II. EXPERIMENTAL METHOD

The binding energies of the various electrons in carbon monoxide were determined by irradiation of a gaseous sample with magnesium K_α x rays (1253.6 eV).[11] The kinetic energies of the photoelectrons were measured in an iron-free double-focusing spectrometer of 50-cm radius.[12] The kinetic energy E_k of an electron is related to its binding energy E_b by conservation of energy:

$$E_b = 1253.6 - E_k$$

(This statement is true for gaseous samples. For solids, where the binding energy is measured relative to the Fermi level, it is necessary to correct for the work function of the spectrometer.[13])

To provide an internal calibration, I ran measurements on a mixture of carbon monoxide and neon, scanning alternately and repetitively the peaks due to electrons from the neon 2s, neon 2p, carbon 1s (carbon monoxide 2σ), and oxygen 1s (carbon monoxide 1σ) orbitals. The ionization potentials for neon are accurately known from spectroscopic measurements.[14] By this technique any effects of instrumental drift or gas pressure on line position are approximately the same for all of the lines. In all of these experiments the pressures in the gas cell ranged from 0.01 to 0.05 Torr. Over the range 0.005 to 0.15 Torr we have found that the position of the fluorine 1s line on fluroform does not vary by more than 0.2 eV.[15] Although there may be larger or different pressure dependences for other systems, we have seen no evidence that this is likely to be a serious problem.

To study the outermost electrons (3σ, 4σ, 1π, and 5σ), I scanned alternately and repetitively the regions of the carbon 1s line (to provide a calibration and a check on stability), the 3σ line, and the 4σ, 1π and 5σ lines. I also obtained some additional data on the 4σ line because it appeared weakly in the spectrum of the neon 2p line. To measure the shifts between the binding energy of the carbon 1s (2σ) electrons on carbon monoxide and those on methane, I ran these two compounds as a mixture. The results obtained in this way agreed within 0.1 eV with those that I obtained by a comparison of the absolute carbon 1s binding energy of carbon monoxide (determined as described in the previous paragraph) with the absolute carbon 1s binding energy of methane.[9] I made a comparison of the oxygen 1s (1σ) binding energy in carbon monoxide with that for oxygen by first running oxygen, then carbon monoxide, and then oxygen again. The two lines were too close together for oxygen and carbon monoxide to be run simultaneously. There was a shift of only 0.07 eV between the two oxygen runs; the carbon monoxide-oxygen shift is taken relative to the average of the two.

III. RESULTS AND DISCUSSION

The results of the energy determinations are summarized in Table I. They are discussed in three parts below: the outermost electrons (4σ, 1π, 5σ), the 3σ electrons, and the innermost electrons (carbon 1s and oxygen 1s).

A. 5σ, 1π, 4σ electrons

The spectrum of the outermost electrons of carbon monoxide excited by magnesium K_α radiation is shown in Figure 1. The solid curve represents a least squares fit to the data assuming all the lines are gaussian with the same width. The energies derived from these fits are given in Table I.

The binding energies of these electrons have been well determined by optical spectroscopy and by ultraviolet photoelectron spectroscopy. A comparison of these determinations with mine is given in Table II. The work of Turner and May[16] indicates that for the 5σ and 4σ electrons the vertical and adiabatic ionization potentials are nearly the same. The agreement between the energies I have determined and those determined by others is quite satisfactory. For the 1π orbital, the most probable transition energy is, according to Turner and May, 16.91 eV and the average transition energy somewhat higher. We would thus expect the binding energy determined by x ray photoelectron spectroscopy, which should be close to the vertical value, to be about 17 eV, in good agreement with the experimental value, 17.2 eV.

