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CONTENTS

I.	INTRODUCTION	1
II.	PHOTOELECTRON SPECTROSCOPY	1
	A. Type I - Retarding Potential Method	5
	B. Type II - Magnetic Analyzing Method	10
III.	ENERGY TRANSFER BETWEEN EXCITED HELIUM ATOMS AND ORGANIC MOLECULES . .	11
IV.	PHOTOIONIZATION AND ABSORPTION SPECTROSCOPY OF OLEFINIC MOLECULES . .	15
V.	CONCLUSIONS	16

Photoelectron Spectroscopy

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ABSTRACT

A photoelectron spectrometer is built which analyzes for the kinetic energy of the photoionized electrons by retardation techniques. The signal to noise ratio is very high due to the use of a new lamp and increasing the aperture of the system. The resolution is found to be extremely low and the sources of difficulties are discussed and are being eliminated.

I. INTRODUCTION

The current activities in the vacuum-ultraviolet spectral region consist basically of four different areas of study. They are as follows: Photoelectron Spectroscopy-Type I (Retarding Potential Method), Photoelectron Spectroscopy-Type II (Magnetic Analyzing Method), Energy Transfer Between Excited Helium Atoms And Organic Molecules, and Photoionization And Absorption Spectroscopy Of Olefinic Molecules.

A detailed report on the present status of these project follows. An overall evaluation of the past, present, and future work is found in the Conclusion section.

II. PHOTOELECTRON SPECTROSCOPY

The now well-established field known as Photoelectron Spectroscopy has to date supplied information with regards to higher ionization potentials which has revolutionized a number of different aspects of the ionization field of Chemical Physics. The first of these is the simple yielding of higher ionization potentials of a large number of molecules. The higher ionization potentials correspond to the ionization of inner (more stable) electrons, which heretofore has rarely been available. A few higher ionization potentials have been obtained for a limited number of small, simple molecules by the techniques of electron impact, photoionization, and spectroscopic Rydberg absorption lines. All of these methods suffer from the same basic limitation in that their spectra yield more information than is desired for the determination of the higher ionization potentials. The excess information manifests itself in the form of a phenomenon known as autoionization. Molecular autoionization is a resonance process by which a ground state molecule is excited by a collisional impact of a photon or an electron into an excited molecular

state above the first ionization potential. After a relatively short time (of the order of 10^{-12} to 10^{-14} seconds) the excited molecule breaks down into an electron and an ion (the energetics of these particles will depend on the energy manifold of the particular ion formed). Since autoionization is a resonance phenomenon the cross section for this process is usually much greater than that for simple photoionization, and hence in the region of an autoionization transition it is found that the current derived from or the absorption due to the ionizing radiation is greatly increased. The fact that the lifetime of the excited autoionizing level is so small means that the line width (halfwidth at half intensity) of the absorption band is rather large (of the order of 530 cm^{-1} or $6 \text{ \AA}$ at λ $1000 \text{ \AA}$). The presence of these broad bands tends to completely mask the entire ionization spectra.

Since in the above mentioned techniques the spectra are obtained by varying the energy of the photons or electrons, the autoionization bands are unavoidably present in their spectra. The absence of autoionization effects in photoelectron spectra, which is the main reason why this method has proven successful, is due to the fact that the energy of the exciting radiation is maintained at a fixed, rather large value (usually 21.21 eV). The photoelectron spectra are obtained by measuring the kinetic energies of the photoelectrons.

In addition to obtaining the higher ionization potentials it is found that much information can readily be acquired by inspecting the shape and structure of the electron distribution curves of the photoelectron spectra. As an example of the type of information that can be obtained from such an inspection, the following is given:

1. A comparison of the shape of the different ionization curves " within a spectrum can be suggestive as to whether a given ionization results from a strongly bonding or weakly bonding type of molecular orbital. For example, a sharper, cleaner ionization curve when compared with another would suggest an ionization from a molecular orbital of less bonding character.
2. If vibrational structure is present on an ionization curve it is immediately suggestive that the ionization process did not radically alter the ion. Hence, the ionized electron most probably did not come from a strongly bonding molecular orbital (e.g. a C-C sigma bond). The converse of this statement is also to be expected.
3. An inspection of the Franck-Condon factors of the vibrational bands can also be instructive. For example, from an inspection of the Franck-Condon envelope it is possible to decide whether the ionization resulted in the formation of an ion which is similar or different geometrically and dimensionally in comparison to the ground state molecule. That is, if the largest Franck-Condon factor is that of the 0,0 transition then one could deduce that the ion is geometrically and dimensionally very similar to the ground state molecule, and furthermore that the ionized electron came from a non- or weakly bonding molecular orbital.
4. Another piece of information that can lead to a better understanding of the ionization process is found in an analysis of the vibrational structure of the ion. If the vibrational structure of the ion can be assigned to a similar vibration in the ground state molecule, it is possible to postulate as to the origin of the

ionized electron from the fact that the ionizing electron will effect those vibrations which are more closely connected with the ionizing molecular orbital.

