

AN ABSTRACT OF THE THESIS OF

Rudy T.M Situmeang for the degree of Master of Science in
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Title: Gas Phase X-ray Photoelectron Spectroscopy of Some
Ketone Compounds

Abstract approved: *Redacted for Privacy*

The photoelectron spectra of a series of ketone compounds have been investigated in the gas phase. Core ionization energies were measured to probe the effects of molecular size and connectivity number on core ionization energies.

It was found that core ionization energies roughly decrease with increasing connectivity number as expected. However, subdividing into several categories based on the molecular type gives improved correlations.

These results show both the effect of molecular size and that of bringing the polarizable group closer to the core ionized center.

In some cases, compounds with the same connectivity number have different core ionization energies and, in others, compounds with different connectivity number have the same core ionization energies. These discrepancies

indicate that the simple method for calculating connectivity numbers must be modified to reflect different molecular types. Other discrepancies indicate that this method does not correctly predict the effects of remote hydrogens or the effects of aromatic substituents, where conjugation may influence the relaxation energy.

Gas Phase X-ray Photoelectron Spectroscopy
of Some Ketone Compounds

by

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A THESIS

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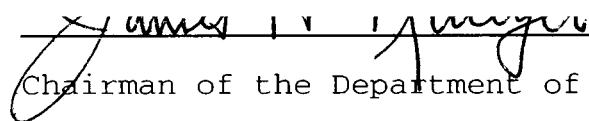
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This work is dedicated to my wife, Iriani and my daughter, Ruth meta.

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GAS PHASE X-RAY PHOTOELECTRON SPECTROSCOPY OF SOME KETONE COMPOUNDS

I. INTRODUCTION

A. General Views

Inside the atom, the nucleus and the electrons attract each other by electrostatic force. When atoms form molecules, the charge distribution of the atom is modified by the molecular bonding. In part this modification is due to a shift of electrons towards the more electronegative atoms and in part it is due to rearrangement of electrons because of resonance effects. The question of charge distribution in molecules is of central importance to chemistry.

Even though inner shells do not participate in this process, core electrons are sensitive to electron redistribution accompanying bond formation. In particular, core ionization energies increase on an atom from which valence electrons have been removed. Therefore, measurement of core ionization energies can provide insight into charge distribution in molecules.

In recent study, Greenberg et al¹. have studied the core ionization in planar and nonplanar amides with the goals of determining how planarity or nonplanarity affects the charge distribution in the amide structure. Analysis of their results was, however, complicated by an additional effect on the ionization energies, which is the effect of molecular size and shape.

The goal of this work is to provide additional information on the effect of molecular size and shape on the core ionization energies in ketones. These were chosen

because amides contain both keto and amine groups. The amine group has been previously studied by Greenberg et al². This work was designed to complement the work on amines, and was to consider the effects of both molecular size and cyclization on the core ionization energies.

B. The Effect of Molecular Size and Molecular Shape

1. The Effect of Molecular Size

To get insight into charge distribution, we have to know what is going on when an electron is ejected from an inner shell of an atom in a molecule. As noted above, the principal effect on the ionization energy is the charge distribution. A second, and often important effect is relaxation of valence electrons in response to the removal of a core electron. This relaxation energy lowers the ionization energy from what it would be if charge distribution were the only factor. To a good approximation the relaxation arises from a polarization of the molecule, and, therefore, increases with molecular size. As a result, core ionization energies decrease with molecular size.

Although the qualitative effect of polarizability (or molecular size) is easily understood, it is not so straightforward to put it on a quantitative basis. Gasteiger and Hutchings^{3,4} have quantified the polarizability by taking into account the attenuation of the effect of remote atoms toward charge flow in the molecule. They have proposed that this effect can be described in terms of connectivity number, N_c , which is defined as

$$N_c = \sum b_n \times (0.5)^{n-1} \quad (1)$$

where b_n is the number of atoms in the n -th neighbor sphere; and the attenuation factor of 0.5 was determined empirically from studies of several systems⁴. Since electron rearrangement is an important factor in relaxation, we can conclude that core ionization energy should decrease with increasing the connectivity number.

2. The Effect of Molecular Shape

As mentioned above the final state relaxation is explicitly related to the molecular geometry. Since one of the nonplanar amides studied by Greenberg et al. was a three-membered ring, we need to know whether ring strain affects the ionization energy. From earlier studies by Greenberg⁵ and by Morton⁶, it was concluded that there is no effect of ring closure in 4- and 5-membered and, presumably larger rings, but possibly an effect in 3-membered rings.

C. A Concept of Probing

The question we will encounter all the way through this thesis is the question of the charge distribution of the molecule. To understand it, we have studied a series of ketones. In this case, we want to see the effect of molecular size on the core ionization energy and also the effect of ring size to core ionization energy. For a ring compound, we intended to collaborate with Greenberg, who was going to synthesize the compound, 2,3-di-tert butyl cyclo-propanone. However, Greenberg has not yet succeeded in synthesizing it. So, the topic of this thesis is the effect of size and connectivity number on the ionization energy.

II. THE EXPERIMENTAL PROCEDURE

A. The X-ray Photoelectron Spectrometer

1. The Cylindrical Mirror Electrostatic Analyzer

All experimental ionization energies were measured on the Oregon State University cylindrical mirror electrostatic analyzer^{7,8}. A cross sectional view of the analyzer is shown in Figure 1. The system consists of three main components. These are the excitation source, the inner and outer cylinders, and the detection system.

The cylindrical mirror analyzer operates on the following basic principle: A gaseous sample is introduced into the gas cell through the gas manifold just above the X-ray tube. The sample molecules are ionized by the X-rays, and the ejected electrons that are travelling at the proper angle with respect to the center axis of the inner cylinder pass through openings in the lower portion of the inner cylinder. Only those electrons having a kinetic energy matched to the voltage applied to the outer cylinder will be focused back through an aperture in the top of the inner cylinder and through a small circular collimator to the channel multiplier where the electrons are multiplied and counted. Electrons are prevented from travelling up the inner cylinder and reaching the detector without passing through the analyzer by a plug inserted into the inner cylinder.

To eliminate fringe effects on the electric field at the ends of the cylinders, the analyzer is equipped with a series of concentric copper rings at the top and bottom of the spectrometer. These are connected to one another, and to the inner and outer cylinders by

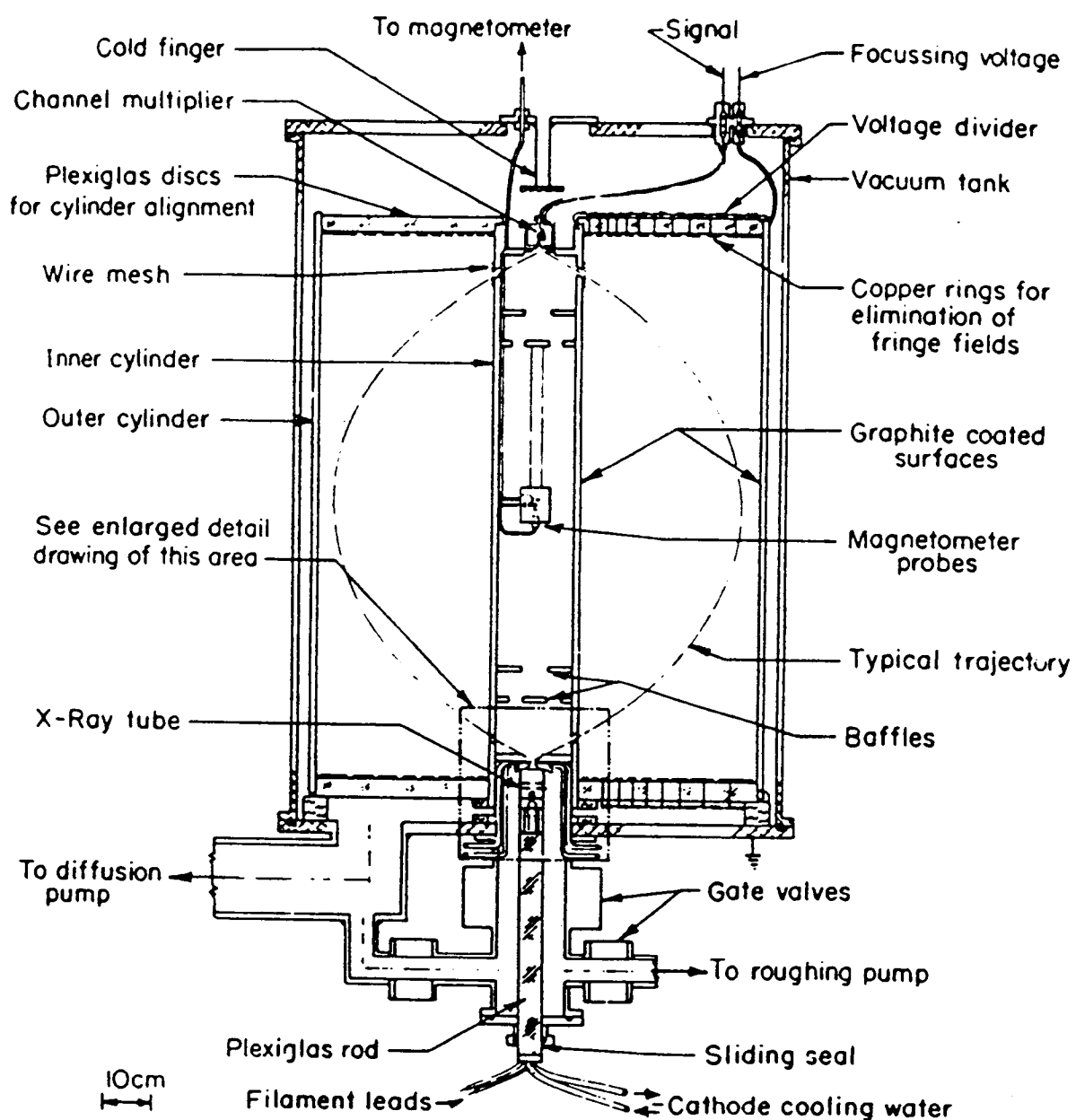


Figure 1. Cross section of Oregon State University Cylindrical mirror electrostatic analyzer⁸.

resistors that form a voltage divider. A voltage gradient at the ends of the cylinders is established that is nearly identical to the gradient for infinitely long cylinders.