Of more interest than the energies, which are better studied by higher resolution techniques, are the intensities. Al-Joboury and Turner[17] have suggested that the intensities of the peaks should be proportional to the population of the orbital, provided that the photon energy is much greater than the binding energy. This is clearly not the case here, for, instead of the expected ratios for $5\sigma/1\pi/4\sigma$ of 1/2/1, we see ratios of 1/0.3/0.3. These data are, however, qualitatively consistent with the theory of the photoelectric effect and with the composition of the molecular orbitals. For excitation with magnesium K_α radiation the cross section for ejection of 2s electrons from carbon or oxygen atoms is expected to be substantially greater than the cross section for ejection of 2p electrons from the same atoms.[10] The cross section for ejection of 2s electrons from oxygen atoms should be greater than that for ejection of 2s electrons from carbon. We expect that these cross sections will be reflected in the intensities from the molecule. The 1π orbitals are composed entirely of oxygen 2p and carbon 2p atomic orbitals (mostly the former).[18] Because of the relatively low photoelectric cross section for the p electrons of these atoms, we expect and find that the intensity due to electrons in a 1π orbital is the lowest of all. The relative intensity of the other two peaks is more or less consistent with this picture. The 4σ orbital is composed of about 21% oxygen 2s, 60% oxygen $2p_z$, and 16% of carbon 2s atomic orbitals.[18] The 5σ is about 59% carbon 2s, and the rest carbon and oxygen p_z. If we say that the p atomic orbitals contribute essentially nothing and that the oxygen 2s contributes about 3 times as much as does the carbon 2s (see section on relative intensities below), then we conclude that the intensity of the 4σ peak should be about 1.3 times the intensity of the 5σ peak. The experimental ratio is slightly more than 3.

We see from the above that the intensities, rather than depending only on the population of the orbitals, reflect to some extent the atomic orbital composition of the molecular orbitals. Perhaps data such as these together with better estimates of the photoelectric cross sections and a more sophisticated analysis can be used to check the population analyses that result from molecular orbital calculations. This possibility is discussed in more detail below.

B. 3σ electrons

The experimental value of the 3σ electron binding energy in carbon monoxide is 38.9 eV; the theoretical value calculated by Huo[19] using Koopmans' theorem[20] is 41.9 eV. The agreement is about as good as can be expected for a theoretical value based on Koopmans' theorem.

The line-width for the 3σ electron is exceptionally broad. Whereas the line-width for the outermost electrons (1.5 eV full width at half maximum) is essentially the instrumental resolution at this energy, the line-width for the 3σ is about 3 eV, full width at half maximum. This extra width probably indicates that the ion is being left in a large variety of vibrational states. Support for this idea comes from calculations by Sahni,[21] who concludes that the equilibrium separation for the C $^2\Sigma^+$ level of CO^+ (the 3σ hole) is about 0.2 Å greater than that for carbon monoxide in the ground state. The vertical transition from the ground state should therefore lead to a variety of vibrationally excited states. The adiabatic ionization potential for the 3σ electron is, therefore, probably somewhat less than 38.9 eV. The width of about 3 eV implies that a substantial number of vibrational states are populated; for the A $^2\pi$ state (1π hole) the vibrational states are spaced at less than 0.2 eV. With ultraviolet as the exciting radiation only about 6 vibrational levels of the A $^2\pi$ are strongly populated for a spread in energy of about 1 eV.[16] The 3 eV width found for the C $^2\Sigma^+$ state is thus remarkably large.

C. 1σ and 2σ electrons

The carbon 1s binding energy in carbon monoxide is 5.4 eV greater than that in methane. This shift is in the expected direction, coinciding with chemical evidence that oxygen is more electronegative than hydrogen and with theoretical evidence, which indicates a charge of between -0.1e -0.5e on the carbon in methane[22, 23] and about +0.3e on the carbon in carbon monoxide.[18] The comparison with methane, however, does not allow us to assign a charge to the carbon on carbon monoxide with any confidence. Ideally we should make the comparison with either atomic carbon or C_2. Unfortunately the current state of the art is such that we cannot yet make these measurements.

