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July 1969

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X-RAY PHOTOELECTRON SPECTROSCOPY OF SIMPLE HYDROCARBONS[*]

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ABSTRACT

Carbon 1s ionization potentials for methane (290.8 eV), ethane (290.6), ethylene (290.7), acetylene (291.2), cyclohexane (290.3), benzene (290.4), 2,2-dimethylpropane (290.4), and fluoroform (299.1), together with the fluorine 1s ionization potential for fluoroform (694.1) and ionization potentials for the $2a_g$ and $2a_u$ orbitals of ethylene (24.5 ± 1 and 19.5 ± 1) and for the $2\sigma_g$ and $2\sigma_u$ orbitals of acetylene (23.5 and 18.5) have been measured. These values, together with those from other measurements, are compared with orbital energies obtained by use of Koopmans' theorem. The comparison indicates that this method of calculation gives orbital energies that are about five percent larger than the experimental ionization potentials for carbon 1s electrons and 10-15 percent greater for the outer electrons. These differences are consistent with calculations of the

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ionization potentials of carbon atoms. The carbon 1s binding energy decreases

with hydrogenation and when a hydrogen is replaced by an alkyl group. The

first of these results is consistent with theoretical calculations and with

other chemical evidence. There is an apparent discrepancy between the second

result and the result of theory or other chemical evidence. A possible source

of this discrepancy is discussed.

I. INTRODUCTION

The ionization potentials of simple hydrocarbons have been the subject of numerous experimental measurements and theoretical calculations. Of particular interest are such series of compounds as ethane, ethylene, and acetylene and methane, ethane, and cyclohexane. In the first case we can see the combined effect on ionization potentials of hydrogenation and changing the type of bonding between the carbons; in the second, the effect of substituting carbons for hydrogens about a given carbon.

Experimental measurements of the ionization potentials have, for the most part, provided reliable information only on the least bound electrons. For these, there are a variety of satisfactory techniques and there is good agreement among the various techniques on the first ionization potential of many substances. For the other loosely bound electrons only photoelectron spectroscopy has given unambiguous results.

Photoelectron spectroscopy with ultraviolet (UV) radiation is capable of giving very precise and detailed information on the outermost electrons.[1] It is, at present, limited to electrons with binding energies of less than 21 eV. Less precise information can be obtained by x-ray photoelectron spectroscopy on both these and more tightly bound electrons.[2] Data from the two types of photoelectron spectroscopy can be combined to give a complete picture of the ionization potentials of a particular molecule.

X-ray photoelectron spectroscopy can give not only the values of the ionization potentials, but also information on the makeup of molecular orbitals. For 1 keV radiation incident on carbon, for instance, the cross section for exciting a 2s electron is considerably larger than that for exciting a

2p electron.[3] Thus, relative intensities can be used to determine whether a

particular photoelectron peak corresponds to a vacancy in a predominantly s

or a predominantly p level. For instance Hamrin, Johansson, Gelius, Fahlman,

Nordling, and Siegbahn[4] have shown for methane that the probability of exciting

electrons from the $2a_1$ orbital (mostly carbon 2s) is three or four times higher

than the probability of exciting one from the $1t_2$ orbital (mostly carbon 2p)

even though there are three times as many electrons in the $1t_2$ orbital as in

the $2a_1$ orbital. They have seen a similar effect in ethane, where the proba-

bility of ionization of the $2a_{1g}$ and $2a_{2u}$ levels (mostly carbon 2s) is con-

siderably greater than that for ionization of the levels that are mostly carbon

2p. This effect is demonstrated in Fig. 1, which shows the spectrum of loosely

bound electrons on acetylene excited with magnesium K x rays. The binding

energies indicated by the two arrows ($3\sigma g$ and $1\Pi_u$) were measured by UV photo-

electron spectroscopy. We see that there is no detectable excitation of

electrons from the two outermost levels, whose wave functions are composed

almost entirely of carbon 2p and hydrogen 1s wave functions.

X-ray photoelectron spectroscopy also provides a technique for pre-

cise measurement of the binding energies of the most tightly bound electrons.

These electrons do not participate in the chemical bond to any great extent;

their binding energies are, however, affected by the removal or addition of

outer electrons. There is an increase of about 15 eV in the binding energy

of an inner electron when an outer electron is removed to infinity.[5] Actual

shifts from one compound to another are rather smaller than this because in

forming chemical bonds the valence electrons are removed not to infinity but

rather to the adjacent atoms in the molecule or, in some cases, only as far

as a larger radius centered on the original atom. The change in energy of
an inner electron will then be (approximately) $-15 + e^2/r$ eV, where r is
the average distance to which the electron has been removed. For r about
1 Å, the second term is about 14 eV and the shift is, therefore, much smaller
than 15 eV. If the amount of charge withdrawn from the atom is greater or
less than one electronic charge, the shift in binding energy of an inner elec-
tron will be proportionally larger or smaller. Similarly, if electrons are
donated to the atom of interest by the surroundings, the binding energy of the
inner electrons will be decreased in magnitude. These binding energy shifts
provide information that can be related to electronegativity or to charges on
the various atoms in a molecule or solid.

I present here the results of measurements of the ionization potentials
of various hydrocarbons by x-ray photoelectron spectroscopy. The compounds studied
are methane, ethane, ethylene, acetylene, 2,2-dimethylpropane, benzene, and cyclohexane.
Because the least bound electrons can be studied most effectively by UV photo-
electron spectroscopy, I have concentrated my efforts on those electrons for
which x-ray photoelectron spectroscopy is particularly useful: those with
binding energies greater than 21 eV and those outer orbitals that have appre-
ciable s character. I have combined my measurements with those of others to
give a fairly complete picture of the ionization potentials for methane,
ethane, ethylene, and acetylene. These results are compared with various theo-
retical calculations. I have given particular attention to an accurate meas-
urement of the rather small differences among the carbon 1s binding energies
of the substances studied. As part of the calibration and standardization
procedure, I have obtained the binding energies for the 1s electron in neon
and for the carbon 1s and fluorine 1s electrons in fluoroform.