The spectrometer is evacuated through two six-inch diffusion pumps, which can be isolated from the spectrometer by gate valves. The analyzer is enclosed in a mu-metal shield and surrounded by helmholtz coils to eliminate external magnetic fields. A complete description of the analyzer is given by Citrin et al⁸.

2. The X-ray Tube

In the determination of the experimental ionization energies the samples were ionized with 1486.553 eV aluminum K α X-rays⁹. The hollow anode X-ray tube, designed and built by Bomben¹⁰, is shown in Figure 2. The anode itself is machined from a solid piece of aluminum. A 10 cm tungsten filament, banded concentric around the anode, functions as an electron supplying cathode. Under the normal vacuum conditions in the X-ray tank (10^{-6} torr) the filament has an average lifetime of about two weeks. The anode was held at about 9.5 kilovolts, and the emission current from the filament to the anode was of the order of 45 milliampere.

The X-ray generation system is also tied into the safety sensor system. Before high voltage can be applied to the anode, five criteria must be met : the cooling ring and X-ray anode cooling water must be turned on, the spectrometer must have adequate vacuum, the lid on the box containing the high voltage safety relay must be closed, and the door leading to the chamber under the spectrometer where the high voltage leads are connected to the X-ray tube must also be closed. The first four safety requirements protect the spectrometer; the last one protects the workers.

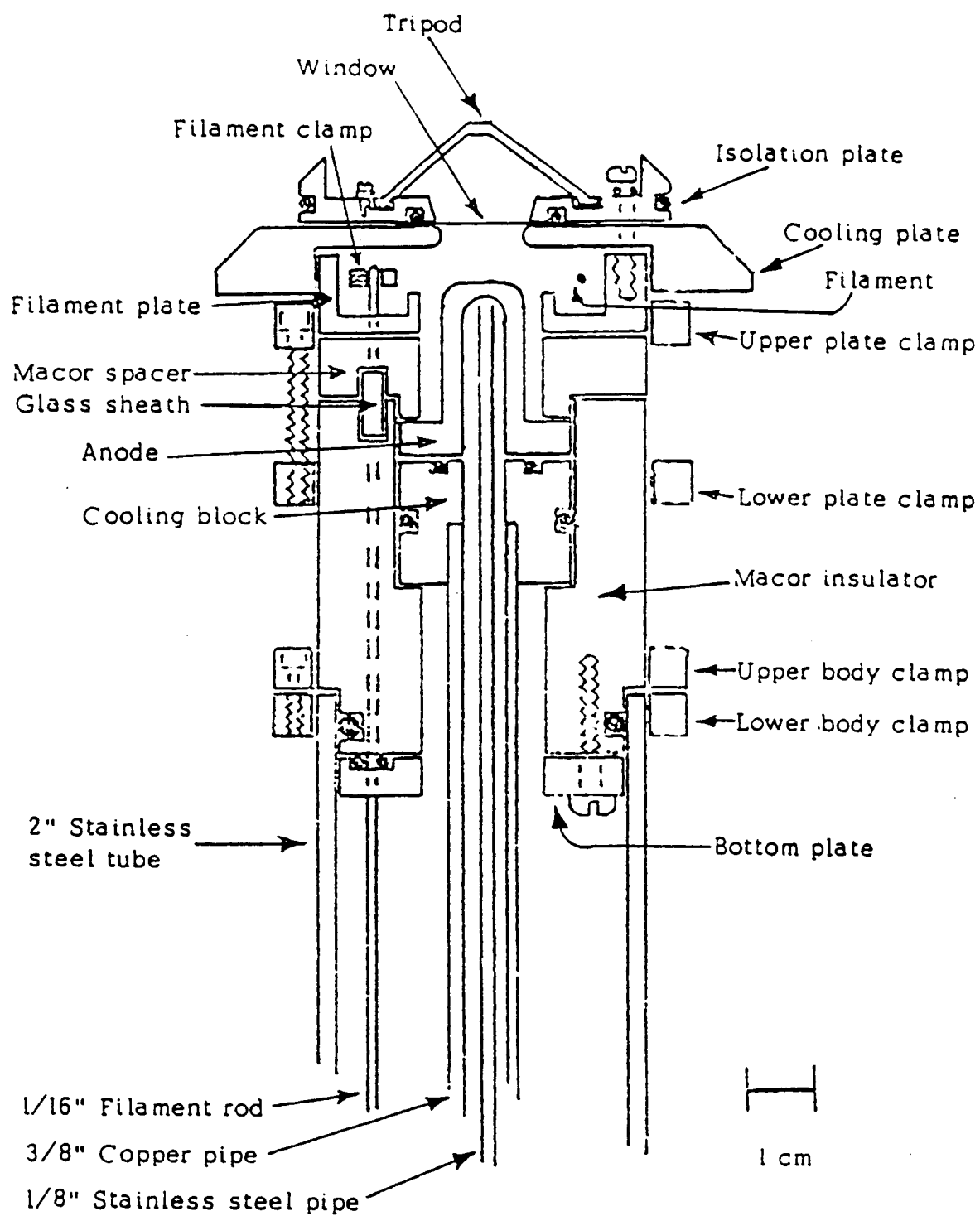


Figure 2. Hollow anode X-ray tube¹⁰.

Should any of the above criteria fail to be met, the high voltage is immediately cut off from the X-ray anode at the relay box, and the connections to the spectrometer are grounded. The safety sensor system is discussed in further detail by Bomben¹⁰.

Data are taken under computer control using the program PESCADO. This program makes it possible to scan the high voltage and record the electron counts in up to 8 different regions. The scans are made sequentially and are repeated until sufficient counts have been accumulated. The output files contain the number of counts recorded at each voltage of the scan, the nominal and measured voltages, date and time. Five regions were scanned in these experiments : Ne1s, O1s, C1s, Ar2p, and Ne2s spectra. For each scan region, the low voltage setting, total number of channels in the particular region, voltage increment (volt/channel) and time per channel per region can be specified. For instance, to scan the O1s region of 3-pentanone, the focusing voltage is set to 758.026 volt which is the low voltage setting given by spectroscopist. For 100 milliseconds electron counts measured by the electron multiplier are accumulated in channel 1 having the label 758.026 volt. Then the focusing voltage is increased automatically by 0.1 volt to 758.126 volt. For the next 100 milliseconds counts are sorted in channel 2 corresponding to the voltage of 758.126 volt. After running through the 101 channels of this region the focusing voltage flips to the low voltage setting of the C1s region, which is next. When the last region, Ne2s, is done the whole cycle is repeated. Finally, calibration voltages are determined by measuring the actual voltages at five points in the spectrum. These are selected by cursors; two of these correspond to the first and last channels in the scan, and the others are selected by spectroscopist to be near the peaks

that appear in the spectrum.

B. Performance

In order to establish optimum operating conditions, tests were made of the performance of the analyzer as a function of pressure. The pressure in the gas cell was measured using a capacitance manometer. Specific tests were concerned with how the pressure affects counting rate, resolution, and position of peak maximum. In these experiments, neon as gas and a tripod (see figure 2), were used. The purpose of this tripod is to block X-rays from hitting the aperture of the gas cell and increasing the background. Pressure was varied from 5 mtorr to 120 mtorr. Counting rate, defined as a peak height divided by the number of scans and time per scan per channel, increases with the increasing pressure as shown in Figure 3a. Therefore, the experiment can still be run at a pressure of 120 mtorr without loss of counting rate.

Resolution is taken to be the full width at half maximum (FWHM) of the peaks in the electron spectra. The resolution depends on the kinetic energy of the electrons, since the analyzer is designed to have a fixed fractional resolution of slightly better than 0.1%. In addition, for photoelectrons, there is a contribution from the X-ray source. Typically, a peak width of 1.2 to 1.3 volts (12 to 13 channels) for photoelectron peaks is acceptable. For Auger electrons, there is no contribution to the resolution from the exciting radiation and the width for NeKLL Auger electrons is typically 0.6 volt and for ArLMM 0.3 volt. In this investigation, the linewidth is nearly independent of pressure up to 120 mtorr, as shown in Figure 3b. So the experiment can be operated at pressure 120

mtorr without influencing the resolution. The position of the peak maximum is related to the kinetic energy of the electrons. Increasing the pressure caused the position to shift significantly at pressure above about 80 mtorr as shown in Figure 3c.

In view of these results, a total gas pressure of 80 mtorr was chosen as giving a high counting rate without a shift in position. As a result, the sample together with neon as calibrant and argon as a check were run at a total pressure of about 80 mtorr.