It is useful to compare the binding energies in carbon monoxide with those in other compounds. The carbon 1s binding energy in carbon monoxide (5.4 eV relative to methane) is practically identical to that in carbon tetrachloride (5.5 eV) and to that expected for difluoromethane (5.6 eV).[24]

To the extent that there is a one-to-one correspondence between the charge on the carbon and the binding-energy shift, these comparisons suggest that the charge on carbon in carbon monoxide is the same as that on the carbon in carbon tetrachloride and in difluoromethane. Gordy[25] has concluded from quadrupole resonance studies that the carbon in carbon tetrachloride has a charge of +0.5e. Schwartz, Coulson, and Allen[26] have concluded from an empirical adjustment of the results of Hartree-Fock calculations that the carbon in difluoromethane has a charge of +0.22e. These comparisons indicate that the carbon in carbon monoxide has a positive charge of between 0.2 and 0.5e.

The oxygen 1s binding energy in carbon monoxide is less than that in molecular oxygen by 1.2 eV, but greater than that in water by 2.9 eV[15] and greater than that in a variety of compounds of oxygen with tetravalent carbon by 1.5 to 4 eV.[15] This result would indicate that the oxygen in carbon monoxide is negatively charged with respect to oxygen in molecular oxygen, but not so negatively charged as oxygen in some other compounds.

As was pointed out, the foregoing analysis assumes that there is a one-to-one correspondence between the 1s binding energies and the charge on the atom from which the 1s electron is removed. This assumption ignores the facts that different molecules have different geometries and that the ion formed has a different charge distribution from that of the neutral molecule. In spite of these problems, it has been shown[1-6] that for a wide variety of nitrogen, sulfur, and chlorine compounds there is a good correlation between the inner electron binding energies and charges calculated by a variety of methods.[27] It seems, therefore, reasonable to conclude from these comparisons that the carbon of carbon monoxide has a slightly positive charge (0.2 to 0.5e) and that the oxygen has a corresponding negative charge. This result is in accord with the population analyses made by

Neumann and Moskowitz.[18] If this is the case, we are left with the problem of explaining the fact that the dipole moment of carbon monoxide has a sign indicating a charge distribution in the opposite direction.[28] If we assume that the dipole moment is due to the charges on the carbon and oxygen atoms and to pairs of electrons localized in the non-bonding orbitals we can show that the dipole should be given as

$$\mu = 0.112 = -1.128\,q + 2(r_C - r_O)\ \text{Debye},$$

where 0.112D is the experimental dipole moment,[29] 1.128 Å is the carbon-oxygen distance in carbon monoxide,[30] qe is the charge on carbon (+) and on oxygen (-), r_C is the distance from the carbon nucleus to the center of charge in the lone pair and r_O is the corresponding distance for oxygen. (This expression does not depend on whether there are 1, 2, or 3 lone pairs on the atoms provided that the angle between lone pairs is 120° for 2, or 109°28' for 3.) If we take q to be between 0.2 and 0.5 then r_C is greater than r_O by 0.17 to 0.34 Å.

D. Comparison between theoretical and experimental binding energies

There are good Hartree-Fock calculations available for carbon monoxide,[19,31] methane,[31,32] and oxygen.[31,33] It is of interest to see to what extent the experimental values of the ionization potentials agree with one-electron energies given by the Hartree-Fock calculations. According to Koopmans' theorem,[20] these energies should be approximately the same. Recently Richards[34] has reviewed the assumptions of Koopmans' theorem, and has shown (with particular reference to the outer electrons on carbon monoxide) that the one-electron energies should not in general and do not agree with the experimental values.

For closed shell molecules Koopmans' theorem fails to give the correct ionization potentials because of neglect of reorganization energy, neglect of differences in the correlation energy between the molecule and ion, and neglect of differences in the relativistic corrections between the molecule and ion. For open shell molecules (such as oxygen) Koopmans' theorem is not applicable. For the molecules considered here the largest source of error is the reorganization energy. This error arises because Koopmans' theorem assumes that the orbitals of the ion are the same as those of the molecule. The true ionization potential is the difference between the total energy of the molecule and that of the ion. The fictitious ion that results if the orbitals of the ion are the same as those of the molecule is at higher energy than the ground state; the ionization potential calculated using this assumption will therefore be too large. Experiments[9] and calculations[35,36] indicate that this error is about 15 eV for the 1s electrons of carbon(compared to a total ionization potential of about 300 eV).