II. EXPERIMENTAL METHOD

In photoelectron spectroscopy, the binding energy of an electron is determined by measuring the kinetic energy of electrons ejected by monoenergetic photons incident on the sample of interest. By conservation of energy the binding energy E_b, or ionization potential, is given as

$$E_b = h\nu - E_k$$

where E_k is the kinetic energy of the ejected electron. This expression 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.[6]

For these experiments the exciting radiation was magnesium K_α x rays (1253.6 eV).[7] The electron energies were measured in an iron-free double-focusing spectrometer of 50-cm radius.[8] The substances studied were introduced into the spectrometer in the gas phase. All were obtained from commercial sources, and were used as supplied without further purification. With the possible exception of acetylene (which is supplied dissolved in acetone) I saw no evidence for impurities in any of the materials studied.

The calibration of the spectrometer was based on the known binding energies of the neon 2s and 2p electrons, 48.5 and 21.6 eV,[9] respectively. During the calibration procedure I measured the binding energy of the 1s electron in neon. In order to compensate for any instrumental drifts during the measurements, I alternately scanned the three lines observed in neon (or in some cases only the 1s and 2s lines). The average of three measurements is 869.7±0.1 eV, where the error is the standard deviation of the three. This is

compared with other determinations of this quantity by a variety of methods

in Table I. Except for the value reported by Hartmann and Chun,[10] which has

a rather large error, the values of Table I, including mine, are within 0.6 eV

of one another.

For measurement of the rather small shifts among the 1s binding energies

of the various hydrocarbons, I used a mixture of two gases, one the sample of

interest, the other fluoroform. Any effects of drift or gas pressure on the

line position are the same for both lines. (The pressure in the gas cell was

between 0.01 and 0.05 Torr. Over the range 0.005 to 0.15 Torr we have found

that the position of the fluorine 1s line from fluoroform does not vary by more

than 0.2 eV.[11] Presumably any differential pressure dependence of two compounds

run together will be substantially less than this.) The carbon 1s line in

fluoroform is well removed from the same line in hydrocarbons and is, therefore,

a convenient standard. The difference between the position of this line and

that of the sample was reproducible to better than 0.2 eV. Figure 2 shows sev-

eral spectra obtained in this way. In order to provide an absolute energy I

made measurements on a mixture of neon and fluoroform taking a series of alter-

nate scans of the neon 1s, 2s, carbon 1s, and fluorine 1s lines. For carbon in

fluoroform the 1s binding energy was found to be 299.1±0.1 eV and for fluorine

in fluoroform 694±0.1 eV. The errors quoted reflect the reproducibility of the

results and do not take into account the possibility of some systematic error.

The agreement of the neon 1s binding energy with that obtained by others sug-

gests that such systematic errors are no more than 0.6 eV at neon and probably

less for carbon 1s electrons which are closer in energy to the calibration

energies. The systematic error should be quite small for the valence electrons.

III. RESULTS

A. Methane

The carbon 1s (or, more correctly, the $1a_1$) binding energy for methane was found to be 8.3±0.1 eV less than that of fluoroform, or 290.8 eV. This is in good agreement with a value of 291 extracted from the first graph given by Hamrin et al.,[4] but disagrees with the value of 288.8±0.2 reported by Chun.[12] (The 2 eV discrepancy here is about the same as the discrepancy between Hartmann and Chun's value for neon 1s and that found by others. See Table I.) The ionization potential of the least bound electron $(1t_2)$ has been measured by a variety of methods and found to be 12.99 eV.[13] Hamrin et al.[4] have reported 13.5 eV. The difference between this value and that measured by others may be the difference between the adiabatic and vertical values. The $2a_1$ level was found by Hamrin et al.[4] to be at 23.1 eV, beyond the range of excitation by the 584 Å line of helium.

The experimental ionization potentials are compared in Fig. 3 with the values calculated theoretically by Palke and Lipscomb[14] and by Arrighini, Guidotti, Maestro, Moccia, and Salveti,[15] and with the semiempirical values of Dewar and Worley.[16] The experimental values are generally smaller than the calculated ones by five to ten percent.

B. Ethane

In ethane the carbon 1s (or $1a_{2a} + 1a_{1g}$) level is found to be 8.5 eV less bound than the corresponding level in fluoroform, giving a binding energy of 290.6 eV in good agreement with a value of 290.5 extracted from the second graph given by Hamrin et al.[4] I have measured values of 24.2 and 20.6 eV for

the $2a_{1g}$ and $2a_{2u}$ levels, within 0.3 eV of those given by Hamrin et al. The

value for the $2a_{2u}$ level is to be compared with a value of 20.13 reported by

Al-Joboury and Turner to be the adiabatic value.[13] Three other levels ($1e_u$,

$3a_{1g}$, and $1e_g$) are expected for ethane; only two have been found, one at

11.49 eV and one at 14.74 eV.[13] Theoretical calculations indicate a spacing

between the $3a_{1g}$ and $1e_g$ levels (the least bound levels) of no more than about

0.5 eV.[14,16-18] It is likely that these levels have not been resolved experi-

mentally.

The experimental results for all but the 1s electrons are compared in

Fig. 4 with the results of various theoretical calculations.[14,16-18] As in

the case of methane the experimental values are smaller in magnitude than are

the theoretical ones. As for methane, the semiempirical results of Dewar and

Worley[16] are in good agreement with the experimental values for the least bound

electrons; the agreement becomes progressively worse as we go to the deeper

levels.

C. Ethylene

Ethylene reacted rapidly with the tungsten filament of the x-ray tube

making it impossible to make measurements over a long time. As a result it

was possible to measure accurately only the binding energy of the innermost

electrons. The carbon 1s binding energy in ethylene is shifted 8.4 eV from

that in fluoroform; the corresponding binding energy is 290.7 eV. The only

observable outer electrons had binding energies of 24.5±1 and 19.5±1 eV.

These presumably correspond to the $2a_g$ and $2a_u$ orbitals, which are primarily

composed of the carbon 2s orbitals. As noted above, the cross section for

excitation of the 2s electrons is considerably higher than that for excitation

of 2p electrons. Al-Joboury and Turner[1] have reported levels in ethylene at

10.48, 12.50, 14.39, 15.63, and possibly at 19.13 eV. The tentative level at

19.13 eV is presumably the same as the one I have seen at about 19.5 eV. Dewar

and Worley[16] agree with Al-Joboury and Turner for the three least bound levels,

but place the fourth at an uncertain value of 18.03 eV.