5. Lastly, the absolute value(s) of the ion vibrational structure when compared to its (their) counterpart in the ground state molecule can lead to an assessment as to the degree of bonding which exists in the molecular orbital of the ground state molecule. By way of an example, imagin the situation in which the energy of the excited vibration of the ion has not changed appreciably from that of the ground state molecule. Then in this case it could be said that the ionized electron was removed from a non- or only slightly bonding molecular orbital. Conversely, if the ion vibrational energy decreased appreciably, then it would be concluded that the ionized electron was removed from a moderately strong bonding molecular orbital (e.g. the ionization of a fairly strong bonding electron will yield an ion which will be enlarged in size compared to the ground state molecule and will tend to result in the lowering of the vibrational energies).

The sum total of all of this discussion on the analysis of the photoelectron spectra is in an ultimate attempt to assign the different ionizations with respect to their origin in the ground state molecule. The ordering and assigning of the molecular orbitals of the ground state molecule with respect to ionization is of paramount importance in attempting to theoretically describe molecular species. In addition, the difference in energy between the different ionization potentials yields directly the energy difference between the molecular orbitals in the ground state molecule. The importance of this information to the chemist and the physicist can not be over emphasized.

A. Type I - Retarding Potential Method

Approximately one year ago it was reported by this author that the construction of a new photoelectron spectrometer was nearly complete, and that higher ionization potential data was forthcoming. It now appears that that expectation was a trifle optimistic. The apparatus has been operational for over a year now as was reported earlier, but the achievement of well-resolved photoelectron spectra has been slow in coming.

In order that an effective description of this past years work be given here, a brief discussion of the general idea behind the apparatus as well as a basic outline of the operation of the apparatus is now given.

A photoelectron spectrometer consists of two basic components, a light source and a ionization chamber. The light source may be one of any number of different types such as microwave discharge, spark discharge, or electron bombardment. The ionizing radiation generally used is the 584 Å helium resonance line. This radiation is directed into an ionization chamber where it ionizes any gas present. The energy of the ionizing radiation (21.21 eV) is normally much greater than the lowest ionization potential of the vapors being studied, and hence a number of different ionizations occur. Nearly all of the excess energy above a given ionization potential results in a kinetically energetic electron. The result is that a number of different electron kinetic energy distributions are formed. The purpose of the photoelectron spectrometer is to measure these electron distributions. By doing so, the values for the different ionization potentials, which resulted in the distributions, can be obtained. For example, the difference between the electron distribution energies and the energy of the ionizing radiation yields directly the different ionization potentials (i.e. $21.21 \text{ eV} - KE_x = I_x$).

In the Type I Photoelectron Spectrometer the kinetic energy distributions are achieved by a retarding grid potential method. This method employs a spherical triode system which consists of a plate for the collection of electrons and a set of two inner grids for the selective retardation of energetic electrons. The retarding potential is achieved by smoothly varying the potential difference between the two inner grids with a sweep generator. When photoelectrons are formed within this triode system and smoothly acted upon by a retarding grid potential the collected ionization current displays sharp breaks on an otherwise smooth curve which correspond to the different ionization potentials (e.g. I_1 , I_2 , I_3 , etc.) of the molecule. The ionization potentials are obtained by subtracting the retardation potentials for the different breaks from the energy of the ionizing radiation.

It is a common practice when working with light of wavelengths less than $1050 \text{ \AA}$ to use an open capillary tube with differential pumping in order to get the light out of a lamp and into a chamber where it is to be used. This set up has two disadvantages in that both lamp and ionization chambers must be designed for continuous flow of gases and the amount of light emanating from the capillary is seriously reduced from what it is in the lamp. As a means of eliminating both of these difficulties a thin aluminum window ($2000 \text{ \AA}$ thick supported on a 80 mesh wire screen) was incorporated into the system between the light source and ionization chamber. The aluminum window possessed the added advantage of acting as a filter to radiation of wavelengths greater than approximately $900 \text{ \AA}$. This means that the potential ionizing Lyman α radiation of hydrogen ($1216 \text{ \AA}$) was completely filter out. Without the restriction of having to use an optical

capillary tube between the two chambers, the optical opening was set at 6 mm. The basic objectives in the above changes were in fact found to be met, but a number of disadvantages arose as a consequence of these changes which completely offset the advantages as will be exemplified below.

Using the above described apparatus, photoelectron spectra were obtained for a number of gases, which included argon, hydrogen, and benzene. The overwhelmingly single feature of these spectra was that they showed little or no structure on the smoothly decreasing current curves indicating poor resolution. Although these spectra were poorly resolved, they did yield the approximate values for the first ionization potentials (i.e. the first point at which no current was detected corresponded approximately to the first ionization potentials). It was therefore concluded that in a gross way, the apparatus did work.

The attempt to improve the resolution has lead this investigator through much literature and has resulted in a number of changes in the apparatus. Some of the more important causes for the lack of resolution as well as the changes that were made to alleviate the problems are enumerated below:

1. Homogeneity of retarding potential - this is important for the achievement of good resolution, for if it is not met the paths of the photoelectrons will be altered and their energies smeared out. It is mandatory that the triode detection system be free of water, oil, or other substances that can support space charge and thereby render the field inhomogeneous. Gold or platinum coating of the triode parts also helps to achieve a homogeneous potential, for

these metals are known to be poor space charge supporters.