Although the absolute binding energies will be in error for the above reasons, we may expect some of these errors to cancel out in comparisons between two different molecules. For instance, the relativistic corrections to the Koopmans' theorem binding energies are small for the molecules considered here and are probably the same for methane as for carbon monoxide (carbon 1s) and the same for molecular oxygen as for carbon monoxide (oxygen 1s). If there are errors between the shifts predicted by Koopmans' theroem and those found experimentally, they are probably due to changes either in the reorganization energy correction or in the correlation energy correction. According to Richards (and as noted above), failure to include the reorganization energy makes the one-electron energies greater than the experimental ionization potentials. On the other hand, the failure to include the correlation energy correction leads to one-electron energies that are smaller than the true ionization potentials; the correlation energy of the ion is smaller than that of the molecule. The decrease in correlation energy between the molecule and an ion with a 1s hole is due primarily to the disappearance of the $1s^2$ correlation energy (about 1.2 eV) plus the disappearance of half of the 1s 2s correlation (half of 0.4 eV).[37] All of the electrons will be drawn in somewhat closer to the nucleus because of the increased positive charge. This contraction presumably leads to a slightly increased correlation energy for the ion. The dominant terms, however, are the negative ones, and the net decrease in correlation energy is probably 1 to 2 eV. The major portion of this is the $1s^2$ correlation energy. Since the 1s wave function will be only slightly affected by changes in the distribution of outer electrons, we can expect this energy to be more or less independent of what molecule the atom is in. Thus, in comparing one-electron energies for 1s orbitals on different molecules we should be able to ignore the correlation energy correction.

From the foregoing, we conclude that the major correction to the one-electron energy must be the reorganization energy. The effect of this correction is that the one-electron energies are larger than the experimental ionization potentials. Whether the difference in one-electron energies between two compounds agrees with the difference in the experimental magnitudes depends on the relative reorganization energies of the two compounds. Davis, Hollander, Shirley, and Thomas[15] have found for a variety of compounds containing carbon, nitrogen, and/or oxygen that the experimental shift in the 1s binding energies (relative to that methane, ammonia, or water, as appropriate) is about 1 eV less than is calculated using Koopmans' theorem. Thus the reorganization energy correction is somewhat larger in the more complex molecules than in the hydrides.

We will, therefore, expect the experimental shift of 1s binding energies between carbon monoxide and methane to be less than that calculated from one-electron energies. This is not the case. The experimental shift is 5.4 eV. The shift calculated from the one-electron energies of Huo (carbon monoxide)[19] and Ritchie and King (methane)[32] is 3.4 eV; that calculated by Basch and Snyder[31] is 5.5 eV. For neither set of calculations is the result significantly greater than the experimental value. For the Huo-Ritchie and King result, which is presumably the more reliable one[38] the calculated value is significantly less than the experimental one, opposite to our expectations.

Comparison of the shift in oxygen 1s binding energies between carbon monoxide and molecular oxygen with that calculated from the one-electron energies is of questionable value. Richards has pointed out that Koopmans' theorem does not hold for open shell molecules, such as molecular oxygen. The experimental shift of the 1s binding energies in carbon monoxide and oxygen[39] is 1.2 eV. According to the calculations of Basch and Snyder, the shift should be 1.0 eV; according to those of Huo[19] and Cade and Malli[33] it should be 1.86 eV. It is perhaps more useful to compare carbon monoxide with water, for which Koopmans' theorem should apply. Experimentally, the oxygen 1s binding energy in carbon monoxide is 2.9 ± 0.1 eV greater than that in water.[15] The calculations of Basch and Snyder[31] give 3.3 eV and those of Huo[19] and Ritchie and King[32] give 2.7 eV. Here, as for the carbon 1s energies, the prediction of Basch and Snyder is somewhat greater than the experimental value and the Huo-Ritchie and King value is somewhat less. The discrepancy is, however, very slight.