Figure 5 shows a comparison of the experimental ionization potentials

for the outermost electrons with theoretical values. The theoretical results

tend to be in good agreement with one another, but in rather mediocre agreement

with the experimental values. The calculations of Dewar and Worley[16] give

results that are in good agreement with experiment for three of the six values.

The theoretical values are, except for the least bound level, greater in magni-

tude than the experimental values.

D. Acetylene

Acetylene reacted with the filament of the x-ray tube, though not so

rapidly as did ethylene. It was possible to obtain reasonably satisfactory

data on some of the outer electrons for acetylene, which are shown in Fig. 1.

The carbon 1s line is shifted 7.9 eV from the same line in fluoroform; the

binding energy is, therefore, 291.2 eV. The only observable outer electrons

were at 23.5 and 18.5 eV. These are most likely the $2\sigma_g$ and $2\sigma_u$ levels,

which are predominantly carbon 2s levels. UV photoelectron spectroscopy[1,20]

gives levels at 11.41, 16.44, 18.42 (Ref. 20), or 18.56 (Ref. 1) eV, and an

undertain level at 20.51 eV. The one at about 18.5 corresponds to the level

at the same energy that I have assigned to $2\sigma_u$: the uncertain level at 20.5

does not agree with my result for $2\sigma_g$.

A comparison of experimental and theoretical[14,17,21-23] results for

the outer electrons of acetylene is shown in Fig. 6. There is fairly good

agreement between experiment and theory for the lowest ionization potential.

Beyond that, the results of the various theoretical calculations resemble one

another more than they resemble the experimental results. The pattern seen

before is apparent in Fig. 6, namely, the theoretical calculations predict

higher binding energies than are found experimentally (except for the least

bound level).

E. Benzene and Cyclohexane

I have measured only the innermost electrons for benzene and cyclo-

hexane. For benzene the shift from fluoroform is 8.7 eV; the ionization

potential is 290.4 eV. The corresponding numbers for cyclohexane are 8.8 and

290.3 eV.

F. 2,2-Dimethylpropane

In the hope of being able to see the difference between the nonequiv-

alent carbons, I have measured the carbon 1s binding energy for 2,2-dimethyl-

propane (neopentane). The spectrum is shown in Fig. 7 together with a least-

squares fit to the experimental data. The centroid of the peak is shifted

8.7 eV from fluoroform, for an average binding energy of 290.4 eV. There is

no obvious evidence in the spectrum for nonequivalent carbons.

There are two features of the data that suggest that the central carbon

has a different binding energy from that of the methyl carbons. In the first place

the average binding energy of neopentane is 0.2 eV less than that for ethane.

We would, however, expect the 1s electrons in the methyl groups of neopentane to have the same binding energy as those in the methyl groups of ethane. The observed shift can be accounted for by assuming that the binding energy for the central carbon is about 1.0 eV less than that of ethane.

Furthermore, the peak shown in Fig. 7 for neopentane is about 10 percent wider than I have found for most other carbon lines. This extra width is consistent with there being a satellite peak one fourth the height of the main peak and displaced about 0.5 eV to higher or lower energies.

The least-squares curve of Fig. 7 was calculated on the assumption that there are two Gaussian peaks in the ratio of 4 to 1, both with the same width, and with a displacement of 0.6 eV. The resulting fit is in reasonable agreement with the data although a single peak gives an equally good fit. When the data are fit with two peaks, in this manner, then the widths are in better agreement with those determined for other compounds, and the position of the main peak is 0.1 eV closer to that of ethane. (An equally satisfactory fit is obtained if I assume the satellite peak is at higher binding energy than the main peak. In this case, however, the main peak position is 0.3 eV from that of ethane.)

The data on neopentane are thus consistent with a difference of 0.5 to 1.0 eV between the carbon 1s binding energies of the central carbon and the methyl carbons. The results suggest that the binding energy is less for the central carbon, in agreement with the trend seen from methane to ethane to cyclohexane.

IV. DISCUSSION

A. Some Preliminary Remarks

For comparing the experimental and theoretical values of the ioniza-
tion potentials it is useful to develop a simple description of the ionization
process. Let us consider the ionization of a 1s electron from carbon by a
magnesium K x ray. The ejected electron has a kinetic energy of about 1 keV,
or a velocity of about 2×10^9 cm/sec. The electron has effectively left the
molecule after traveling a few Å, or in about 10^{-17} sec. The molecule is left
with a hole in the K shell, which fills by the Auger effect in a time longer
than about 2×10^{-15} sec—much later than the time of the electron ejection.
After the Auger process, the molecule is left doubly ionized and either is
neutralized in a subsequent collision or breaks into fragments. The lifetime
of the species formed upon ejection of an electron from the K shell is not
long compared to the time for a molecular vibration (as it is when outer elec-
trons are ejected). For this reason, the question of whether the transition
is "vertical" or "adiabatic", which is relevant for transitions involving outer
electrons, is probably of little significance for transitions leaving the mole-
cule with a K-shell vacancy.

Ignored in the above description is any rearrangement of the remaining
electrons during the ejection of the 1s electron. Before the arrival of the
photon, all of the electrons are in eigenstates of the neutral molecule. After
the ejection of the electron and before the Auger process takes place, the
electrons are in eigenstates of the ion, (although not necessarily stationary
states). There must be a relaxation taking place after the electron is ejected.
If the relaxation is fast compared with the emission time (10^{-17} sec), the

electron is ejected with full energy (hν - the ionization potential). If the relaxation time is slow, then the electron is ejected with an energy that is less than the full energy by an amount equal to the relaxation energy.

The preceding paragraph gives a classical description of the process. Quantum mechanically we can describe the eigenstates of the neutral molecule as linear combinations of the eigenstates of the ion. In order to determine the final state of the ion, we must solve the time-dependent Schrödinger equation, with the leaving electron providing the time-dependent portion of the Hamiltonian. If the electron leaves in a time long compared to the relaxation time of the other electrons, the wave functions will evolve into those of the lowest eigenstates of the ion. If the electron leaves quickly, the ion will be left in some excited state. As seen above, the relaxation time for the 1s hole in carbon is about 10^{-15} sec compared to an ejection time of about 10^{-17} sec. We expect (and find experimentally) that the ion will be formed with a 1s hole.