2. Scattered radiation - the effect of scattered radiation is two fold. The first is to produce photoelectrons from metal and non-metal surfaces alike, which appears as background current. This current reduces the signal to noise ratio. The second is to create space charge on nonmetal surfaces which "drastically" alters the amount and energies of collected photoelectrons. To remedy the scattered radiation problem a number of things can be done. The first is to have the radiation beam focused such that it does not significantly diverge while it is within the triode system. This can be accomplished by first collimating the entering light through a "capillary" tube and second by installing a radiation exit tube in optical alignment with the entering tube but slightly larger in its inner diameter to accommodate for some divergence of the beam. A second measure that should be taken is to coat all surfaces with a blackening agent such "aqua dag", platinum black, or benzene soot. This helps to reduce multiple reflections of the ionizing radiation. Thirdly, and this is of extreme importance, as little non-conducting materials as possible should be exposed to direct or indirect radiation. This should be carried out to the extreme extent of coating the tips of the glass optical tubes with a gold or platinum film. It was found that this was the single most important cause for the lack of resolution.
3. Photoelectrons from aluminum window - this problem is unique to this apparatus and manifests itself in the form of a flood of electrons down the entering light tube. The effect of this is to (1)

lower the signal to noise ratio and (2) to enhance space charge effects in the very near vicinity of the photoionization. The seriousness of this effect is probably comparable to the space charge problem caused by scattered radiation incident on non-conducting materials as discussed above. The removal of the aluminum window eliminates this problem.

4. Magnetic shielding of triode system - the problem here arises from the earth's magnetic field as well as other stray fields. Its effect is to bend the nearly retarded electrons in a circular path which increases the total number of collisions experienced by the electrons with gaseous species in their attempt to be collected. These collisions destroy the discreteness of the electron energies and tends to broaden out the electron distribution. This can be remedied by surrounding the triode system with "Mu-metal".
5. Signal to noise ratio - in addition to the effects described above relating to the signal to noise ratio, other areas of difficulty are caused by such things as an unstable light source, magnetic and/or rf lamp noise, and the noisiness of the sweep generator. These problems, which are not of a serious nature, can be eliminated with proper adjustment of the equipment and sufficient shielding.

All of the above difficulties have been or are presently being remedied as described.

B. Type II - Magnetic Analyzing Method

Recently Turner has shown that photoelectrons formed in a photoelectron spectrometer can be analyzed for their kinetic energies by acting upon them with a magnetic field. The principle of the method is identical to that used in a mass spectrometer except that in a mass spectrometer one is normally observing positively charged species. This type of spectrometer differs in a number of ways with of Type I; they are listed below:

1. In the Type II system the photoelectrons are formed very near a slit which provides an opening into a 180° analyzer. The slit is so arranged that only photoelectrons with a velocity perpendicular to the direction of the light beam can enter into the analyzer. The reason for observing only perpendicularly directed photoelectrons is an attempt to improve resolution.
2. The detection of the photoelectrons is accomplished by employing a partical multiplier which is situated directly behind a second, focusing slit. This exit slit is located in the same plane as the entrance slit and at a distance of approximately 4 cm. from it.
3. The photoelectron spectra are obtained by varying the magnetic field, which is aligned parallel to the entering photoelectrons, in a smooth manner. The out-put current from the partical multiplier is displayed on the X-axis of an XY recorder. A measurement of the strength of the magnetic field is displayed on the Y-axis.
4. In the Type I spectrometer one observes all photoelectrons which have kinetic energies greater than any particular retardation potential, whereas in the Type II spectrometer one observes only

Energy Transfer Between Excited He Atoms and
Organic Molecules

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ABSTRACT

The transfer process between excited triplet helium atoms and benzene molecules resulting into benzene ionization has been demonstrated and is now being studied.

those photoelectrons which have a given kinetic energy, which is determined by the applied magnetic field. The result is that in the Type II spectrometer one obtains the photoelectron distribution profiles.

5. The resolution of the Type II spectrometer is an order of magnitude or so better than that of Type I. This is primarily due to the fact that better than 95 per cent of the photoelectrons are not being analyzed. The remaining photoelectrons are most likely swept into the analyzer without ever experiencing a single collision, thereby retaining the discreteness of their energies.
6. The Type II spectrometer, however, is more difficult to construct, develop, and maintain, so that the Type I spectrometer would still seem to be worthy of having if for no other reason than it can yield rough data quickly.

This investigator has recently embarked on the construction of a Type II photoelectron spectrometer, which will probably take upwards of two years to complete.

III. ENERGY TRANSFER BETWEEN EXCITED HELIUM ATOMS AND ORGANIC MOLECULES

The vast area of research known broadly as Energy Transfer is presently, as it has for many years, enjoying a considerable degree of interest and popularity. The main reason, of course, is that much information can be acquired about the energetics of atoms and molecules by studying their responses to energetic bodies in a more or less close proximity to them. Studies have shown that numerous types of systems exhibit energy

transfer, such as atom-atom, atom-molecule, molecule-molecule, ion-atom, and ion-molecule, all of which have been shown to occur in both the gaseous and condensed phases. In the first three examples a more or less resonance condition must be met in order for energy to be transferred between the two species, whereas in the last two examples the electron affinities of the two species are the most important factors.