The carbon monoxide results thus appear to be an exception to the general trend observed by Davis et al.[15] that the experimental shifts in ionization potential relative to that of the hydride are less than those calculated using Koopmans' theorem. For carbon monoxide either the agreement between calculation and experiment is fairly good or the disagreement is in the direction opposite to that expected.

E. Relative intensities

In the discussion of the outermost electrons we saw how the intensity data can be correlated with the molecular orbital population analyses and the atomic photoelectric cross sections. In principle it is possible to do a more thorough comparison of these quantities, although all of the data necessary are probably not yet available.

The cross section for the photoelectric effect will be proportional to, among other things, $|M|^2$, where M is the matrix element connecting the initial molecular orbital via the perturbation of the photon to a final state consisting of an ion and a free electron. Writing the n th molecular orbital ψ_n as a linear combination of atomic orbitals χ_j we have that

$$\begin{aligned} M_n &= \left\langle \psi_{final} \left| H \right| \psi_n \right\rangle \\ &= \sum_j C_{nj} \left\langle \psi_{final} \left| H \right| \chi_j \right\rangle \phi_j \\ &= \sum_j C_{nj} \quad H_j \; \phi_j \end{aligned}$$

where the C_{nj}'s are the expansion coefficients and the H_j's are the matrix elements for the atomic photoelectric effect. The ϕ's are phase factors to take into account the fact that the phase of the incident radiation will be different at different atoms. If the photon can be represented as a plane wave, then $\phi_j = \exp(i\,k_z Z_j)$, where k_z is the Z component of the photon momentum and Z_j is the distance (along the Z direction) of the atom from the origin of the sytem. The photoelectric cross section is proportional to the square of the matrix element.

$$\left|M_n\right|^2 = \sum_j \sum_\ell C^*_{nj} \, C_{n\ell} \, H^*_j \, H_\ell \, \phi^*_j \, \phi_\ell$$

For orbitals on the same atom, the product $\phi^*_j \, \phi_\ell$ is 1. For orbitals on different atoms if the wave length of the incident radiation is long compared to the molecular dimensions, the real part of $\phi^*_j \, \phi_\ell$ will be close to unity and the imaginary part very small. Since this condition is satisfied for the radiations considered here, we will assume that this product is 1. The C's are known for carbon monoxide and many other molecules from molecular orbital calculations. The atomic matrix elements should, in principle, be easily calculated.

It is of interest then to examine the relative intensities of the various peaks in the carbon monoxide spectrum and to compare them with theoretical predictions. The experimental relative intensities are given in Table III. The 1σ and 2σ orbitals are essentially pure oxygen 1s and carbon 1s and we may expect that the relative intensities for these orbitals will be given by the atomic cross sections. For the outer electrons this will not be the case and it will be necessary to use the above formula. However, rather than use this formula, which involves two theoretical quantities, C_{nj} and H_j, I believe that it is useful to compare the total intensity for the outer orbitals with the intensities for the carbon and oxygen 1s orbitals.

As we shall see below, this total intensity is approximately proportional to the sum of the atomic cross sections for the carbon and oxygen 2s and 2p electrons. We thus have an opportunity to compare the measured and theoretical intensities without the additional uncertainties introduced by molecular orbital calculations.

The molecular orbitals for the 3σ, 4σ, 1π, 5σ orbitals are, to a good approximation, linear combinations of the carbon and oxygen 2s and 2p orbitals. The intensity of photoelectrons from these orbitals is given by the formula above. The sum of the intensities for these four orbitals is given as

$$\sum_n |M_n|^2 = \sum_j \sum_\ell H^*_j H_\ell \sum_n C^*_{nj} C_{n\ell}$$

If the matrix C is unitary, then it is easy to show that the sum over n is equal to $\delta_{j\ell}$ and

$$\sum |M_n|^2 = \sum_j |H_j|^2$$

That is, the sum over the molecular intensity equals the sum over the intensity for the isolated atoms. The condition that the matrix C be unitary is that the overlap integrals $S_{j\ell} = \langle \chi_j | \chi_\ell \rangle$ be equal to $\delta_{j\ell}$. This is met for the orbitals centered on the same atom. For the orbitals centered on different atoms, let us assume that the S's are small enough to be neglected. Then the above equation is approximately correct.