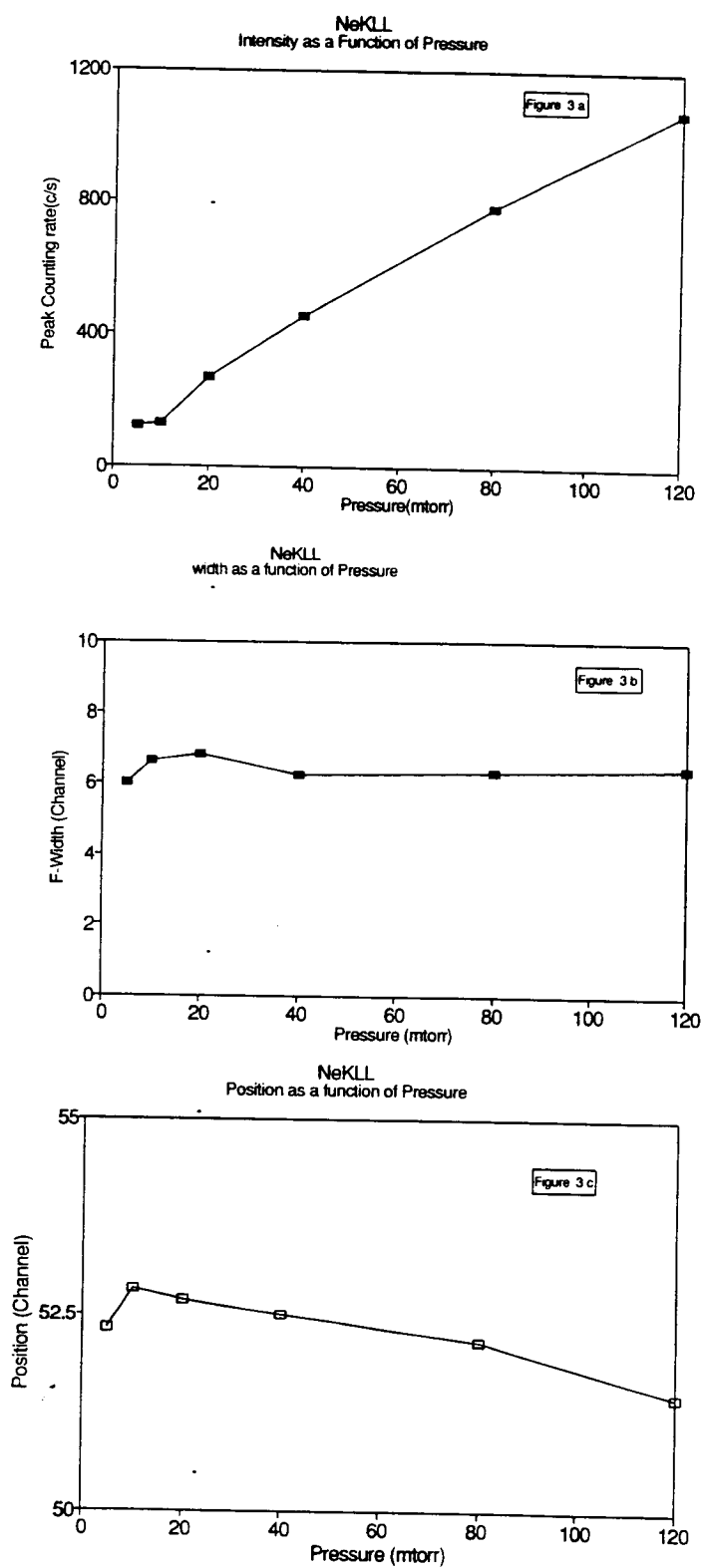


Figure 3. NeKLL as a function of Pressure.

C. Ketone Compounds

In this experiment, the samples investigated are acetone, 2-butanone, 2-pentanone, 3-pentanone, 3-methyl-2-butanone, 2-hexanone, 3-hexanone, 3-methyl-2-pentanone, 4-methyl-2-pentanone, 2-methyl-3-pentanone, 2-heptanone, 3-heptanone, 4-heptanone, 4,4-dimethyl-2-pentanone, 2,4-dimethyl-3-pentanone, 5-methyl-2-hexanone, 2-methyl-3-hexanone, and 2-octanone. Some of these were purchased directly from Aldrich and some, also originally from Aldrich, were donated from Dr Pastorek's lab. All samples were run four or five times with about 200 scans and 1000-2000 counts at the peak heights.

When running the sample, it is admixed with neon as a calibrant and argon as a check. Neon is used as calibrant because it has a widely spaced lines between Ne1s and Ne2s; therefore the calibration per unit energy has less uncertainty¹¹. Argon was included in each run to obtain an idea of the overall reproducibility of the measurements.

Beside the sample runs, the oxygen and carbon background spectra were checked. A typical background spectrum for this time period consisted of only randomly scattered points. It means there was no leaking of air and water vapor into the system. Small amounts of water present as an impurity in some of the samples caused an extra peak in some of the oxygen 1s spectra. Removing the water by using anhydrous magnesium sulphates gave spectra that were free of this contamination. However, the results obtained both with and without water in the sample were not different as shown in table I.

III. TREATMENT OF DATA

A. Least Squares Fittings

All spectra in the series of the ketones were fit using the LSMV program, written by T.X. Carroll. In the program non-linear least squares fitting is done with Voigt functions and a linear background. Theoretically, a photoelectron peak should have the shape of a lorentzian function. The finite resolution of the instrument, however, superimposes a gaussian function on top of the natural line shape. The voigt function, a convoluted gaussian-lorentzian function, fits the peak best.

The fitting procedure yields the peak position, peak area, as well as width parameters describing the relative contributions of gaussian and lorentzian shapes to the overall peak shape and total width of the peak. As an example, the carbon 1s and oxygen 1s of 3-pentanone fitted with the LSMV program are attached in the next page (Fig. 4).

The final steps to calculate the ionization energy of a particular core electron from the peak positions, focusing voltage, and kinetic energy of the electron of interest together with those for the calibration standard is done by the Calibration program consisting of both MICAL and NECAL subroutine programs.

B. Calibration

The energy conservation law for electron spectroscopy¹² must be refined for the purpose of experimental measurement.

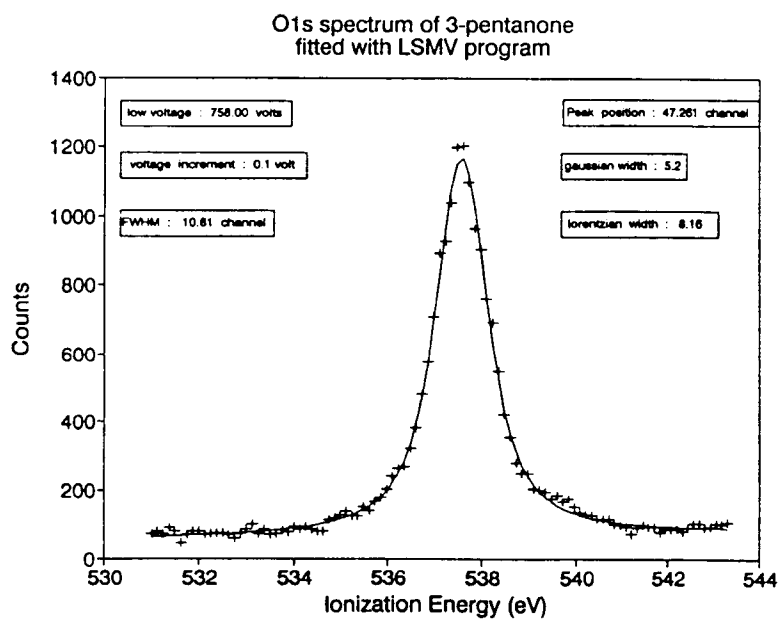
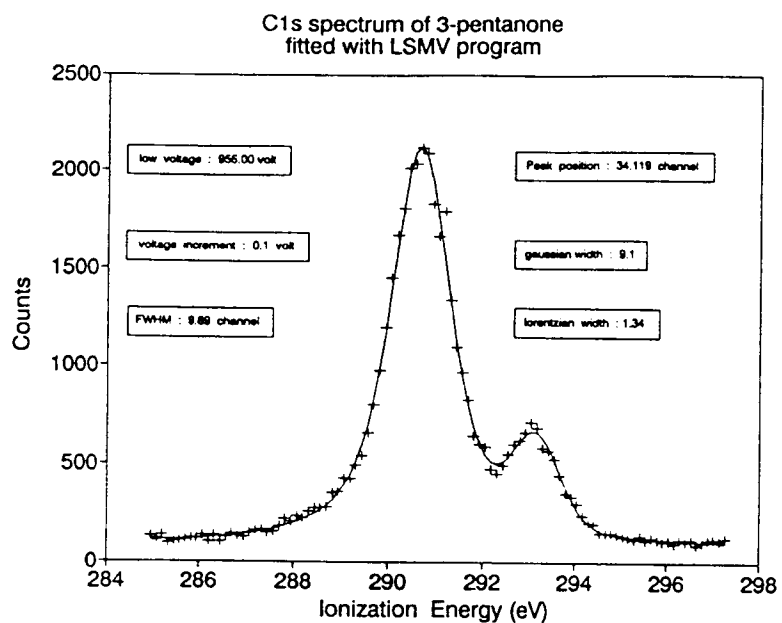


Figure 4. The carbon and oxygen 1s spectra of 3-pentanone fitted with the LSMV program

$$I = h\nu - \frac{mV^2}{2} - (-w + r_e) \quad (2)$$

Here I is the ionization energy, $mV^2/2$ is the translational energy of the ejected electron, and $h\nu$ is the energy of the X-ray source. The expression in the bracket can be considered as a correction factor¹³. The second term, r_e , refers to the recoil energy imparted by the ejected electron to the remaining ion. The fraction of recoil carried away by the ion when an electron is ejected from neon is, according to conservation of momentum, less than 0.003 % and much less than this for most molecules. The recoil energy is, thus, small but not negligible; its effect is included in the calibration program.

The work function, w is significant. When the electron passes from the gas cell into the analyzer, it passes from one potential field to another, and there is a resulting change in kinetic energy of the electron. The differences between the work function (or potential) of the gas cell and that of the rest of the analyzer may arise because of differences in materials, because of charging of the gas in the cell, and because electrons escape more rapidly than ions. The factors mentioned above make the absolute determination of the work function difficult. To get around the difficulties with the work function, neon as a reference is admixed with the sample that is to be measured. Since the various potentials will affect the kinetic energy of the ejected electrons of both sample and neon identically, a calibration of kinetic energy can be made with certainty.

For electrons entering the analyzer, the required focusing voltage is related to the

kinetic energy of the electron K by the expression,

$$V = C K + B \quad (3)$$

The spectrometer constant, C has been calculated from the dimensions of spectrometer to be $0.8019 \pm 0.0002 \text{ V/eV}^9$. The spectrometer has been slightly modified since then and the present calculated value is 0.803 V/eV^{14} . The existence of an offset voltage B in equation (3) reflects the change in the work function. Experimental values of C and B were determined from Ne1s and Ne2s calibration which are discussed below.