Whether there will be additional excitation of the ion beyond that due to a 1s hole depends on the relaxation time for the various electrons involved. For instance, the 1s wave function must change from one appropriate to neutral carbon, where one of the 1s electrons is shielded by the other, to a wave function appropriate to ionized carbon, where this shielding has disappeared. We can make a simple estimate of the time required for this relaxation. On the average, the 1s electrons in a carbon atom have a kinetic energy of about 300 eV, or a velocity of about 10^9 cm/sec. About half of the 1s electron density is within 0.2 Å of the nucleus. The electron can move from one part of the orbital to any other part in about 4×10^{-18} sec—a time comparable

to the time for ejection of the other electron. Relaxation of the 1s elec-
tron is presumably completed by the time the ejected electron has left the
molecule. The outer electrons, however, move more slowly and cover a larger
volume than the 1s electrons do. The relaxation times are correspondingly
longer and it seems likely that the ion will sometimes be left with a higher
excitation than that due to a 1s hole alone. Electrons emitted in such a
process will appear in the spectrum at kinetic energies lower than the usual
value. Some evidence for such processes has been found for x-ray excitation
of the rare gases.[24]

B. Comparison Between Experimental and Theoretical Results

According to Koopmans' theorem,[25] the orbital binding energies cal-
culated by the Hartree-Fock method are equal to the ionization potentials of
the molecule. The theorem is true only if the wave functions for the elec-
trons of the ion are identical to those for the same electrons of the molecule.
As noted above, this is not the case, and the orbital energies given by
Hartree-Fock calculations will be greater than the actual ionization potentials
by the relaxation energy. The correct value of the ionization potential is
obtained by taking the difference between the total energies of the ion and of
the neutral molecule.

Siegbahn and co-workers have calculated ionization potentials for atoms
using Koopmans' theorem and by taking the difference between the energy of the
neutral atom and that of the ion.[26] For carbon they find that Koopmans' theorem
gives binding energies that are 4 percent too great for the 1s orbital, 10 per-
cent (2 eV) for the 2s, and 16 percent (1.5 eV) for the 2p. The difference

between the calculated orbital energies and the experimental values is there-
fore, about as one would expect. That the measured carbon 1s energies are
about five percent less than the calculated values is consistent with the dif-
ference of four percent calculated by Siegbahn et al. for atomic carbon.[26]
The situation for the outer electrons is similarly in accord with the calcula-
tion for atomic carbon.

C.   Carbon 1s Binding Energies

The carbon 1s binding energies of the compounds studied are summarized
in Table II. Included in this table is the reference value for fluoroform. The
ionization potentials for the hydrocarbons cluster around 291 eV. The Koopmans'
theorem values are about 305 eV; the discrepancy of five percent is about as
expected.

Of more interest than the absolute values of the binding energies are
the relative values. Although theoretical orbital energies based on Koopmans'
theorem should not agree exactly with the experimental values, the theoretical
calculations should give the distribution of electrons in the molecule with
some accuracy. Since the shifts of the 1s binding energies result largely
from changes in the distribution of the outer electrons, we may hope that the
calculations will predict these shifts with some accuracy. Failing this, they
should at least account for the direction of the shifts. However, the error in
the ionization potential obtained from use of Koopmans' theorem is about 5 per-
cent of the absolute value of the ionization potentials. The shifts in the
carbon 1s binding energies among the hydrocarbons studied are less than 0.3
percent of the absolute value. If the error in the Koopmans' theorem value

varies from compound to compound, then comparison between shifts calculated

using Koopmans' theorem and experimental shifts may not be very useful. There

is some evidence that Hartree-Fock calculations do not give the correct rela-

tive energies for the carbon 1s ionization potentials in the fluorinated

methanes.[27]

A comparison of the experimental and theoretical shifts for the com-

pounds acetylene, ethylene, ethane, and methane is shown in Fig. 8. The

energies are all plotted relative to that of acetylene taken as zero. The

hatched areas represent the errors in each measurement and include the error

in the acetylene measurement. For the series acetylene, ethylene, ethane the

agreement between theory and experiment is quite good. With the exception of

the ethane-acetylene difference calculated by Buenker, Peyerimhoff, and

Whitten,[17] and by Basch and Snyder[28] the theoretical values for the shift

are rather close to the experimental values. The direction of the shift indi-

cates that each additional hydrogen increases the electron density at the

carbon and makes the carbon 1s electron slightly less bound. The calculations

of Palke and Lipscomb[14] for these compounds are in agreement with this conclu-

sion and show that the carbon is negatively charged and the hydrogen positively.

According to their results, the charge on the carbon increases from -0.188 for

acetylene to -0.372 for ethane. This point of view is consistent with the fact

that the electronegativity of carbon is greater than that of hydrogen.[29] We

see a similar result on comparing benzene with cyclohexane. Adding six hydro-

gens to benzene causes a decrease of 0.1 eV in the carbon 1s binding energy,

the same as between ethylene and ethane. In both cases the bonding changes

from sp^2 to sp^3. Adding carbons across a triple or double bond also causes a

decrease in the ionization potential. There is an 0.8 eV shift between acet-
ylene and benzene and an 0.4 eV shift between ethylene and cyclohexane. These
shifts are larger than those for addition of a hydrogen. This result suggests
that an alkyl group is electron donating relative to hydrogen.

For the methane, ethane, cyclohexane comparison, theory and experi-
ment are not in agreement. The 1s electron in ethane is less bound than that
in methane by 0.2±0.2 eV, and that in cyclohexane is less bound than that in
ethane by 0.3 eV. Similarly, there is a shift of 0.3 eV between ethylene and
benzene. The replacement of a hydrogen attached to a carbon with a carbon
apparently results in an increased electron density at the carbon. This
result is not consistent with the molecular orbital calculations. Those of
Palke and Lipscomb[14] and those of Basch and Snyder[28] indicate a shift of 0.2 eV
between methane and ethane in the direction opposite to that observed. Palke
and Lipscomb calculate a charge of -0.452 on the methane carbon and -0.372 on
those of ethane--reversed from what one might conclude from the experimental
data. A comparison of the results calculated by Cade and Huo[30] for CH with
those of Greenshields[31] for C_2 indicates the 1s electron in C_2 is bound by
1.15 eV more than that in CH--again in the opposite direction to the observed
methane-ethane shift. The discrepancy between theory and experiment may be due
to the inapplicability of Koopmans' theorem.