The particular system of interest here is the transfer of energy from an atom to a molecule. As was stated above, this process is not a novel one, but what is new to this process is the possible resultant products, namely an atom and an ion. More specifically, the prospect for the following energy transfer scheme was envisioned:

whereby excited helium atoms in the 2^3S state (19.81 eV) interact with ground state benzene molecules in such a way that energy be transferred from the helium atoms to the benzene molecules. Subsequently, the benzene molecules, which now possess energy in excess of their ionization potential ($I_1 = 9.24$ eV), would break down into ions and electrons.

If such an energy transfer does occur, some questions that would be interesting to pose and attempt to answer are as follows:

1. To what extent would a matching of a higher ionization potential of the molecule to the energy of the excited helium atom play in determining the efficiency of the energy transfer?
2. Into what ionic states are the ions formed, and what subsequently happens to those ions (e.g. nature of degradation products)?

3. What emissions are observed, if any, from either the ions or recombined molecules?
4. What would be the measured "reaction" cross sections for a series of molecules and their implications?

With the above consideration in mind, an attempt was made to transfer energy from helium (2^3S) [hereafter "He triplet"] to benzene. The initial experiments employed a helium electron bombardment lamp for the production of the He triplets. A flow system was used, whereby the He triplets were swept out of the lamp chamber and into an adjoining reaction chamber where they were mixed with benzene vapor. In order to determine whether any ions were formed in this chamber, a series of potential plates were mounted within the reaction chamber and an electrometer installed in the circuit to measure the current. An elaborate baffling system was installed between the two chambers to insure that no ionizing radiation entered the reaction vessel. In addition, all potential reflecting surfaces were coated with "aqua dag".

Using a wide range of pressures of both helium and benzene gases it was found that current derived from benzene (approximately 10^{-9} amp) was definitely achieved. That is, no ionization current was ever measured in the absence of benzene, and that only over a relatively short range of helium pressures was there ever any ionization current. The fact that benzene is necessary for any ionization current is substantial proof that the current is derived from the benzene molecules. The problem of whether ionizing radiation is possibly the cause for the benzene ionization can readily be discounted from the fact that ionization current is measured only over a small helium pressure range, namely approximately 5-15 mm Hg.

The particular helium gas pressure range is understandable when it is realized that the lifetime of the helium triplets goer through a maximum in this range. It appears as though the distance the He triplets must travel (30 cm) in order to cause ionization which is detected verges on being too long for the pumping speed of this system. The lifetime of the He triplet decreases by two orders of magnitude in going from either 10-1 or 10-50 mm Hg. The lifetime of the He triplet is known to be 2×10^{-2} seconds at its maximum (10 mm Hg at 300°K).

In a further attempt to be certain that the ionization current requires the presence of the He triplets, an absorption cell was built into the reaction chamber such that the optical axis of the cell was situated immediately in front of the detecting potential plates and between the plates and the He triplet source. The idea behind this alteration was to attempt to detect He triplets by means of the known near infrared transition of He (2^3S) + 10829 Å → He (2^3P) simultaneously with the occurrence of ionization current. Such an observation would conclusively establish the validity of equation [1]. At present, work is continuing on attempts to observe the triplet → triplet absorption, which may possibly have been seen once. Some difficulty has been experienced in attempting to maintain a stable and reproducible He triplet source over the helium pressure range necessary for the observance of the ionization current. A typical discharge type lamp is now being employed in hopes of eliminating this problem.

Photoionization and Absorption
Spectroscopy of Olefinic Molecules

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ABSTRACT

The absorption spectra and the lowest photoionization potential are measured and compared for a large number of simple and cyclic olefins. The effect of the structure on the value of the ionization potential is examined.

During the year 1966-67, the vacuum ultraviolet absorption spectra and photoionization potentials of a number of compounds were studied, using the McPherson Model 225 vacuum monochromator. The compounds studied were primarily olefins, ranging from simple olefins to complicated diolefinic compounds like norbornadiene, . In addition, other compounds with structures similar to norbornadiene were studied.

To date, the primary interpretation of this data has been the correlation of their ionization potentials. The absorption spectra have proven more difficult to interpret, as will be discussed later.

The compounds studied were isolated and collected by A. Lee of Dr. S. Winstein's research group.

ABSORPTION SPECTRA

Most of the spectra have been obtained with a krypton discharge lamp, and cover a range from 2100 Å to 1300 Å.

The compounds studied were:

trans-3-hexene

1-octene

cis-di-t-butyl ethylene

trans-di-t-butyl ethylene

methylene cyclobutane

methylene cyclohexane

cyclopentene

cyclohexene

cyclopentadiene

1,3 cyclohexadiene

1,4 cyclohexadiene

1,4 cyclooctadiene

1,4 cyclononadiene

1,4,7 cyclononatriene

norbornene, bicyclo(2,2,1)hept-2-ene

norbornadiene, bicyclo(2,2,1)hept-2,5-diene

benzene

bicyclo (3,2,1)oct-2,6-diene

bicyclo(3,2,1)oct-2-ene

and a tricyclic compound,

, and two tetracyclics,

and

In benzene, or in a "normal" olefin, the electrons in the pi orbitals of the atoms involved in the double bond are orthogonal to, and therefore separate from, those in sigma orbitals, which hold together the framework of the molecule. Observed absorption maxima near 56 kilokysers in the absorption spectra of these compounds have been assigned as $\pi - \pi^*$, transitions located within this system. In order to study steric effects, and effects of enforced configuration, a program was begun, in which substituted and cyclic olefins were studied, with the hope that this particular transition and others would become more fully understood.