Theoretical relative intensities calculated using the Stobbe formula (nonrelativistic)[10] are compared in Table IV with the experimental values. We see from this comparison that the theoretical calculations predict a much wider range of intensities than is found experimentally. The theoretical ratio for oxygen 1s to carbon 1s is 3.4 compared to an experimental value of 2.2. (We have found the same experimental value for the ratio of oxygen 1s intensity per atom of oxygen to carbon 1s intensity per atom of carbon in nitropropane.[40]) The ratio of the total outer orbital intensity to the carbon 1s intensity is predicted to be about 1/6 the observed value. The intensity for 2p electrons is predicted to be vanishingly small whereas the experimental intensity for the π electrons is comparable to the experimental intensities for the σ electrons.

This is not the appropriate place to explore in detail these discrepancies. Either the model used to calculate the cross sections is inadequate, or the measured intensities do not reflect the photoelectric cross sections. There are a number of reasons why either or both of these statements are true. At least one of these is that there is a non-linear pressure-dependence of the intensity. If this dependence varies with the electron energy there will be a pressure-dependence of the intensity ratio. Until we are more confident on these points, it will not be fruitful to use this method to explore the atomic composition of the molecular orbitals.

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Table I

Electron binding energies in carbon monoxide and oxygen determined by x ray photoelectron spectroscopy

	Orbital	Binding energy(eV)
Carbon monoxide	5σ	14.0
	1π	17.2
	4σ	19.8
	3σ	38.9
(carbon 1s)	2σ	296.2*
(oxygen 1s)	1σ	542.3
Oxygen	1s	543.5†

* 5.4 MeV greater than that of methane

† This is a weighted average of the $^4\Sigma$ and $^2\Sigma$ states. The splitting between these is 1.13 eV, with the $^4\Sigma$ state having the lower energy.

Table II

Comparison of outer electrons binding energies of carbon monoxide as determined by various techniques
(eV)

Orbital	Spectroscopic	Photoelectron spectroscopy		
		UV[c]	UV[d]	x ray[e]
5σ	14.009[a]	14.00	14.01	14.0
1π	16.539[b]	16.54	16.55	17.22
4σ	19.667[b]	19.65	19.69	19.8

a. G. Herzberg, Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules. (D. Van Nostrand Co., Inc., New York 1950).

b. Donnees Spectroscopiques Concernant les Molecules Diatomique, B. Rosen, ed. (Hermann & Cie, Paris 1951) 70.

c. Reference 16

d. J. E. Collin and P. Natalis, Int. J. Mass Spectry. and Ion Physics 2, 231 (1969).

e. This work

Table III

Experimental relative intensities for electrons ejected from carbon monoxide orbitals with magnesium K_α radiation

Orbital	Intensity relative to carbon 1s
1σ (oxygen 1s)	2.21 ± 0.15
2σ (carbon 1s)	1
3σ	0.077± .007
4σ	0.070± .005
1π	0.021± .003
5σ	0.021± .003

