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Publication Date
1969-07-01
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July 1969

AEC Contract No. W-7405-eng-48
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X-RAY PHOTOELECTRON SPECTROSCOPY OF SIMPLE HYDROCARBONS

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July 1969

ABSTRACT

Carbon ls 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 ls 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 2g_u and 2g_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 ls electrons and 10-15 percent greater for the outer electrons. These differences are consistent with calculations of the

* Supported in part by the U. S. Atomic Energy Commission.

† Permanent address.
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.\textsuperscript{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.\textsuperscript{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. 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 have shown for methane that the probability of exciting electrons from the 2a₁ orbital (mostly carbon 2s) is three or four times higher than the probability of exciting one from the 1t₂ orbital (mostly carbon 2p) even though there are three times as many electrons in the 1t₂ orbital as in the 2a₁ orbital. They have seen a similar effect in ethane, where the probability of ionization of the 2a₁g and 2a₂u levels (mostly carbon 2s) is considerably 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 (3σg and 1Πu) were measured by UV photoelectron 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 precise 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. 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 electron 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 photoelectron 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 appreciable 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 theoretical calculations. I have given particular attention to an accurate measurement of the rather small differences among the carbon ls binding energies of the substances studied. As part of the calibration and standardization procedure, I have obtained the binding energies for the ls electron in neon and for the carbon ls and fluorine ls 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.

For these experiments the exciting radiation was magnesium $\text{K}_\alpha$ x rays (1253.6 eV). The electron energies were measured in an iron-free double-focusing spectrometer of 50-cm radius. 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, 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 $869.7 \pm 0.1$ 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,\textsuperscript{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 ls 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 ls line from fluoroform does not vary by more than 0.2 eV.\textsuperscript{11} Presumably any differential pressure dependence of two compounds run together will be substantially less than this.) The carbon ls 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 several 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 alternate scans of the neon ls, 2s, carbon ls, and fluorine ls lines. For carbon in fluoroform the ls 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 ls binding energy with that obtained by others suggests that such systematic errors are no more than 0.6 eV at neon and probably less for carbon ls 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 $8.3 \pm 0.1 \text{ eV}$ less than that of fluoroform, or $290.8 \text{ eV}$. This is in good agreement with a value of $291$ extracted from the first graph given by Hamrin et al., but disagrees with the value of $288.8 \pm 0.2$ reported by Chun. (The $2 \text{ eV}$ 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 $12.99 \text{ eV}$. Hamrin et al. have reported $13.5 \text{ eV}$. 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. to be at $23.1 \text{ eV}$, beyond the range of excitation by the $584 \text{ Å}$ line of helium.

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

B. Ethane

In ethane the carbon $1s$ (or $1a_2 + 1a_1$) level is found to be $8.5 \text{ eV}$ less bound than the corresponding level in fluoroform, giving a binding energy of $290.6 \text{ eV}$ in good agreement with a value of $290.5$ extracted from the second graph given by Hamrin et al. I have measured values of $24.2$ and $20.6 \text{ eV}$ 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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{14,16-18} It is likely that these levels have not been resolved experimentally.

The experimental results for all but the $ls$ electrons are compared in Fig. 4 with the results of various theoretical calculations.\textsuperscript{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 $ls$ 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\textsuperscript{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\textsuperscript{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\textsuperscript{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 magnitude 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\textsubscript{g} and 2\sigma\textsubscript{u} levels, which are predominantly carbon 2s levels. UV photoelectron spectroscopy\textsuperscript{1,20} gives levels at 11.41, 16.44, 18.42 (Ref. 20), or 18.56 (Ref. 1) eV, and an uncertain 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\textsubscript{u}; the uncertain level at 20.5 does not agree with my result for 2\sigma\textsubscript{g}.\textsuperscript{20}
A comparison of experimental and theoretical\textsuperscript{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 cyclohexane. 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 nonequivalent carbons, I have measured the carbon 1s binding energy for 2,2-dimethylpropane (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 ionization 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 $2 \times 10^9$ 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 $2 \times 10^{-15}$ 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 electrons 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 molecule 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 ($h\nu$ - 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 $4 \times 10^{-18}$ sec—a time comparable
to the time for ejection of the other electron. Relaxation of the ls electron 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 ls 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 ls 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.