The more simple olefins studied, 1-octene and the like, display similar absorption spectra. In each, there is an absorption which begins to rise near 50-52 kK, with a maximum near 56-57 kK, and less absorption past 60 kK. This absorption is the one which has been assigned $\pi - \pi^*$, an assignment which is valid only in the case that one can meaningfully talk of such levels. In the instances of these compounds, such an assignment seems valid, for, near the double bond, the molecules can become planar, with no particular interaction between the double bond and the remainder of the molecule.

Beyond 70 kK, these compounds show a smooth, rising absorption or series of absorptions. This is due to transitions within the sigma-bonded parts of the molecule. Larger molecules, such as those with t-butyl groups, show more absorption in this

region than do the smaller ones, relative to the $\pi - \pi^*$.

Between these regions, there may or may not occur some sharper transitions which appear to be molecular Rydberg in nature. In trans-3-hexene, for example, there are three peaks which seem to fit the formula

$$E \text{ (cm}^{-1}\text{)} = 72,100 - R/(n + .15)^2$$

Methylene cyclobutane shows 5 members of the series

$$E = 73,840 - R/(n + .88)^2$$

Methylene cyclohexane also appears to show a molecular Rydberg series, as well as other structure. Benzene, of course, has much structure.

Molecular Rydberg transitions are similar to the atomic ones, in that electrons are excited to large orbits around the entire molecule, rather than being excited within the sigma or pi parts of the molecule. They seem to occur in the smaller, more symmetrical and rigid molecules studied. Apparently there is more overlap between the ground state orbitals and those of the Rydberg state. Larger molecules would require that electrons be further away to be in Rydberg orbitals, than would the smaller ones. Thus molecular Rydberg transitions would be more likely to be observed in smaller compounds.

The spectra of methylene cyclobutane and methylene cyclohexane are unlike those of the simple olefins. Methylene cyclobutane, for example, has two absorption peaks with maxima near 53 kK and 62 kK, neither of which are where the normal $\pi - \pi^*$ is expected. This is likely due to non-planarity

of the cyclobutane ring causing interaction of the pi and sigma levels, which mix and give the observed spectra.

The cyclic olefins, cyclopentene and cyclohexene, seem to be "normal". They seem to have $\pi-\pi^*$ transitions with maxima near 56 kK. Cyclopentene has a good deal of structure in its absorption, not all of which appears to be vibrational, but no molecular Rydberg series have been determined. Cyclohexene also appears to have structure in its spectrum, but the roughness of the continuum of the lamp used to record its spectrum precludes further analysis of the present spectrum. Both compounds have a broad rising absorption at higher energy.

The cyclic conjugated dienes, cyclopentadiene and 1,3 cyclohexadiene, have considerable structure in their spectra, plus $\pi-\pi^*$ transitions rising around 60 kK, with maxima near 65 kK. These are at higher energy than those in the simple olefins because they are higher transitions of those possible where there are several π states and several π^* states, because there are several double bonds interacting in these compounds. In both compounds, there are lower peaks in the 48-52 kK region, which may be lower $\pi-\pi^*$ transitions, or the much discussed "mystery" band. The ionization potentials of both compounds lie on the high energy slope of the $\pi-\pi^*$, and so ^{some} ~~any~~ molecular Rydberg absorption would lie in the same region as the strong absorption, and could be buried.

The cyclic, nonconjugated 1,4 dienes all show broad absorptions. The six carbon compound had several sharper peaks, but no others were observed throughout the series. The hexa-

diene shows a strong maximum at 64 kK, the heptadiene has one at 60 kK, while the octadiene has a less definite maximum near 57 kK. The nonadiene has no observable maxima in its spectrum, just a smoothly rising absorption. Thus, throughout the series, a particular transition becomes lower in energy and either less intense or broader, until, in the highest member of the series, no peak is observable. Because the heavier molecules are more flexible, they have less symmetry, which allows more transitions to appear, perhaps to the point where no particular transition can be picked out, as in 1,4 cyclononadiene. If 1,4 cyclohexadiene is considered as having D_{2h} symmetry, the lowest expected $\pi - \pi^*$ transition is symmetry forbidden. This would explain why only a higher than "normal" transition is seen. In 1,4 cyclooctadiene, the transition appears where most olefins have one; thus there is probably not much interaction between the double bonds in this larger molecule. The addition of more "sigma" parts to the molecule, lessening interaction, and lowered symmetry likely all contribute to the broad spectra observed as one looks at larger molecules. However, it does seem that there is interaction and splitting between the olefinic groups.