Neon calibration was accomplished by recording the neon 1s and neon 2s photoelectron peaks along with the Cls or O1s spectrum from a mixture of neon and sample gas. The focusing voltage was controlled and collected, and the data stored by using a personal computer and accompanying electronics¹⁵. The measured focusing voltages and known energies of the neon peaks sufficed to determine both C and B , allowing the energy corresponding to each sample peak to be computed.

C. Programs

Graphs of the measured spectra, least squares fits and calculation of the ionization energies were formerly made by using the chemistry department VAX computer. In anticipation of the demise of the VAX, we have rewritten these programs for a PC. Basically, the programs used in the PC are the same as the programs used in the VAX. The difference is in the program language, that is Lahey Fortran 77. Those programs are

RGPH3 program which graphs sample spectra, LSMVRS program which does the least squares fit to the data and plots a graph of the fitted data, and CALBTN program which calculates the spectrometer constant and kinetic energy of sample.

IV. RESULTS

Typical spectra for oxygen 1s and carbon 1s of several ketones are shown in Figure 5a and 5b. The oxygen 1s spectra (Fig. 5a) show only one peak, which arises from the carbonyl oxygen. The carbon 1s spectra of ketones (Fig. 5b) typically show two peaks, one from the carbonyl carbon (higher ionization energy) and the other from hydrocarbons (lower ionization energy). Although these hydrocarbon carbons are inequivalent and, therefore, have different core ionization energies, the differences are small and can not be resolved in these experiments.

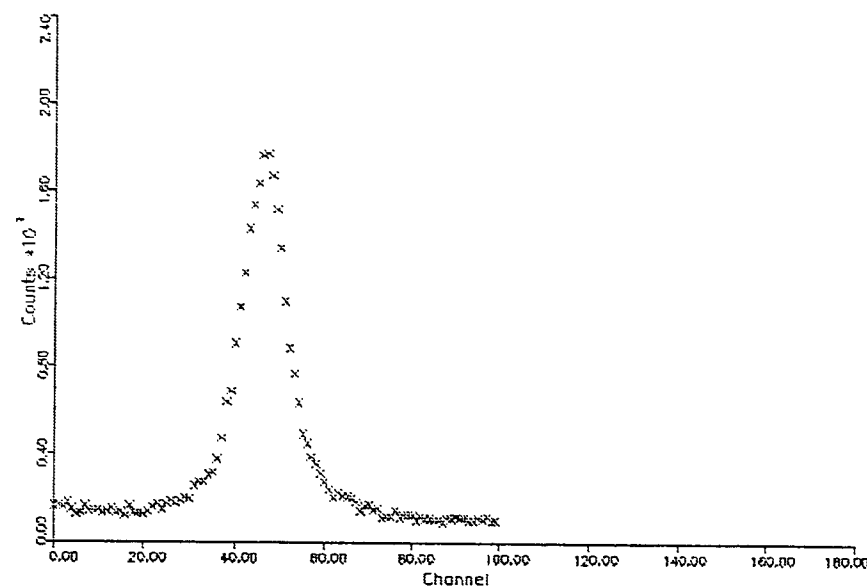
The oxygen and carbon gas phase core ionization energies of eighteen measured ketones are listed on table II. These oxygen and carbon ionization energies are ordered on the basis of the increasing connectivity number¹⁶. This is described in the discussion section.

Argon 2p spectra were measured with each sample as a check on the operation of the spectrometer and to obtain an idea of the precision of the measurements. From the table, the core binding energy for Ar2p_{3/2} is 248.60 eV. This is in good agreement with the results taken from the literature, 248.60¹⁷, 248.62¹⁸, and 248.63^{19,20} eV. These results indicate that our measurements are characterized by an accuracy of about 0.02 eV and a standard deviation of about 0.03 eV for each measurement. For a set of 4 or 5 measurements, the overall accuracy should be about 0.03 eV.

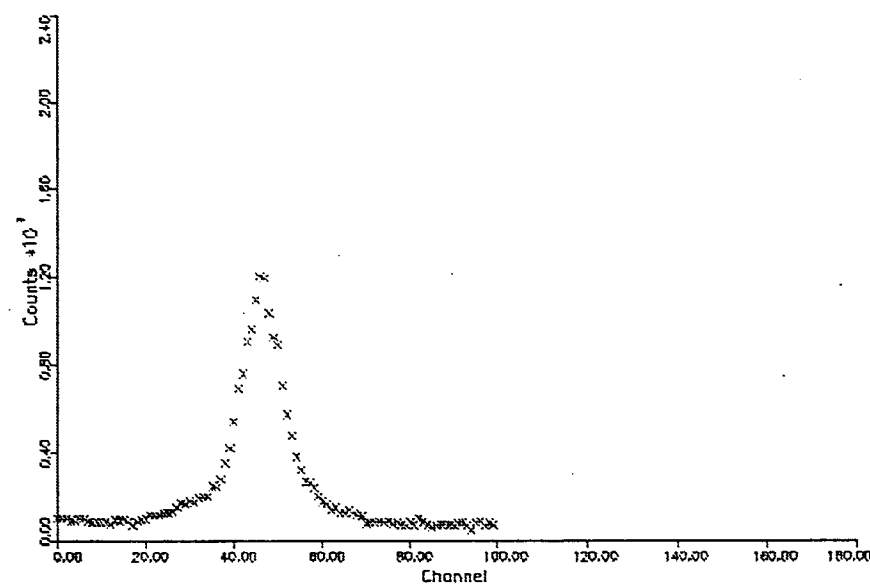
Only a few data on ketones are available in the literature. In general, our measurements are in good agreement with the literature results for both C1s and O1s

ketones as shown in table III. This literature values are known with an estimated uncertainty about 0.05 eV.

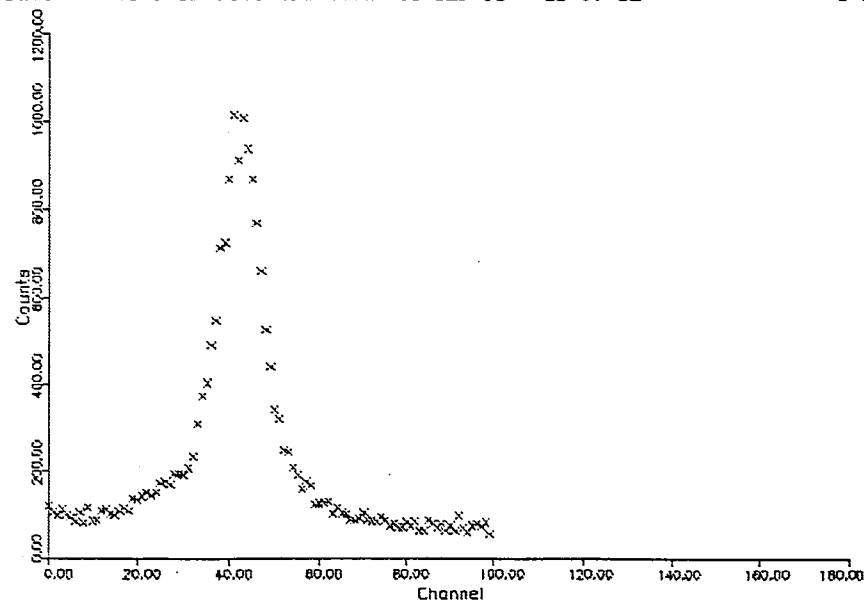
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4,4 DiMeth 2 Pentanone, 01s, 9.5KV, 40-50 mA, P=20, September08'93
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3-Heptanone, 01s, 9.5KV, 40-50mA, P=20, Feb02'94
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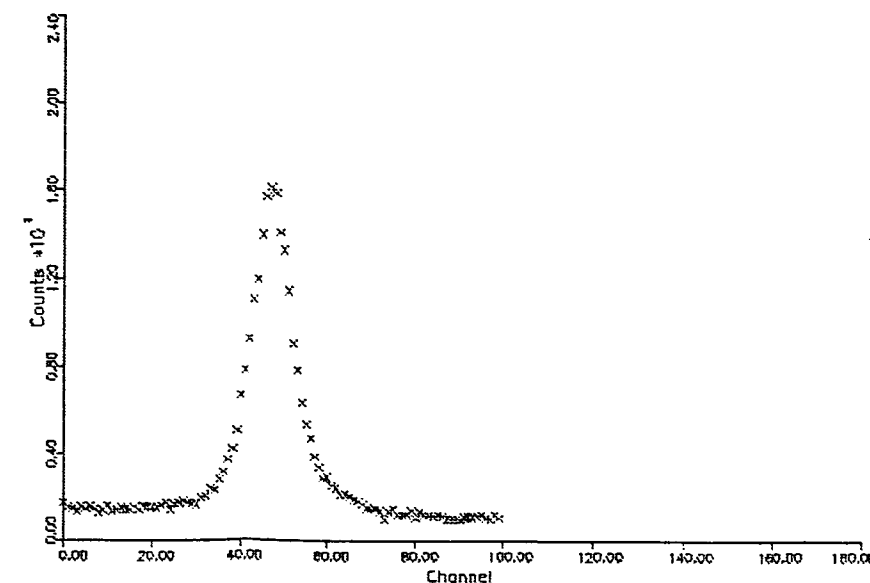
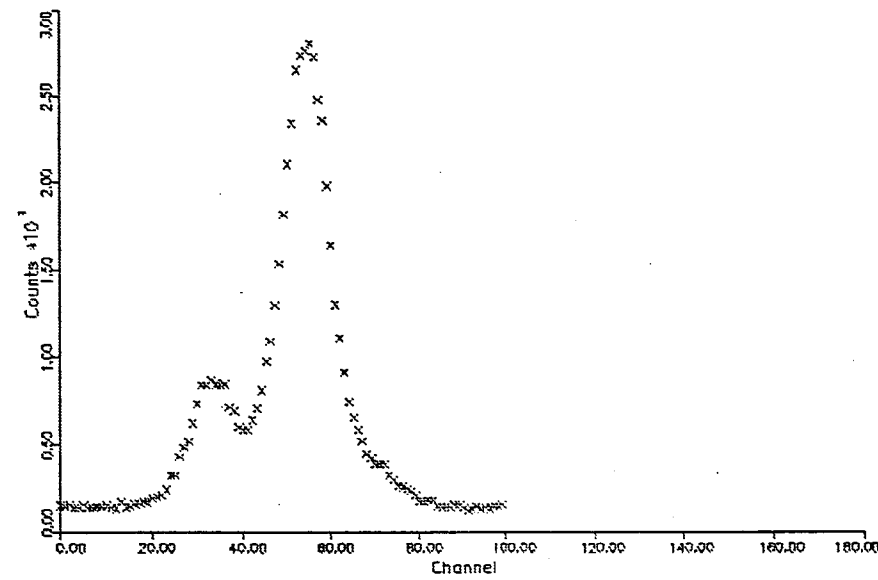
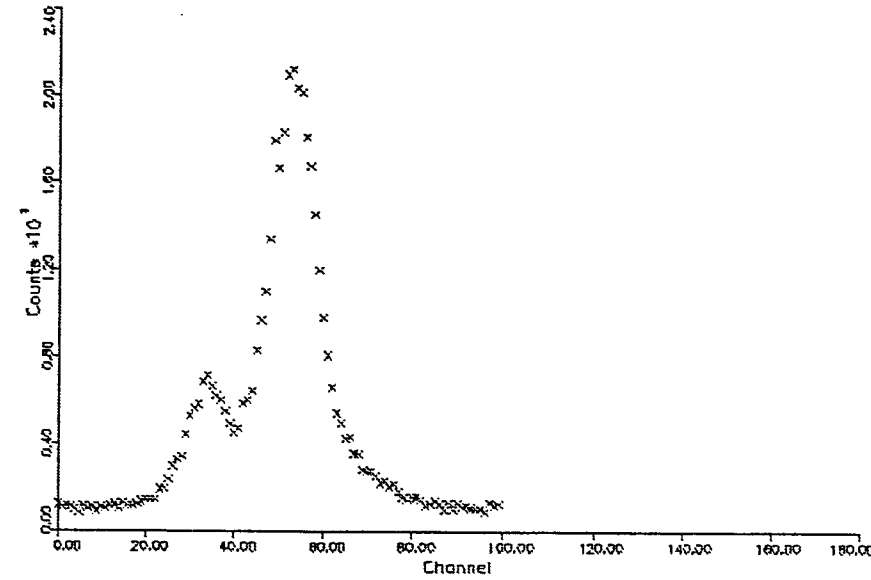