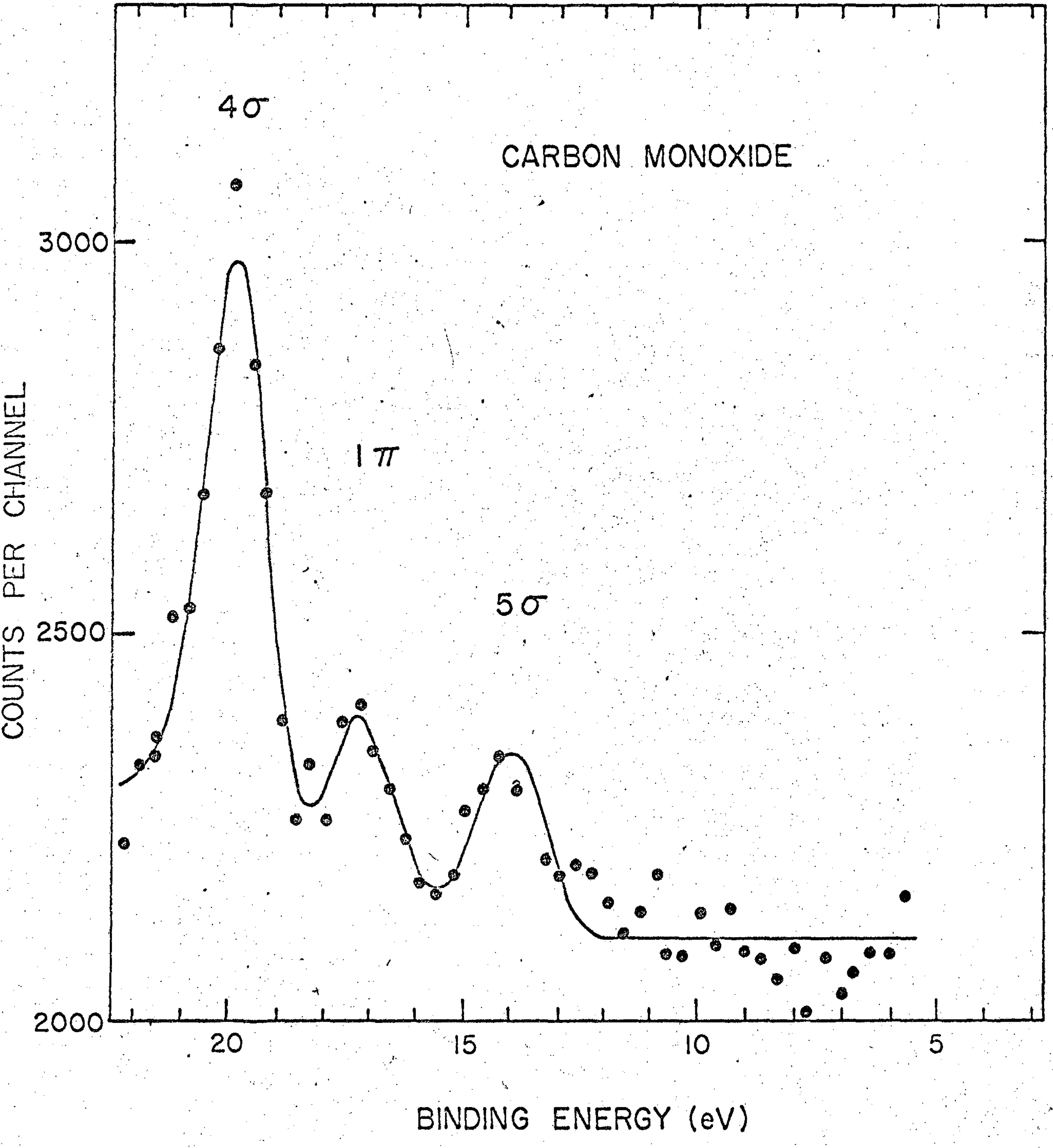
Table IV

Comparison of experimental and theoretical intensities for electrons ejected from carbon monoxide orbitals with magnesium K_{α} radiation

Orbital	Relative intensity Theoretical (atomic)	Experimental (molecular)
O 1s (1σ)	3.39	2.21
C 1s (2σ)	1.	1.
O 2s	.0217	
C 2s	.00749	
O 2p	.00018	
C 2p	.00003	
Sum of n =2	.0294	.189

FIGURE CAPTION

Fig. 1. Spectrum of outer electrons of carbon monoxide. The solid line represents a least squares fit to the data. Exciting radiation is magnesium K_α x rays.


4σ
CARBON MONOXIDE
1π
5σ
COUNTS PER CHANNEL
3000
2500
2000
20
15
10
5
BINDING ENERGY (eV)

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