In addition, however, the measured shift seems to be in the opposite
direction from that suggested by chemical evidence. For instance, the elec-
tronegativity of carbon is greater than that of hydrogen, suggesting that an
alkyl group should be electron withdrawing relative to hydrogen. Although
for unsaturated carbons alkyl groups are known to be electron donating,[32]

there is some evidence that a methyl group attached to a saturated carbon is electron withdrawing relative to hydrogen.[33]

There is an important difference between the other determinations of the electron withdrawing power of alkyl groups and those reported here. The previous investigations have determined this property for neutral molecules. In photoelectron spectroscopy, the result is affected by the properties of both molecule and ion. The positively-charged carbon left after ionization withdraws electrons from the neighboring atoms, reducing the total energy of the ion, and, hence, reducing the ionization potential. We can estimate the relative electron donating powers of an alkyl group and of hydrogen towards a positively-charged carbon by looking at the carboxylic acids. In these the carbon will be positively charged since oxygen is more electronegative than carbon. (Measurements of the carbon 1s binding energies give results in agreement with this conclusion.[34]) The higher acidity of formic acid relative to acetic acid indicates that the carboxyl carbon in acetic acid is more negative than that in formic acid and that, in this situation, the methyl group is electron donating relative to hydrogen. (This is not a new conclusion.[32]) Thus there are two opposing effects determining the ionization potential. The carbon 1s electron in methane sees a higher negative potential than does that in ethane (in agreement with the theoretical results and other chemical evidence). This effect tends to make the ionization potential larger for ethane than for methane. In the ion, the greater electron donating power of methyl relative to hydrogen towards the positively-charged carbon causes a greater reduction in energy for the ethane ion than for the methane ion. This effect, which is apparently dominating, tends to make the ionization potential smaller

for ethane than for methane, which is the case. In cyclohexane, where there
are two ends of an alkyl chain to contribute electrons to the ionized carbon,
the effect is even greater.

V.   ACKNOWLEDGMENTS

REFERENCES

1. M. I. Al-Joboury and D. W. Turner, J. Chem. Soc. 1964, 4434.

2. Siegbahn, Nordling, Fahlman, Nordberg, Hamrin, Hedman, Johansson, Bergmark, Karlsson, Lindgren, and Lindberg, ESCA – Atomic, Molecular, and Solid State Structure Studied by Means of Electron Spectroscopy, (Almqvist and Wiksells, Uppsala, 1967).

3. A. H. Compton and S. K. Allison, X-Rays in Theory and Experiment, (D. Van Nostrand, Inc., New York, 1935) p. 561.

4. K. Hamrin, G. Johansson, U. Gelius, A. Fahlman, C. Nordling, and K. Siegbahn, Chem. Phys. Letters 1, 613 (1968).

5. Ref. 2, Chapter V.

6. Ref. 2, Chapter II.

7. Ref. 2, Appendix 6.

8. J. M. Hollander, M. D. Holtz, T. Novakov, and R. L. Graham, Arkiv Fysik 28, 375 (1965); T. Yamazaki and J. M. Hollander, Nucl. Phys. 84, 505 (1966).

9. Charlotte E. Moore, Atomic Energy Levels, Vol. I, NBS Circular 467, (U. S. Government Printing Office, 1949) p. 76, 81.

10. H. Hartmann and H.-U. Chun, Theor. Chim. Acta 2, 1 (1964).

11. D. A. Shirley and T. D. Thomas, unpublished work.

12. H.-U. Chun, Z. Naturforsch. 23, 1415 (1968).

13. M. I. Al-Joboury and D. W. Turner, J. Chem. Soc. 1967, 373B.

14. W. E. Palke and W. N. Lipscomb, J. Am. Chem. Soc. 88, 2384 (1966).

15. G. P. Arrighini, C. Guidotti, M. Maestro, R. Moccia, and O. Salveti, J. Chem. Phys. 49, 2224 (1968).

16. M. J. S. Dewar and S. D. Worley, J. Chem. Phys. 50, 654 (1969).

17. R. J. Buenker, S. D. Peyerimhoff, and J. L. Whitten, J. Chem. Phys. 46, 2029 (1967).

18. R. M. Pitzer and W. N. Lipscomb, J. Chem. Phys. 39, 1995 (1963).

19. U. Kaldor and I. Shavitt, J. Chem. Phys. 48, 191 (1968).

20. C. Baker and D. W. Turner, Chem. Commun. 1967, 797.

21. A. D. McLean, J. Chem. Phys. 32, 1595 (1960).

22. J. W. Moskowitz, J. Chem. Phys. 43, 60 (1965).

23. U. Kaldor, J. Chem. Phys. 46, 1981 (1967).

24. M. O. Krause, T. A. Carlson, and R. D. Dismukes, Phys. Rev. 170, 37 (1968).

25. T. Koopmans, Physica 1, 104 (1933).

26. Ref. 2, Appendix 2.

27. T. D. Thomas, to be published.

28. H. Basch and L. C. Snyder, Chem. Phys. Letters 3, 333 (1969).

29. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, (Interscience, New York, 1962) p. 92.

30. P. E. Cade and W. M. Huo, J. Chem. Phys. 47, 614 (1967).

31. J. B. Greenshields, unpublished data quoted in Ref. 17.

32. G. E. K. Branch and M. Calvin, The Theory of Organic Chemistry, (Prentice-Hall, New York, 1946) p. 204.

33. V. W. Laurie and J. S. Muenter, J. Am. Chem. Soc. 88, 2883 (1966) and other references listed therein.

34. Ref. 2. pp. 78-9.

Table I.　Various measurements of the
1s binding energy in neon.

Brogren	870.3±0.1	a
Backovsky	870.2	b
Hartmann and Chun	867.8±1.8	c
Körber and Melhorn	870.0±0.4	d
Kunzl and Svobodova- Joanelli	869.7	b
Moore and Chalkin	869.9±0.1	b
This work	869.7	

[a] G. Brogren, Nova Acta Regiae Soc. Sci.

Upsaliensis, Ser IV, 14, no. 4 (1949).

[b] Quoted by (d).

[c] Ref. 10.

[d] H. Körber and W. Melhorn, Z. Physik 191,

217 (1966).