Figure 5a. Oxygen 1s spectra for carbonyl oxygen in ketones

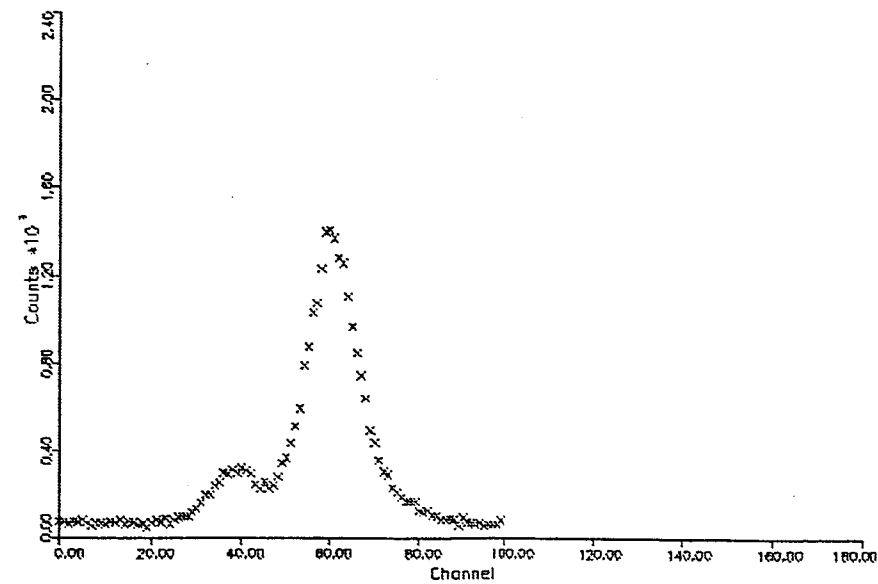
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4,4 DiMeth 2 Pentanone, C1s, 9.5KV, 40-50 mA, P=20, September08'93
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3-Heptanone, C1s, 9.5KV, 40-50mA, P=20, Feb02'94
 Lo Voltage Setting: 956.0 Voltage at Channel 1. : 955.851 V
 Voltage Increment : 0.100 Voltage at Channel 36. : 959.353 V
 Time/Channel/Scan : 0.100E+03 Voltage at Channel 56. : 961.352 V
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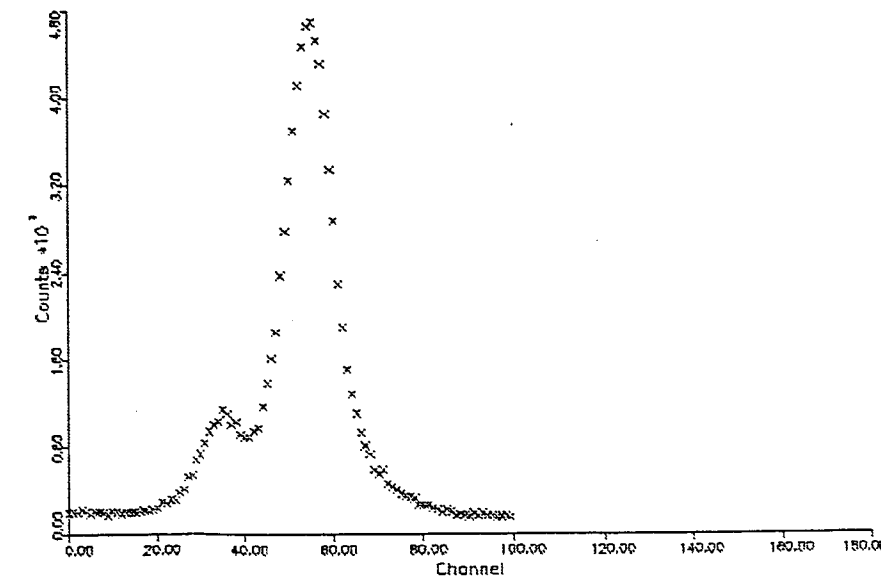


Figure 5b. Carbon 1s spectra for carbonyl carbon in ketones

V. DISCUSSION AND CONCLUSIONS

A. What does core ionization energy depend on?

As known, the core-ionization energy I , depends not only on the charge distribution in the neutral molecule but also on the charge rearrangement that happens when a core electron is removed. Therefore, by comparing with another molecule, the shifts in core ionization energy can be expressed as^{22,23}

$$\Delta I = \Delta V - \Delta R \quad (4)$$

where V is the potential energy of a unit positive charge at the site of the core electron in the neutral molecule, which reflects the charge distribution of the unionized molecule, and R is the lowering of the energy of the final state by rearrangement of electrons in response to the removal of the core electron.

The potential at the atom of interest is affected by the potential due to the charge distribution in the entire molecule, V can be expressed approximately as²⁴

$$\Delta V = \Delta \left(-\sum_k N_{ik} \left\langle \frac{1}{r_i} \right\rangle_k + \sum_{i \neq j} \left\langle \frac{q_j}{R_{ij}} \right\rangle \right) \quad (5)$$

where i refers to the atom of interest, j refers to the other atoms in the molecule, and q_j

represents the charges on the atoms. R_{ij} is the distance between atom i and atom j and $\langle 1/r_i \rangle_k$ is the expectation value of $\langle 1/r \rangle$ for orbital k . N_{ik} is the number of electrons in orbital k of atom i .

From equation (5), it can be concluded that the potential at the atom of interest depends not only on the valence population of that atom but also on the nature of the other atoms to which it is attached. Since the compounds of our experiments are all ketones, the surrounding atoms to which the atom of interest is attached are almost the same. Thus the difference in the potential among the molecules is not much. As a result, the major role in the shift of core ionization energy is the final state relaxation which depends on the polarizability.

Based on theoretical calculations, the relaxation energy or reorganization energy is defined as²⁵,

$$R = -\epsilon_{HF} - (E_{ion} - E_{mol}) \quad (6)$$

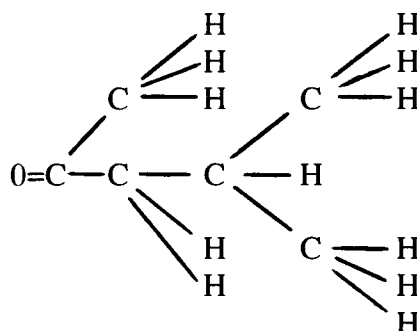
where ϵ_{HF} is the orbital energy of a Hartree-Fock calculation and E_{ion} and E_{mol} are the total energies of the ion and molecule. The term in parenthesis is the true ionization energy and $-\epsilon_{HF}$ is the ionization energy for an unrelaxed molecule (Koopmans' theorem approximation). Since relaxation depends not only on local electron density around the atom of interest but also on the charge redistribution in the whole molecule, the total molecular reorganization energy for an ionization in the core of an atom, R_{total} , can be expressed as,

$$R_{total} = R_{contr} + R_{flow} \quad (7)$$

where R_{contr} is the reorganization showing up from the contraction of the local electron density around the atom of interest, as a result of the increasing electron-nuclear attraction. R_{flow} is the additional reorganization energy which originates from the charge redistribution in the whole molecule.

B. Connectivity number

The charge redistribution that accompanies ionization is affected by geometry and size of molecule, and the electronegativity of atoms in the whole molecule. For instance, in larger molecules, core electron binding energies will decrease because of an increase on the relaxation energy since they have greater polarizability^{26,27}. In order to explain the chemical shifts, in fact, there are several empirical methods. One of these is based on the connectivity number, N_c , which is developed by Gasteiger and Hutchings²⁸. Based on their theoretical calculations, there is a correlation between the effective polarizability and connectivity number. In general, the way to calculate a connectivity number, N_c , is described in Fig 6.