The first of the rigid molecules, norbornene, , has a smooth spectrum with maxima at 51 and 59 kK. Norbornadiene has several maxima and shows vibrational structure. The most notable maxima are around 55 kK and 63 kK. The eight-membered bicyclic monocolefin has a transition occurring around 54 kK, but no other notable maxima, while the diene , appears

to have broad maxima near 55 and 62 kK. The transitions in these compounds near 55 kK are undoubtedly to be classified as $\pi - \pi^*$ in nature, as are the diene transitions in the 62-65 kK range. If one considers two double bonds interacting and splitting each other one arrives at a picture in which there are several $\pi - \pi^*$ transitions, with various energies. It is, however, difficult to explain why norbornene should have two transitions of comparable intensity. There are the $\pi - \sigma^*$ arguments put forward by Robin; but it must be remembered that we are no longer dealing with purely planar systems, and that pi and sigma are no longer orthogonal and separable. This becomes more evident when the tetracyclics are examined.

The tetracyclics, and , have odd absorption spectra. The first has an absorption maximum near 55 kK, even though it has no formal double bonds; the other has what might be more normal for such a compound: just a constantly increasing absorption.

A case in between is that of the tricyclic . It has very little structure, but there is a small maximum near 56 kK.

Thus the absorption spectra of these compounds are very difficult to assign. The peaks seen are due to $\pi - \pi^*$ or perhaps it should be said mostly pi to mostly pi star transitions, for in these complicated molecules, pi and sigma can

no longer be thought of as separate. It is perhaps even surprising that many of the transitions occur near 55kK, the place where $\pi - \pi^*$ transitions occur in simple olefins. But, as the pi and sigma levels mix, the intensities of absorption bands change radically. Thus more analysis is needed before unambiguous assignments can be made.

1,4,7 cyclononatriene has absorption maxima at 51 and 60 kK, with the absorption rising to 72 kK, with a substantial falling off beyond this energy. This falling off of absorption beyond the ionization potential is unusual behavior, at least among the compounds studied.

Thus, among the olefins, the smaller compounds have absorption of a molecular Rydberg nature, as well as $\pi - \pi^*$ in nature, while the larger nonplanar molecules become featureless in absorption. In addition, the transitions in the larger molecules lose their identity as $\pi - \pi^*$, other transitions being mixed in, to the point at which even a mono-olefinic compound, such as norbornene, can have several absorptions of comparable intensities.

IONIZATION POTENTIALS

Photoionization potentials have been determined on the Mc Pherson model 225 in the following manner: Two parallel plates are mounted inside the absorption cell, just outside the path of light; one is connected to a battery, the other to an electrometer. As the spectrum is scanned upward in energy, the output of the electrometer is displayed on a strip chart recorder. When a plot is made of the amount of current divided by the amount of light absorbed versus the energy of the incoming light, the photoionization potential becomes evident. There is a steep upward slope, due to ionization from excited ground state levels (hot bands), followed by a gentler slope due to increasing ionization from excited ions. The plot is done on semilogarithmic paper, which linearizes the steep slope due to the Boltzman distribution of the ground state, and makes the break much more evident. The break in this curve is the photoionization potential.

The same compounds were studied as in the absorption spectra, with the addition of two compounds, and , both of which have the basic bicyclic structure of norbornene, but apparently have too low a vapor pressure at room temperature for their absorption spectra to be determined with the present cell. They did, however, yield enough current to obtain a fairly good photoionization potential.

Ionization potentials determined to date are:

trans-3-hexene	8.915 [±] .61 eV
1-octene	9.43 .01
cis di-t-butyl ethylene	8.68 .01
trans di-t-butyl ethylene	8.734 .01
methylene cyclobutane	9.16 .01
methylene cyclohexane	8.97 .01
cyclopentene	9.02 .01
cyclohexene	8.945 .01
cyclopentadiene	8.574 .01
1,3 cyclohexadiene	8.25 .03
1,4 cyclohexadiene	8.82 .02
1,4 cyclooctadiene	8.64 .02
1,4 cyclononadiene	8.60 .04
1,4,7 cyclononatriene	8.40 .04
norbornene	8.81 .02
norbornadiene	8.42 .02
7.79-7.94
8.62
8.44 .01
8.42 .01
8.24 .03
Benzene	8.25 .01
8.40 .03
8.40 .61

CYCLOPENTADIENE

T 583
A 949, 950

IP 1446A

8.574 eV

yield

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4 CYCLES X 70 DIVISIONS
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It can be seen that, in general, the larger the size of the molecule, the lower is its ionization potential. It is easier to pull one electron away from several atoms than from a fewer number. It is also apparent that the electron which is removed from the molecule comes from the double bond. Thus 1-octene, which has only one group larger than a hydrogen attached to the olefinic carbons, has a much higher (9.43 eV) ionization potential than does trans-3-hexene (8.94 eV), which is a smaller molecule, but one having two ethyl groups attached to the double bond. A further example is tetramethyl ethylene (2,3-dimethyl-2-butene), which has a well established IP (ionization potential) of only 8.30 eV.^{2,3,4} Thus, the more substitution at the double bond, the lower the ionization potential.

The effect of increasing the size of a group attached to a double bond diminishes rapidly, as can be seen from the following series taken from the literature.^{5c}

1-propene	9.73 eV
1-butene	9.58
1-pentene	9.50
1-hexene	9.46 and our value of
1-octene	9.43

This illustrates the point that it is what is near the double bond that is important in determining the compound's ionization potential.