Table II. Carbon 1s binding energies
in simple hydrocarbons.

Compound	Shift from fluoroform (eV)	Binding (eV)
Methane	-8.3	290.8
Ethane	-8.5	290.6
Ethylene	-8.4	290.7
Acetylene	-7.9	291.2
Cyclohexane	-8.8	290.3
Benzene	-8.7	290.4
2,2-dimethylpropane	-8.7	290.4
Fluoroform	0	299.1

FIGURE CAPTIONS

Fig. 1. Spectrum of outer electrons from acetylene excited by magnesium K

x rays. The dashed curve represents a least-squares fit to the data

assuming a linearly decreasing background and two Gaussian peaks of the

same width. The energies marked $3\sigma_g$ and $1\Pi_u$ have been determined from UV

photoelectron spectroscopy (Refs. 1, 20).

Fig. 2. Spectra of the carbon 1s electrons on acetylene, ethylene, and ethane

relative to fluoroform. Radiation is magnesium K x rays.

Fig. 3. Experimental values for the binding energies of outer electrons on

methane compared to theoretical values. Palke and Lipscomb: Ref. 14.

ACMMS: Ref. 15. Dewar and Worley: Ref. 16.

Fig. 4. Experimental values for the binding energies of outer electrons on

ethane compared to theoretical values. Buenker, Peyerimhoff, and Whitten:

Ref. 17. Pitzer and Lipscomb: Ref. 18. Palke and Lipscomb: Ref. 14.

Dewar and Worley: Ref. 16.

Fig. 5. Experimental values for the binding energies of outer electrons on

ethylene compared to theoretical values. Buenker, Peyerimhoff, and Whitten:

Ref. 17. Kaldor and Shavitt: Ref. 19. Palke and Lipscomb: Ref. 14.

Dewar and Worley: Ref. 16.

Fig. 6. Experimental values for the binding energies of outer electrons on

acetylene compared to theoretical values. McLean: Ref. 21. Moskowitz:

Ref. 22. Palke and Lipscomb: Ref. 14. Kaldor: Ref. 23. Buenker,

Peyerimhoff, and Whitten: Ref. 16.

Fig. 7. Spectrum of carbon 1s electrons from 2,2-dimethylpropane. Curves

represent a least-squares fit to the data, assuming two Gaussian peaks

with an area ratio of 4 to 1, the smaller peak being displaced 0.6 eV to
lower binding energies. The solid curve shows the sum of the two peaks
plus background. The dashed curves show the component peaks.