Sphere n	1	2	3	4	5
No of atoms, b_n	1	2	6	3	6
$N_c =$	$1(1) + 2(0.5) + 6(0.5)^2 + 3(0.5)^3 + 6(0.5)^4 = 4.25$				

Figure 6. Calculation of Connectivity number, N_c , for 4-methyl-2-pentanone, starting at oxygen atom.

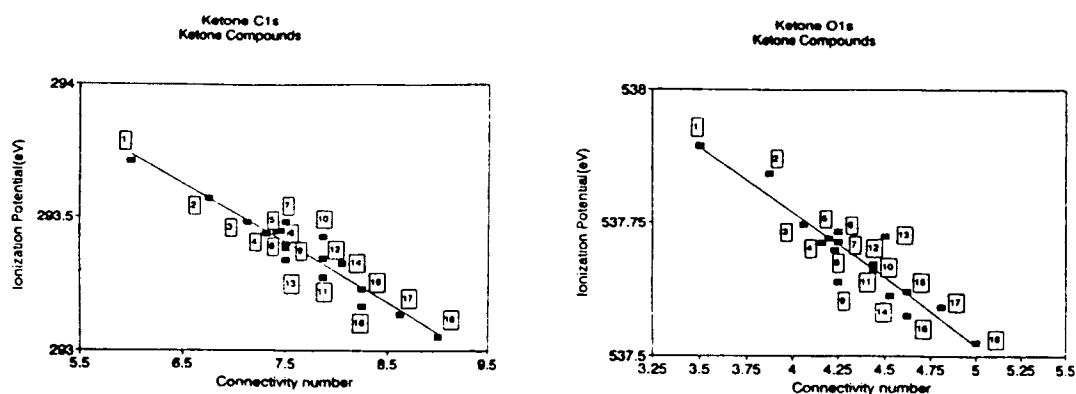


Figure 7. All ketones, ionization energy vs N_c for carbonyl carbon and oxygen 1s.

C. Correlations with Connectivity number

1. Overall Correlation

The general relationship between core-ionization energy and connectivity number, is shown in figure 7, where the measured ionization energies are plotted against connectivity number. From figure 7, we see there is, as expected, a decrease in core-ionization energies with increasing connectivity number. However, there is considerable scatter in the intermediate region. There is a trend to a better correlation if the data are subdivided into several categories, such as those in which the carbonyl group is symmetrically located as in molecules RCOR , 2-ketone compounds CH_3COR , in which we see the effect of changing the size of the alkyl group on one side of the carbonyl group, and 3-ketone compounds $\text{CH}_3\text{CH}_2\text{COR}$, where we have a series similar to that for 2-ketone compounds. Table IV shows the regression data for each of their subdivisions, and it can be seen that the values of R^2 are significantly improved by this subdivision. The various subdivisions are discussed in the following sections.

2. Correlations according to molecular type

a). Symmetrical ketone Compounds

In molecules, RCOR , in which the carbonyl group is symmetrically located, with $\text{R} =$ -methyl, -ethyl, -n-propyl, and -i-propyl, the connectivity number increases and the ionization energy decreases, as expected (see Fig. 8a and 8c). These results are explained as alkyl group, an inductive agent, will allow the electron to flow to the carbonyl functional group, therefore; molecule is more polarizable. Since ionization energy depends

mostly on the polarization of the molecule, the more polarizable molecule will increase the relaxation energy, which causes a corresponding decrease in electron binding energy.

Data are also available on two similar compounds, formaldehyde ($R=H$) and benzophenone ($R=phenyl$). These have been added to the plots in figure 8b and 8d. In figure 8b (carbonyl carbon 1s) we see that the point for formaldehyde fits well on the same correlation line as the other compounds and the point for benzophenone is reasonably close. However, for the oxygen correlations, these points fall far from the correlation line for the other four compounds (see figure 8c). In figure 8d we see that the point for formaldehyde falls well above the correlation line of figure 8c and the point for benzophenone falls well below it. The discrepancy for formaldehyde indicates less relaxation than expected and might be explained by a failure of the connectivity model to correctly predict the polarizability of remote hydrogens. However, even eliminating the contribution from the hydrogens does not bring formaldehyde to the correlation line for the other molecules. The discrepancy for benzophenone indicates a higher than expected relaxation energy. This can be accounted for by contributions to the relaxation from conjugation, which are present when the oxygen of benzophenone is core ionized, but not present in any other situation.

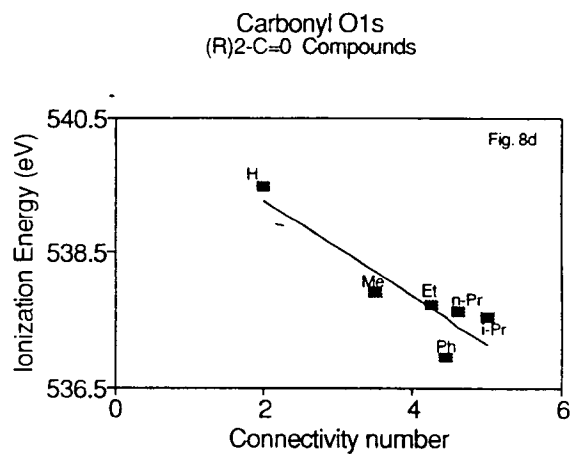
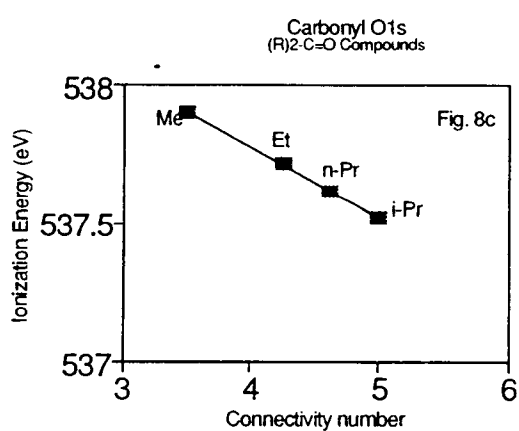
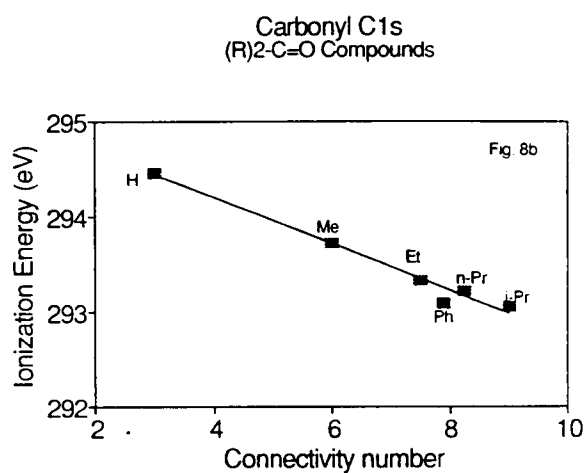
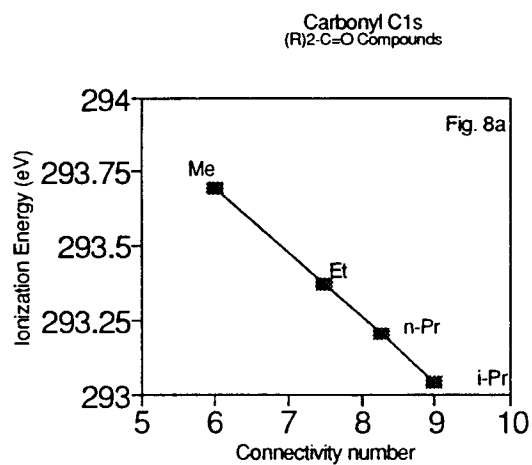


Figure 8. I.E vs N_c for carbonyl carbon and oxygen 1s of symmetrical ketones.

b. 2-ketone compounds, CH_3COR

In all 2-ketone compounds, R^2 for carbonyl carbon and oxygen 1s are 0.883894 and 0.872678 respectively. These are worse compared with the 2-ketones with normal alkyl substituents (see table IVa and IVb). So it is better to distinguish between normal and branched 2-ketones.

For 2-ketone compounds with R as normal alkyl substituents (see Fig. 9a and 9c), the carbon 1s ionization energy decreases with increasing connectivity number, except for $R = \text{-n-butyl}$, -n-amyl , and -n-hexyl which have about the same values. Figure 9b and 9d show the correlation including acetaldehyde. As we have seen for the symmetric ketones, the carbonyl carbon 1s ionization energy in acetaldehyde correlates well with the other carbon 1s ketone energies, but the carbonyl oxygen 1s ionization energy does not correlate well with the other oxygen 1s ketone energies. This result provides further evidence that the simple connectivity model does not correctly treat the effect of a remote hydrogen.

c. 3-ketone compounds

From figure 10, we see again that with increasing connectivity number the core ionization energy decreases. In addition, here we have the opportunity to see the effect of chain branching on the ionization energy. In table VIIa, we see that for a given number of carbon atoms, the substituent with the most branched chain has the largest shift. For example, in molecules $\text{CH}_3\text{CH}_2\text{COR}$, in which R is n-propyl and i-propyl, the shifts of the carbon 1s energies (relative to 3-pentanone) are 0.06 and 0.17 eV, respectively. The

addition of a methyl group at the end of the chain is less effective in shifting the ionization energy than addition of one close to carbonyl group.

A similar effect is seen in the heptanones, where the shifts of the carbon 1s energies relative to 3-pentanone are -0.01 eV for 3-heptanone ($R=n$ -butyl), -0.20 eV for 2-methyl-3-hexanone ($R=$ sec-propyl), and -0.28 eV for 2,4 di-methyl-3-pentanone ($R, R'=$ sec-propyl).

Inspection of Table VIIb shows that similar effects are seen for the oxygen 1s ionization energies.