An interesting pair of molecules studied are the cis and trans 2,2,5,5-tetramethyl-3-hexenes, the cis and trans di-*t*-butyl ethylenes ($\text{X} \begin{array}{c} \diagup \diagdown \\ \text{C}=\text{C} \\ \diagdown \diagup \end{array} \text{X}$ and $\text{X} \begin{array}{c} \diagup \diagdown \\ \text{C}=\text{C} \\ \diagdown \diagup \end{array} \text{X}$). Because of interference between the large *t*-butyl groups, one would expect that the cis compound would not be planar in the region of the double bond, and this should have an effect on the ionization potential. The ionization potentials determined were 8.68 eV for the cis compound, and 8.73 for the trans. These are both lower than the 8.945 eV of trans-3-hexene, due to the additional size of the groups, and the difference between the two is due to the interference. Because the cis compound cannot become planar, the pi level is destabilized, and it is thus easier to remove a pi electron. The more planar trans compound, while it shows the general lowering of IP due to the general size of the groups attached to the double bond, has a lower energy pi level than the cis compound, giving it a higher ionization potential.

Methylene cyclobutane, , presented interesting results. Its ionization potential, 9.16 eV, was very close to that of 2-methyl-1-butene, reported by Watanabe as 9.12 eV. The two compounds are of nearly identical structure and molecular weight, differing in that the cyclobutane ring of one replaces the methyl and ethyl groups of the other, forming a ring and reducing the molecular weight by one. Because the ionization potentials are so similar to one another, it appears that the strain incorporated in the molecule by the inclusion of an olefinic carbon in a four-membered ring has very little effect on the ionization potential of the molecule.

Incidentally, the cis and trans 2-pentenes, other compounds of the same molecular weight, have reported electron impact ionization potentials⁶ of 9.11 and 9.06 eV, slightly lower. These compounds have their two groups attached to different carbons of the double bond, whereas the other two had groups on only one of the carbons, even though the size of the groups was identical. In fact, the differences are even larger, for electron impact values of ionization potentials⁷ are invariably larger than photoionization values, for the same compounds. A further example is that of cyclopentene, which gave an IP of 9.02 eV. It thus appears that a group attached to each carbon of the double bond will give the compound a lower ionization potential than if the two were both on the same compound.

The other exocyclic olefin, methylene cyclohexane, had

an ionization potential of 8.97 eV, which is about what would be expected with respect to methylene cyclobutane. The ring again appears to have little if any effect on the IP.

Cyclopentene had an ionization potential of 9.02 eV, which is supported by other work. This number can be compared to those of the non cyclic 2-pentenenes stated above. It is lower, but, as stated, the 2-pentenenes have only electron impact IP's. It does not appear that the cyclic olefin has an appreciably different IP from comparable non cyclic olefins. Further support for this is the 9.945 eV IP obtained for cyclohexene. This is only about .07 eV lower than that of cyclopentene, a difference easily accounted for by cyclohexene's larger size. Trans-3-hexene, a straight chain olefin comparable to cyclohexene, gave the identical result of 8.945 eV. The other available data on 2 and 3-hexenes is electron impact data,³ with IP's between 9.1 and 9.2 eV. Since a typical difference between electron impact and photoionization is about .2 eV, it is evident that putting the double bond in a ring does not appreciably alter its ionization potential, at least for five and six membered rings.

The ionization potentials of conjugated dienes are lower than monoolefinic compounds in general. The 8.57 eV and 8.25 eV obtained for cyclopentadiene and 1,3 cyclohexadiene are good examples. Literature examples are 1,3 butadienes^{5a} (9.07 eV) compared with 1-butene^{5b} (9.58 eV). These results can be explained on a simple basis: if one considers two pi systems interacting strongly, they become split. One goes to

lower energy, the other to higher energy; both levels are still occupied. The lower level is now more stable than the lone double bond was, but the higher one is less stable. Ionization can occur from the higher level, and this accounts for a lower ionization potential. The more the two systems interact, the more they are split, and the more the ionization potential is lowered. Conjugated dienes have a great deal of interaction; therefore, their IP's are substantially lowered.

In the molecular orbital description, two double bonds are brought into interaction; they split into a lower orbital, on the left, and a higher one, on the right. Ionization occurs

from the higher level, giving a lower IP than the monoolefinic compound. It should be noted that the ionization potential

of 1,3 cyclohexadiene is .32 eV lower than that of cyclopentadiene, a much larger difference than one would expect from simply increasing the size of the molecule by one CH_2 group. Cyclopentene had an IP less than 1. eV higher than cyclohexene, and even propene had one only .15 eV higher than butene. It appears that orientational factors come heavily into play in these cases. The interaction in 1,3 cyclohexadiene must be stronger than that in cyclopentadiene, as the cyclohexadiene IP is lower than expected, indicating more splitting.