B. Comparison Between Experimental and Theoretical Results

According to Koopmans' theorem, the orbital binding energies calculated 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 electrons 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. For carbon they find that Koopmans' theorem gives binding energies that are 4 percent too great for the ls orbital, 10 percent (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 therefore, about as one would expect. That the measured carbon ls energies are about five percent less than the calculated values is consistent with the difference of four percent calculated by Siegbahn et al. for atomic carbon. The situation for the outer electrons is similarly in accord with the calculation for atomic carbon.

C. Carbon ls Binding Energies

The carbon ls 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 ls 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 percent of the absolute value of the ionization potentials. The shifts in the carbon ls 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 relative energies for the carbon 1s ionization potentials in the fluorinated methanes. 27

A comparison of the experimental and theoretical shifts for the compounds 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 Snyder28 the theoretical values for the shift are rather close to the experimental values. The direction of the shift indicates that each additional hydrogen increases the electron density at the carbon and makes the carbon 1s electron slightly less bound. The calculations of Falke and Lipscomb14 for these compounds are in agreement with this conclusion 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 hydrogens 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 sp2 to sp3. Adding carbons across a triple or double bond also causes a
decrease in the ionization potential. There is an 0.8 eV shift between acetylene 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 experiment are not in agreement. The ls 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 Falke and Lipscomb\textsuperscript{14} and those of Basch and Snyder\textsuperscript{28} indicate a shift of 0.2 eV between methane and ethane in the direction opposite to that observed. Falke 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\textsuperscript{30} for CH with those of Greenshields\textsuperscript{31} for C\textsubscript{2} indicates the ls electron in C\textsubscript{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 electronegativity 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,\textsuperscript{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 ls 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 ls 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

I would like to express my appreciation to Professor David A. Shirley
for many stimulating discussions and provocative suggestions and to Dr. J. M.
Hollander for making the electron spectrometer available to me. Thanks are
due to C. S. Fadley for his patient instruction in the use of the spectrom-
eter and for the many ideas he has contributed to the understanding of the
results. I am indebted to Charles Butler for assistance in constructing various
pieces of apparatus needed in these experiments. Finally, I would like to thank
the John Simon Guggenheim Memorial Foundation for fellowship support.
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6. Ref. 2, Chapter II.


25. T. Koopmans, Physica 1, 104 (1933).
27. T. D. Thomas, to be published.
34. Ref. 2. pp. 78-9.
Table I. Various measurements of the $1{s}$ binding energy in neon.

<table>
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<th>Binding Energy (eV)</th>
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<tr>
<td>Brogren</td>
<td>870.3±0.1</td>
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<tr>
<td>Backovsky</td>
<td>870.2</td>
<td>b</td>
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<td>d</td>
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<td>Kunzl and Svobodova-Joanelli</td>
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<td>b</td>
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<td>Moore and Chalkin</td>
<td>869.9±0.1</td>
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<tr>
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b Quoted by (d).

c Ref. 10.

<table>
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<th>Compound</th>
<th>Shift from fluoroform (eV)</th>
<th>Binding (eV)</th>
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<td>Methane</td>
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</tr>
<tr>
<td>Ethane</td>
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</tr>
<tr>
<td>Ethylene</td>
<td>-8.4</td>
<td>290.7</td>
</tr>
<tr>
<td>Acetylene</td>
<td>-7.9</td>
<td>291.2</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>-8.8</td>
<td>290.3</td>
</tr>
<tr>
<td>Benzene</td>
<td>-8.7</td>
<td>290.4</td>
</tr>
<tr>
<td>2,2-dimethylpropane</td>
<td>-8.7</td>
<td>290.4</td>
</tr>
<tr>
<td>Fluoroform</td>
<td>0</td>
<td>299.1</td>
</tr>
</tbody>
</table>
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. 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 Falke 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

Counts per channel vs. Binding energy (eV) for \( \text{C}_2 \text{H}_2 \) with points at 8 min/point. Peaks labeled as 2\( \sigma_g \), 2\( \sigma_u \), 3\( \sigma_g \), and 1\( \pi_u \).
Fig. 2
Fig. 3

Ionization potential (eV)

Methane

$\text{Exp.}\quad \text{Palke & Lipscomb} \quad \text{AGMMS} \quad \text{Dewar & Worley}$

$1t_2$

$2a_1$
Fig. 5
Fig. 6
Fig. 7
2,2-Dimethylpropane

C 1s

Counts per channel

3.5 min/channel

Binding energy (eV)

Fig. 8
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