These results show the effect of bringing the polarizable group closer to the core ionized center. This attenuation of the polarization with distance from the core hole is one of the important features included in the definition of the connectivity number.

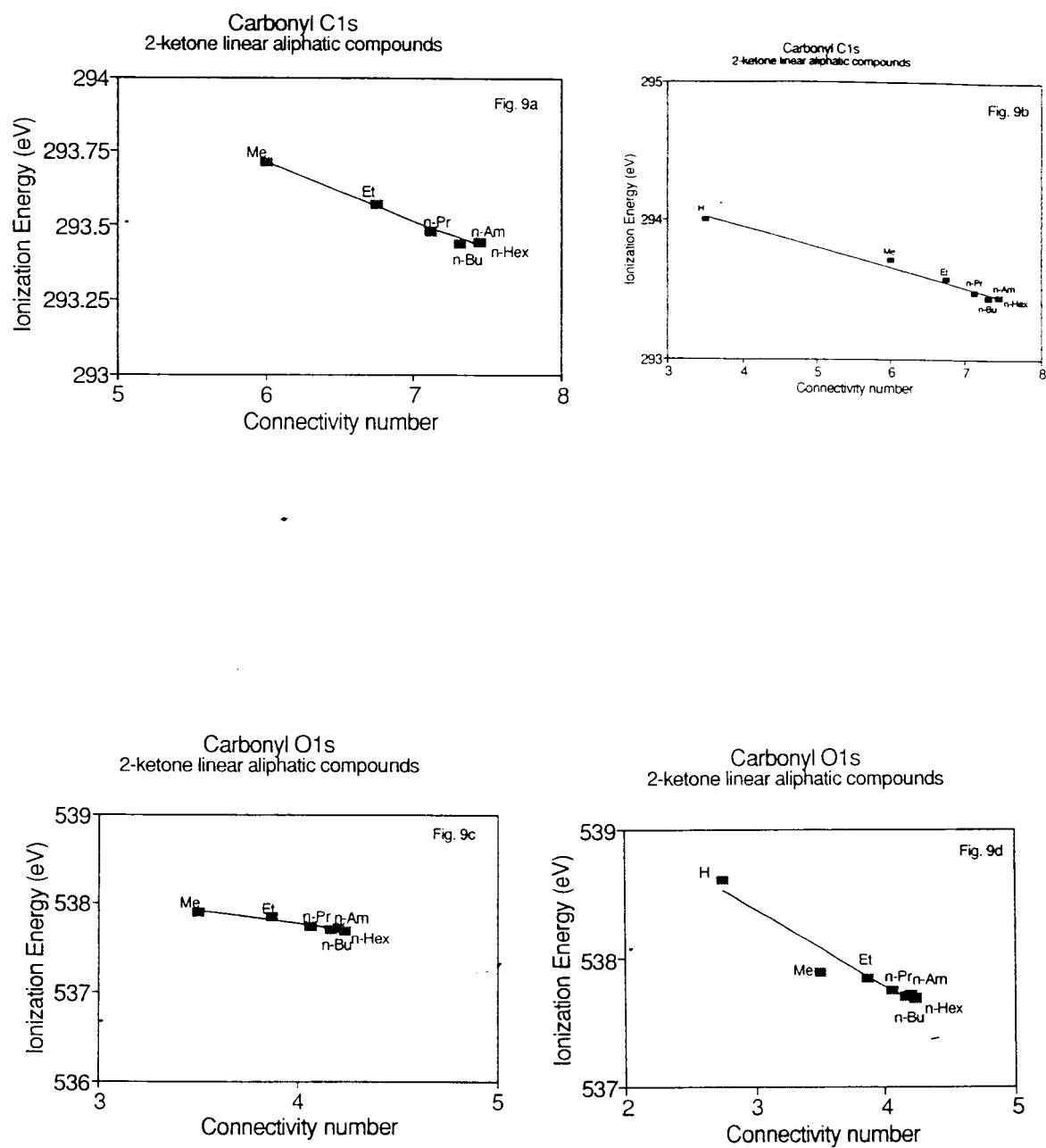


Figure 9. I.E vs N_c for carbonyl carbon and oxygen 1s of 2-ketones, CH_3COR .

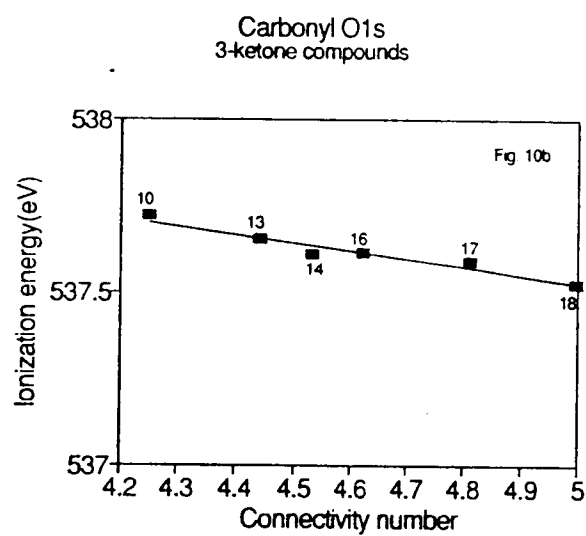
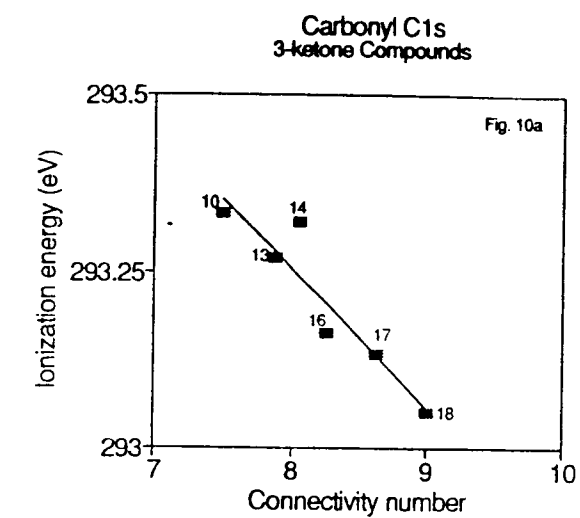


Figure 10. I.E vs N_c for carbonyl carbon and oxygen 1s of 3-ketone compounds.

D. Conclusions

The ketone compounds have been shown to provide a convenient series for the study of the effect of the molecular size on the core ionization energy and also to give information about correlation among molecular size, connectivity number, and the core ionization energy. As shown in Fig. 7 and table II.1 and II.2, there are some features that look strange. For instance, some compounds have the same connectivity number but different core ionization energies and some have different connectivity numbers with the same core ionization energy. Therefore, we conclude that there is only a rough correlation between connectivity number and core - ionization energy.

However, by subdividing the ketones into several categories based on the molecular type, we have a better correlation, with connectivity number.

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APPENDIX

Appendix 1.

Table I. O1s spectrum of 2-pentanone
both with and without water impurity

Water impurity	F-Width	I.E	K.E
Yes	11.84	537.758	948.789
No	11.56	537.750	948.797

Table II.1. Carbon 1s ionization energies for ketones

No	Compounds	Nc	C1s (eV)
1	propanone	6.0	293.713
2	2-butanone	6.75	293.571
3	2-pentanone	7.12	293.479
4	2-hexanone	7.31	293.437
5	2-heptanone	7.41	293.445
6	2-Octanone	7.45	293.445
7	4-methyl-2-pentanone	7.50	293.480
8	3-methyl-2-butanone	7.50	293.390
9	5-methyl-2-hexanone	7.50	293.377
13	3-pentanone	7.50	293.332
10	4,4-dimethyl-2-pentanone	7.87	293.422
12	3-methyl-2-pentanone	7.87	293.338
11	3-hexanone	7.87	293.268
14	3-heptanone	8.06	293.319
15	4-heptanone	8.25	293.225
16	2-methyl-3-pentanone	8.25	293.161
17	2-methyl-3-hexanone	8.62	293.131
18	2,4-dimethyl-3-pentanone	9.0	293.049

Nc= connectivity

Appendix 2.

Table II.2. Oxygen 1s ionization energies for ketones

No	Compounds	Nc	O1s (eV)
1	propanone	3.50	537.897
2	2-butanone	3.87	537.845
3	2-pentanone	4.06	537.745
4	2-hexanone	4.16	537.709
5	2-heptanone	4.20	537.718
6	2-octanone	4.23	537.695
7	4-methyl-2-pentanone	4.25	537.711
8	3-methyl-2-butanone	4.25	537.731
9	5-methyl-2-hexanone	4.25	537.636
10	4,4-dimethyl-2-pentanone	4.44	537.668
11	3-hexanone	4.44	537.657
12	3-methyl-2-pentanone	4.44	537.657
13	3-pentanone	4.50	537.721
14	3-heptanone	4.53	537.610
15	4-heptanone	4.62	537.573
16	2-methyl-3-pentanone	4.62	537.617
17	2-methyl-3-hexanone	4.81	537.589
18	2,4-dimethyl-3-pentanone	5.0	537.524

Nc = connectivity

Appendix 3.