Fig. 8. Experimental values for the carbon 1s binding energies of ethylene,
ethane, and methane relative to acetylene compared with theoretical values.
The hatched areas represent the experimental values and their uncertainties.
The solid lines refer to the calculations of Palke and Lipscomb (Ref. 14),
the dotted lines to those of Buenker, Peyerimhoff, and Whitten (Ref. 17),
the short-dashed lines to those of Kaldor and Shavitt (Ref. 19, 23), the
long-dashed lines to those of Basch and Snyder (Ref. 28).
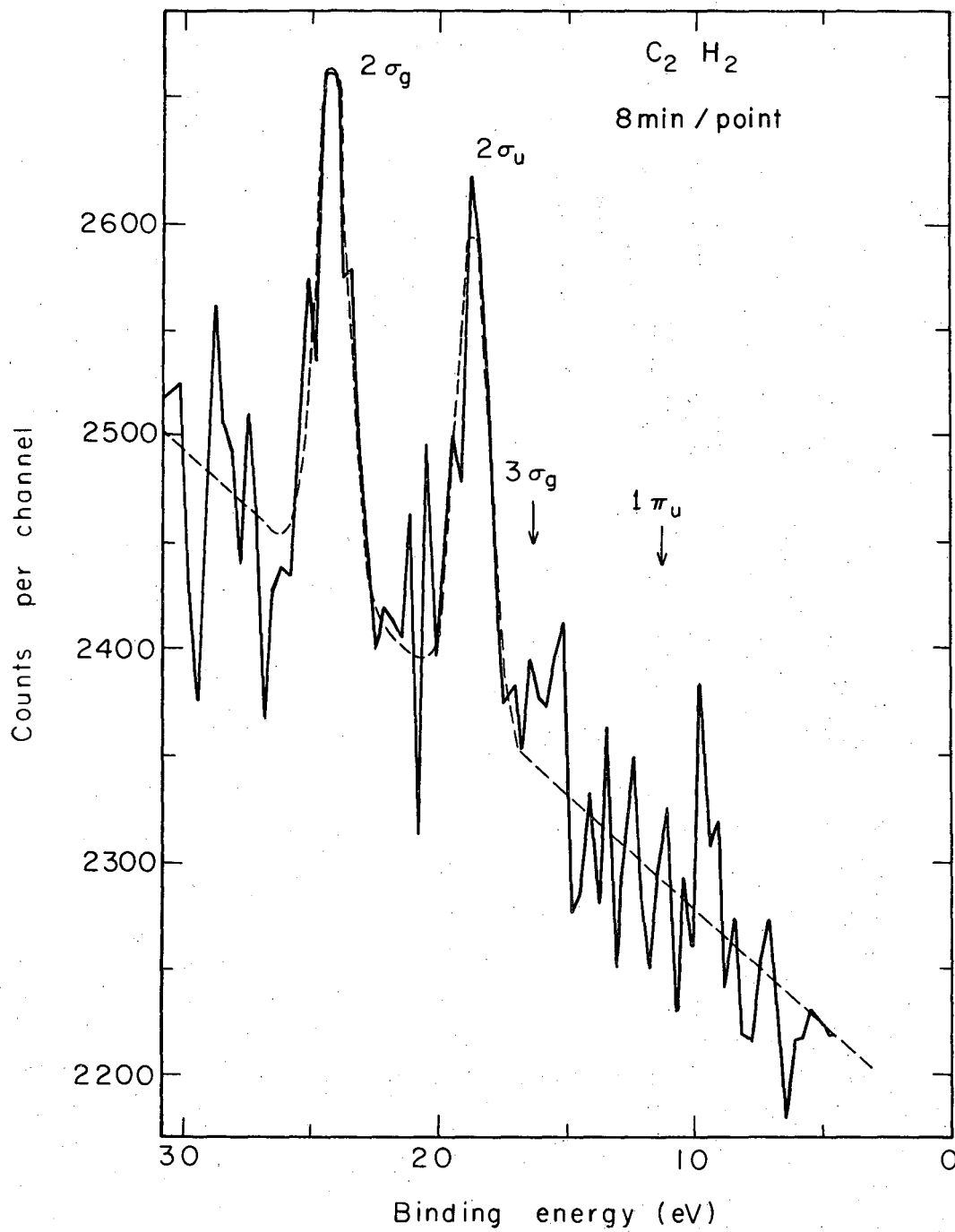
Fig. 1