One might expect the same sort of behavior for interacting, nonconjugated dienes, except that the interaction should be weaker and should depend strongly on orientational factors. 1,4 cyclohexadiene had an IP of 8.82 eV, while the ionization potentials of the 1,4 cyclooctadiene and nonadiene were 8.64 and 8.60 eV, respectively. The heptadiene IP will be determined in the near future. The photoionization potentials of these compounds are lower than those of monoolefinic compounds of comparable size, and, more significantly, lower than those of compounds with more widely separated olefinic groups, such as 1,5 hexadiene (9.51 eV)⁶. The ionization potentials are, however, much higher than those of conjugated dienes. As an example, 1,4 cyclohexadiene has an IP of 8.82 eV, compared with 8.25 for the 1,3 compound and 8.95 for cyclohexene. This indicates that interaction is occurring even though the double bonds are not directly connected (conjugated).

Now the problem of what occurs in more rigid systems might be studied. What is the effect of putting olefins in a more fixed environment, and interacting them in more definite ways? Let us examine the ionization potentials of bicyclic and other more rigid systems, ones in which double bonds are held in close (interacting) proximity to one another.

Beginning with the more rigid bicyclic systems, norbornene, , has an ionization potential of 8.81 eV. This molecule can be looked at as cyclohexene with a 3,6 methylene bridge. The IP is .13 eV lower than that of cyclohexene, a result which is expected, due to its larger size, with more substitution near the double bond. This compound thus appears to be a "normal" olefin with regard to its ionization potential. The eight membered olefin, , however, has a somewhat lower IP, 8.62 eV, which cannot be accounted for by the addition of another methylene group to the molecule. The photoionization curves for this compound are very broad; it is possible that an impurity was present in the sample examined. Looking at the raw curve, aside from a long tail, the region near 8.75 eV would be a likely choice for the IP. This is more reasonable and in line with what would be expected for this compound. Another sample of this compound will be examined in the near future.

The two bicyclic dienes, and , had ionization

potentials of 8.42 and 8.44 eV respectively. Norbornadiene, , and be considered as 1,4 cyclohexadiene with a 3,6 methylene bridge. 1,4 cyclohexadiene had an IP of 8.82 eV, and the difference between it and norbornadiene cannot be explained by the additional size of the molecule. It must be due to the enforced interaction of the two pi systems, with splitting occurring as explained previously. Note that the eight membered diene, , had a higher ionization potential, 8.44 eV, than norbornadiene, despite the fact that it is a larger molecule. Apparently, because of the additional carbon, the olefinic systems are further apart, and thus interact less, leading to less splitting and therefore a higher ionization potential. The eight membered diene can be compared to 1,4 cycloheptadiene, which will be determined in the near future.

The larger, multi-bicyclic compounds, and , both had ionization potentials of 8.40 eV. They are very similar compounds; both have the same molecular weight, and both have interaction between the pi cloud of the double bond and some other part of the molecule. In both compounds, there are hydrogen atoms disrupting the double bond. This appears to have a marked affect on lowering the ionization potential, as such low IP's could not be accounted for by just the additional size of the molecules.

Tri- and tetracyclic compounds gave rather odd ionization potentials. 7.94 eV, 8.62 eV, and 8.24 eV were the results obtained. In two of these compounds, there are no double bonds formally, only cyclopropane rings. Cyclopropane rings are very strained, and for that reason are more

easily ionized than the usual sigma type systems, which normally have ionization potentials above 10 eV. One might expect that the most easily ionized systems would be those with the most strained bonding; thus it is not unexpected that has an unusually low ionization potential. Has a higher one, probably because the additional methylene group significantly reduces the strain in the structure. The more open tricyclic, , is between the others. These compounds cannot really be interpreted at present, as they have quite different structures and bonding from the olefins studied. Their ionization potentials are quite low, however, compared to saturated compounds in general, and even cyclopropane,^{5c} about 10.1 eV, in particular.

Benzene, pyridine, and the diazines have also been studied. Benzene, for example, had an IP of 9.25 eV, higher than what would be expected for such a large compound with three unsaturations. This is, however, in line with the stabilization expected in the pi levels of an aromatic system. The heterocyclics gave similar results.

Thus it is possible to correlate the ionization potentials of olefins in general on the basis of pi type systems, with the IP decreasing with increases in size of the molecule, and substitution on the double bond, with further decreases found in the cases of interactions of two or more double bonds. On the other hand, more compounds containing cyclopropane rings must be studied before their IP's can be correlated.

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V. CONCLUSION

The research presently being conducted in the vacuum-ultraviolet spectral region is in an active and productive state. Shortly, the Type I photoelectron spectrometer will be yielding a large amount of data on the higher ionization potentials and related information on azabenzenes, azanaphthalenes, and bicyclo compounds. All of these groups of compounds have already been studied from the photoionization and absorption spectroscopy stand point; the comparison of these data are anxiously anticipated. As for the Type II spectrometer, it will be in the construction and development stages for sometime in the future.

The Energy Transfer research is presently receiving considerable attention, for a major break through seems eminent. The photoionization and absorption spectroscopy study of the olefinic compounds will continue on its present course of measuring their spectra with the intension of trying to understand their absorption and photoionization processes through correlation of the series of molecules. In addition, attempts will be made in the future to obtain absolute measurement of absorption and photoionization cross sections. Furthermore, the lines already observed in the absorption spectra and thought to be molecular Rydberg lines will be investigated in depth by obtaining the absorption spectra using photographic techniques. The accurate determination of these lines and the ionization potentials which result are good spectroscopic information and should always be accumulated for any in depth study.