Table II.3 Electron Spectroscopy Data of Some Ketone Compounds
(X-ray source : Al =1486 eV)

Compounds	Spectrometer Constant	Ionization energy		
		Ar 2p	*C1s	*O1s
propanone (FW=58.08)	0.804058	248.605	293.688	537.910
	0.804018	248.599	293.760	537.897
	0.804044	248.554	293.660	537.838
	0.804090	248.616	293.754	537.879
	0.803966	248.603	293.643	537.922
	0.804096	248.605	293.778	537.909
	0.804075	248.595	293.709	537.924
Average			293.713	537.897
Standard Dev.			0.048	0.028
2-butanone (FW=72.11)	0.804059	248.607	293.535	537.839
	0.804073	248.577	293.570	537.839
	0.804123	248.611	293.611	537.863
	0.804063	248.600	293.568	537.838
Average			293.571	537.845
Standard Dev.			0.027	0.010
3-methyl-2- butanone (FW=86.13)	0.804089	248.603	293.362	537.719
	0.804104	248.708	293.476	537.736
	0.804097	248.593	293.362	537.739
	0.804097	248.609	293.361	537.728
Average			293.390	537.731
Standard Dev.			0.049	0.008
2-pentanone (FW=86.13)	0.804092	248.581	293.508	537.767
	0.804084	248.600	293.534	537.758
	0.804003	248.565	293.478	537.715
	0.803975	248.502	293.399	537.727
	0.804118	248.641	293.483	537.753
	0.804126	248.596	293.469	537.750
Average		293.479	537.745	
Standard Dev.		0.042	0.018	

Compounds	Spectrometer		Ionization energies	
	Constant	Ar 2p	*C1s	*O1s
3-methyl-2-pentanone (FW=100.16)	0.804037	248.621	293.396	537.650
	0.804000	248.553	293.283	537.665
	0.804057	248.612	293.336	537.657
Average			293.338	537.657
Standard Dev.			0.046	0.006
4-methyl-2-pentanone	0.804214	248.594	293.477	537.704
	0.804107	248.627	293.496	537.721
	0.804107	248.612	293.466	537.709
Average			293.480	537.711
Standard Dev.			0.012	0.007
4,4-dimethyl-2-pentanone	0.804147	248.603	293.426	537.688
	0.804138	248.580	293.419	537.659
	0.804190	248.606	293.421	537.657
Average			293.422	537.668
Standard Dev.			0.003	0.014
3-pentanone (FW=86.13)	0.804094	248.613	293.338	537.743
	0.804054	248.599	293.320	537.705
	0.804095	248.757	293.328	537.705
	0.804095	248.605	293.340	537.731
Average			293.332	537.721
Standard Dev.			0.056	0.032
2-methyl-3-pentanone (FW=100.16)	0.804111	248.582	293.110	537.630
	0.804089	248.658	293.218	537.672
	0.804076	248.597	293.186	537.637
	0.804094	248.614	293.129	537.530
Average			293.161	537.617
Standard Dev.			0.043	0.053

Compounds	Spectrometer Constant	Ar 2p	Ionization energies	
			*C1s	*O1s
2,4-dimethyl- 3-pentanone (FW=114.19)	0.804153	248.640	293.015	537.525
	0.804113	248.628	293.034	537.530
	0.804103	248.620	293.069	537.515
	0.804101	248.640	293.162	537.523
	0.804110	248.626	293.014	537.518
	0.804106	248.612	293.054	537.540
	0.804100	248.625	293.023	537.541
Average			293.049	537.524
Standard Dev.			0.072	0.013
2-hexanone (FW=100.16)	0.804065	248.584	293.499	537.705
	0.804099	248.583	293.452	537.738
	0.804071	248.571	293.360	537.683
Average			293.437	537.709
Standard Dev.			0.058	0.023
3-hexanone (FW=100.16)	0.804166	248.602	293.248	537.659
	0.804094	248.627	293.280	537.655
	0.804083	248.597	293.277	537.657
Average			293.268	537.657
Standard Dev.			0.014	0.002
2-methyl-3- hexanone (FW=114.19)	0.804121	248.606	293.122	537.607
	0.804083	248.613	293.141	537.579
	0.804056	248.592	293.129	537.582
Average			293.131	537.589
Standard Dev.			0.008	0.013
2-heptanone (FW=114.19)	0.804075	248.587	293.476	537.744
	0.804066	248.602	293.431	537.690
	0.804090	248.605	293.428	537.719
Average			293.445	537.718
Standard Dev.			0.022	0.022

Compounds	Spectrometer Constant	Ar 2p	Ionization energies	
			*C1s	*O1s
3-heptanone (FW=114.19)	0.804129	248.619	293.377	537.613
	0.804078	248.626	293.405	537.594
	0.804084	248.613	293.355	537.567
	0.804103	248.606	293.398	537.625
	0.804073	248.585	293.246	537.628
	0.804125	248.604	293.237	537.620
	0.804088	248.615	293.218	537.624
Average			293.319	537.610
Standard Dev.			0.076	0.020
4-heptanone (FW=114.19)	0.804027	248.558	293.198	537.566
	0.804116	248.657	293.279	537.599
	0.804060	248.605	293.198	537.553
Average			293.225	537.573
Standard Dev.			0.038	0.019
5-methyl-2- heptanone	0.804110	248.602	293.391	537.711
	0.804084	248.620	293.454	537.677
	0.804092	248.579	293.285	537.521
Average			293.377	537.636
Standard Dev.			0.070	0.083
2-octanone (FW=128.22)	0.804089	248.605	293.488	537.727
	0.804061	248.603	293.478	537.717
	0.804099	248.618	293.399	537.689
	0.804131	248.610	293.434	537.690
	0.804152	248.598	293.437	537.658
	0.804155	248.642	293.432	537.691
Average			293.483	537.722
Standard Dev			0.005	0.005

Appendix 4.

Table III. Comparison of experiment and literature values for both C1s and O1s ketones.

Compounds	Literature ²⁰		Experiment	
	C1s(eV)	O1s(eV)	C1s(eV)	O1s(eV)
propanone	293.71	537.92	293.71	537.90
2-butanone	293.47	537.82	293.57	537.85
2-pentanone	293.40	537.77	293.48	537.75
3-pentanone	293.26	537.73	293.31	537.72

Table IVa. Regression results for C1s ketones

Group	Slope	Intercept	R-squared
All ketones	-.22638	295.0991	0.919654
Symmetric R-group			
no aldehydes	-.21832	295.0081	0.991228
with aldehydes	-.24536	295.1839	0.977323
Linear R-group			
no aldehydes	-.19246	294.8648	0.981389
with aldehydes	-.18169	294.7901	0.926209
3-ketones	-.19797	294.8366	0.969792

Table IVb. Regression results for O1s ketones

Group	Slope	Intercept	R-squared
All ketones	-.25007	538.7695	0.879087
Symmetric R-group			
no aldehydes	-.24980	538.7745	0.998818
with aldehydes	-.71104	540.6848	0.812112
Linear R-group			
no aldehydes	-.28778	538.9204	0.938814
with aldehydes	-.18169	540.1529	0.926209
3-ketones	-.23951	538.7234	0.937221

Appendix 5.

Table Va. Ionization energies for carbonyl carbon 1s of symmetrical ketone compounds, RCOR

Compounds	Nc	Ionization energy C1s	
		rel. to formaldehyde	Absolute I.E
Formaldehyde	3.0	-	294.470
propanone	6.0	-.757	293.713
3-pentanone	7.50	-1.138	293.332
Benzophenone	7.88	-1.370	293.100
4-heptanone	8.50	-1.245	293.225
2,4dimethyl-3-pent	9.00	-1.421	293.049

Table Vb. Ionization energies for carbonyl oxygen 1s of symmetrical ketone compounds, RCOR

Compounds	Nc	Ionization energy O1s	
		rel. to formaldehyde	Absolute I.E
formaldehyde	2.0	-	539.480
propanone	3.50	-1.583	537.897
3-pentanone	4.25	-1.759	537.721
Benzophenone	4.44	-2.540	536.940
4-heptanone	4.62	-1.863	537.617
2,4dimethyl-3-pent	5.00	-1.956	537.524

Appendix 6.

Table VIa. Ionization energies for carbonyl carbon 1s of 2-ketone compounds, CH_3COR , with R = normal alkyl

Compounds	Nc	Ionization energy C1s	
		rel. to acetaldehyde	Absolute I.E
acetaldehyde	3.50	-	294.000
propanone	6.00	-.287	293.713
2-butanone	6.75	-.429	293.571
2-pentanone	7.12	-.521	293.479
2-hexanone	7.31	-.563	293.437
2-heptanone	7.45	-.555	293.445
2-octanone	7.45	-.555	293.445
4-meth-2-pentanone	7.50	-.520	293.480
3-meth-2-butanone	7.50	-.610	293.390
5-meth-2-hexanone	7.50	-.623	293.377
4,4-dimeth-2-pent	7.87	-.578	293.422
3-meth-2-pentanone	7.87	-.662	293.338

Table VIb. Ionization energies for carbonyl oxygen 1s of 2-ketone compounds, CH_3COR , with R = normal alkyl

Compounds	Nc	Ionization energy O1s	
		rel. to acetaldehyde	Absolute I.E
acetaldehyde	2.75	-	538.620
propanone	3.50	-.723	537.897
2-butanone	3.87	-.775	537.845
2-pentanone	4.06	-.875	537.745
2-hexanone	4.16	-.911	537.709
2-heptanone	4.20	-.901	537.719
2-octanone	4.23	-.925	537.695
4-meth-2-pentanone	4.25	-.909	537.711
3-meth-2-butanone	4.25	-.889	537.731
5-meth-2-hexanone	4.25	-.984	537.636
4,4-dimeth-2-pent	4.44	-.962	537.668
3-meth-2-pentanone	4.44	-.973	537.657

Appendix 7.

Table VIIa. Ionization energies for carbonyl carbon 1s of 3-ketone compounds.

Compounds	Nc	Ionization energy C1s	
		rel. to 3-pentanone	Absolute I.E
3-pentanone	7.50	-	293.332
3-hexanone	7.87	-.064	293.268
2-meth-3-pentanone	8.25	-.171	293.161
3-heptanone	8.06	-.013	293.319
2-meth-3-hexanone	8.62	-.201	293.131
2,4dimeth-3-pent	9.00	-.283	293.049

Table VIIb. Ionization energies for carbonyl Oxygen 1s of 3-ketone compounds.

Compounds	Nc	Ionization energy O1s	
		rel. to 3-pentanone	Absolute I.E
3-pentanone	4.25	-	537.721
3-hexanone	4.44	-.064	537.657
2-meth-3-pentanone	4.62	-.104	537.617
2-heptanone	4.53	-.111	537.610
2-meth-3-hexanone	4.81	-.135	537.589
2,4dimeth-3-pent	5.00	-.197	537.524