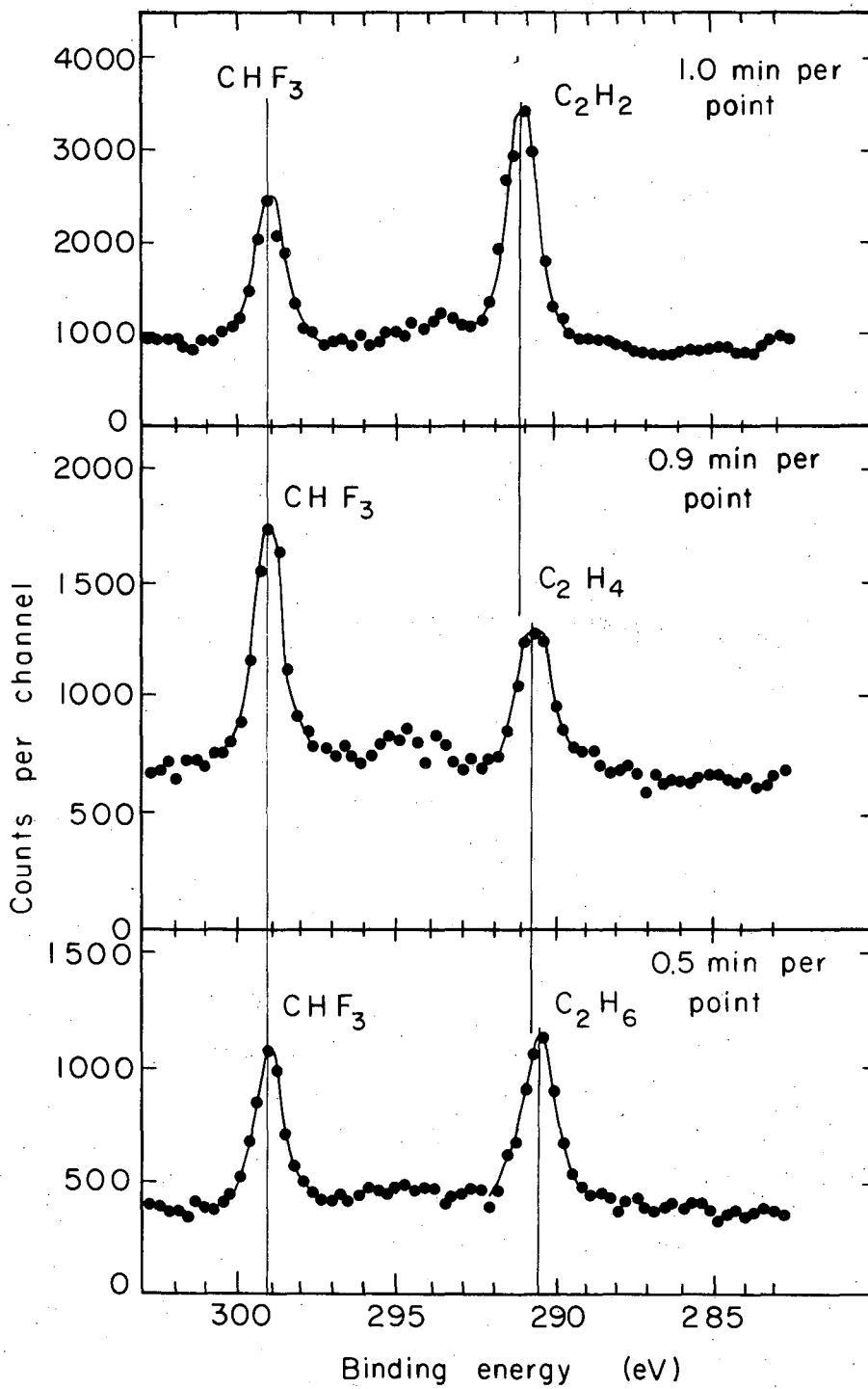
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Fig. 2
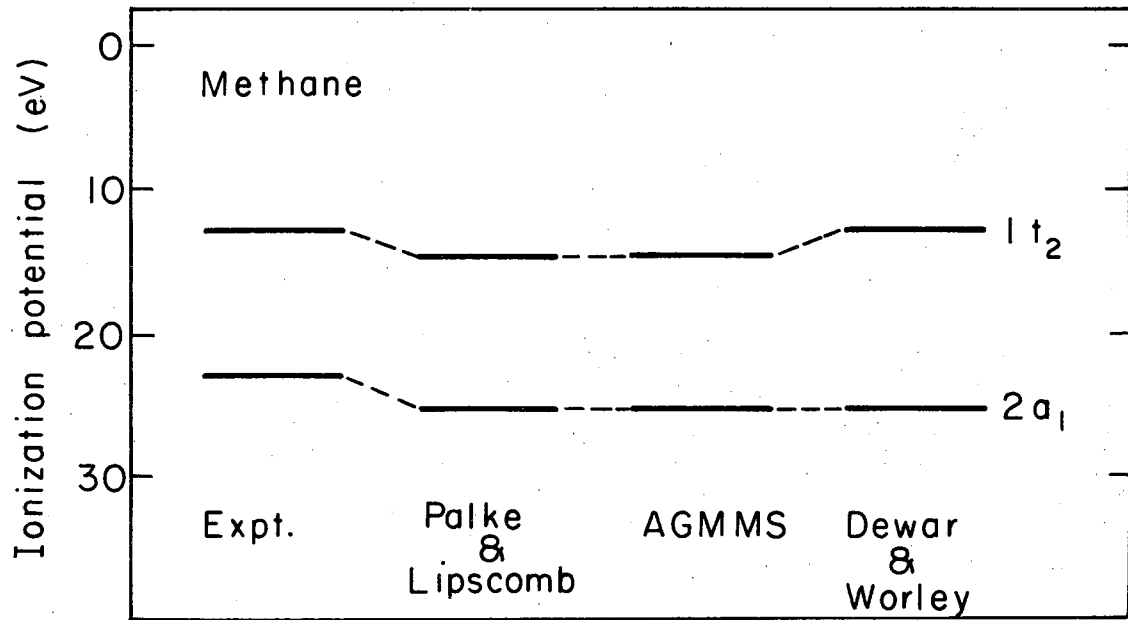
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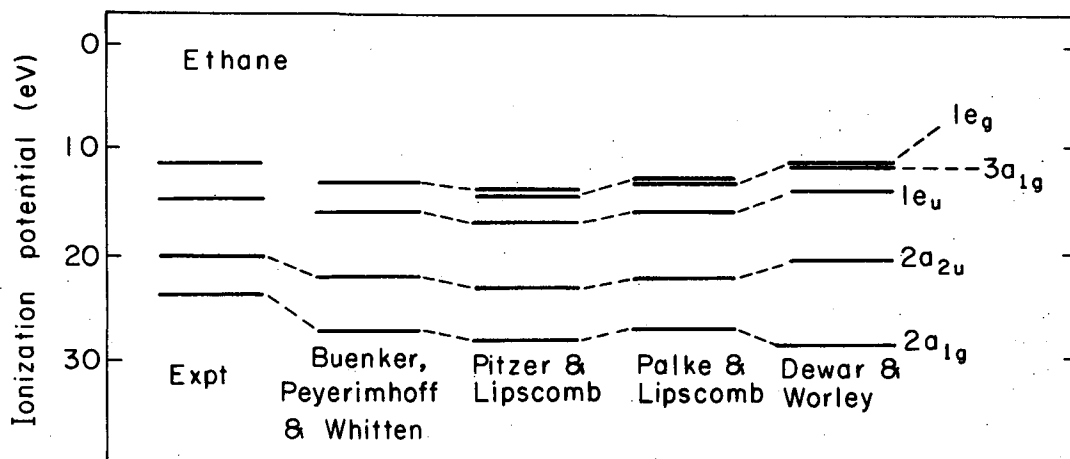
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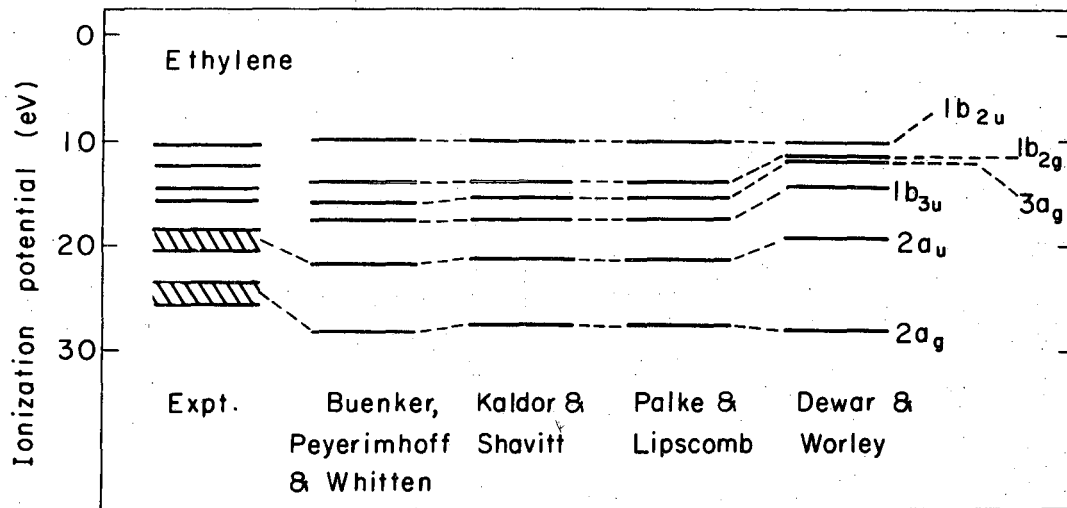
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Fig. 5
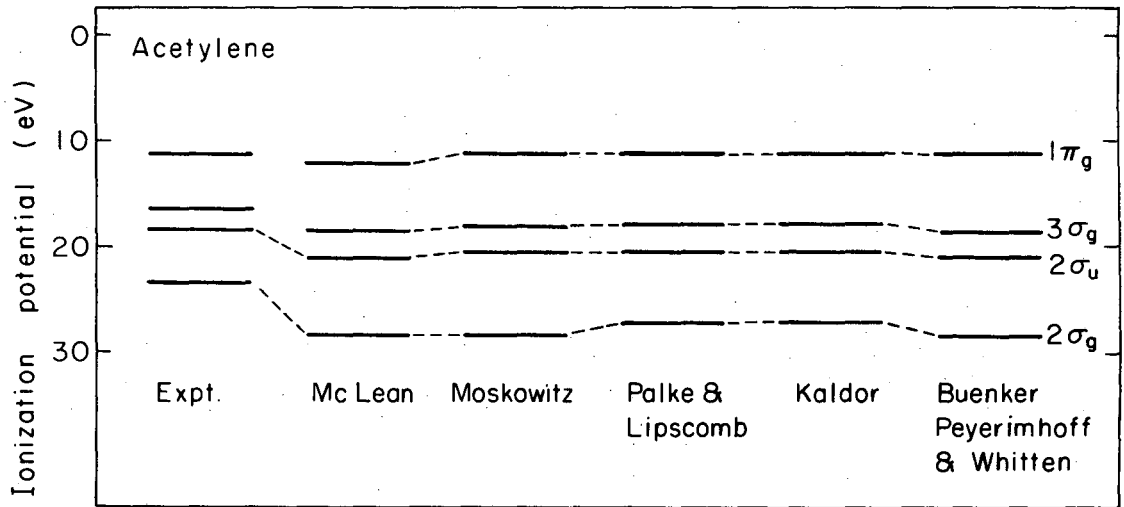
XBL697-3307

Fig. 6

XBL697-3306

Fig. 7

2,2 - Dimethylpropane

C 1s

3.5 min / channel

Binding energy (eV)

XBL697-3303

Fig. 8