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Electronic Transitions in Mono-Olefinic Hydrocarbons.

Freddie Howard Watson Jr
Louisiana State University and Agricultural & Mechanical College

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ELECTRONIC TRANSITIONS IN MONO-OLEFINIC HYDROCARBONS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by

Freddie Howard Watson, Jr.
B.S., Louisiana State University, 1960
M.S., Louisiana State University, 1963
August, 1969

This dissertation is dedicated to my parents,
Mr. and Mrs. Freddie H. Watson, Sr., who have done
so very much for me. Certainly they are due much
of the credit for the completion of this work.

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ABSTRACT

Mulliken-Wolfsberg-Helmholz calculations which predict certain trends as methyl groups are appended to ethylene have been performed on the series of methyl substituted ethylenes. Predicted shifts in energy verify the assignment by Mulliken that the transition between 5 - 7 ev is $N \rightarrow R(3s)$ in nature.

However, spin-orbit coupling calculations indicate that the weakest olefin band at $\sim 2700\text{\AA}$ is too intense to be a triplet as is usually assumed. The shifts predicted by our computations for a $\pi \rightarrow \sigma^*(3s, 2s)$ transition agree well with the positions of these weak bands in the absorption spectra of liquid olefins.

That the predicted trends are believable is supported by the fact that the computations accurately predict shifts in ionization potential and in the $N \rightarrow V$ transition with increased methylation. They further predict that the excitation energy of the $N \rightarrow V$ transition is strongly dependent on molecular geometry as is observed experimentally.

On the basis of intensity calculations it is postulated that the $N \rightarrow R(3s)$ transition gains at least part of its intensity via vibronic stealing from the $N \rightarrow V$ transition. This mechanism explains the anomalies observed in the isotopic ratios and intensities of the Rydberg doublets in the ethylene spectrum. The validity of

the vibronic stealing mechanism is supported by the appearance of non-totally symmetric vibrations in the Rydberg spectrum of cyclopentene.

Computations on cyclic olefins predict the possibility of several low-lying π, π transitions, explaining the unusual broadening of the $N \rightarrow V$ transition in these molecules. Computations on methylenecycloalkanes and cycloalkylidenecycloalkanes reveal that σ -strain can lead to low-lying $\pi \rightarrow \sigma^*$ (valence-shell) transitions.

In general it is concluded that the 3s atomic orbital can mix appreciably, in both bonding and antibonding combinations, with valence-shell orbitals.

CHAPTER I

A HISTORY OF THE ELECTRONIC STRUCTURE AND ULTRAVIOLET ABSORPTION SPECTRUM OF ETHYLENE IN THE FORM OF AN ANNOTATED BIBLIOGRAPHY

This bibliographical history of the ethylene molecule and its electronic transitions is intended to be rather complete as regards experimental work. Only those theoretical papers which we feel are pertinent to the development of the presently accepted molecular orbital theory of the structure of the double bond are included. No attempt has been made to catalogue the vast number of papers which have appeared in the literature dealing with computations on ethylene. Only those are included which led to new assignments of electronic transitions. Being a history, references are presented in their chronological order of appearance in the literature.

We reproduce in each case the notation used in the individual paper without attempting to update any trends or convert to uniform notation. For example, in the coordinate frame used by Mulliken, one might find, depending on the time of the particular publication, the lowest allowed valence-shell singlet-singlet transition in ethylene being represented by any of the following:

$$\begin{aligned} & {}^1A \rightarrow {}^1B, {}^1B \leftarrow {}^1A, {}^1A_{1g} \rightarrow {}^1B_{1u}, {}^1B_{1u} \leftarrow {}^1A_{1g}, \pi \rightarrow \pi^*, \pi^* \leftarrow \pi, \\ & N \rightarrow V, V \leftarrow N, (b_{3u})(b_{2g}) \leftarrow (b_{3u})^2, (b_{3u})^2 \rightarrow (b_{3u})(b_{2g}), \\ & [x + x]^{-1} \rightarrow [x - x]^1, [x - x]^1 \leftarrow [x + x]^{-1}. \end{aligned}$$

All refer to the same transition.

- (1) J. Stark, W. Steubing, C.J. Enklaar and P. Lipp, "Die ultravioletten Absorptionbanden der wechselseitigen Bindung von Kohlenstoffatomen. I. Methodik, Äthylenbindung."

Jahrbuch der Radioaktivität und Elektronik, 10, 139-174 (1913).

- (1a) J. Stark und P. Lipp, "Einfluss der innermolekularen Relativbewegung auf die Intensität der Absorption und Fluoreszenz von Valenzelektronen."

Z. für Physik Chem., 86A, 36-41 (1914).

These two references report the first ethylene absorption spectrum to appear in the literature. It is very qualitative, showing the onset of absorption to be below 200 millimicrons and having two peaks at about 193 and 197 millimicrons.

- (2) R.S. Mulliken, "Electronic Structure of Polyatomic Molecules and Valence. II. Quantum Theory of the Double Bond."

Phys. Rev., 41, 751-758 (1932).

Mulliken first examined a CH_2 radical situated so that the z-axis bisects the H-C-H angle, the x-axis being perpendicular to the CH_2 plane. He described the ground state in terms of molecular orbitals as

$$1s^2[s]^2[y]^2[z]^2, {}^1\Gamma_1,$$

where $[s]$ is composed mostly of 2s, some 1s, and a little $2p_z$; $[x]$ of $2p_x$ only; $[y]$ of $2p_y$ and 1s; $[z]$ of $2p_z$, some 1s and a little 2s. The probable lowest excited state would be

$$1s^2[s]^2[y]^2[z][x], {}^3\Gamma_3.$$

Using the criterion of maximum overlap, he formed the ethylene molecule by situating two ${}^3\Gamma_3$ methylene radicals in the same plane so that their z-axis coincide. This allows the two [z] orbitals to form a strong σ -bond, the two [x] orbitals forming a less strong π -bond. This yields the ground state of plane ethylene as

$$1s^2 1s^2 [s]^2 [s]^2 [y]^2 [y]^2 [z+z]^2 [x+x]^2, {}^1\Gamma_{1g}.$$

This process also yields what are probably the two lowest excited states of plane ethylene:

$$1s^2 1s^2 [s]^2 [s]^2 [y]^2 [y]^2 [z+z]^2 [x+x][x-x], {}^3\Gamma_{4u}, {}^1\Gamma_{4u}.$$

He next considered what would happen if the two ${}^3\Gamma_3$ methylene radicals were brought together with their planes perpendicular. The [z] orbitals would overlap as before but the [x]'s would overlap not at all, leading to:

$$1s^2 1s^2 [s]^2 [s]^2 [y]^2 [y]^2 [z+z]^2 [x][x], {}^3\Gamma_3, {}^1\Gamma_2.$$

This non-bonding situation of the [x] orbitals in perpendicular ethylene, ${}^1\Gamma_2$, is probably more stable than the plane form, ${}^1\Gamma_{4u}$, because the [x-x] is more antibonding than the [x+x] is bonding. Thus one would expect the lowest allowed transition in ethylene to be ${}^1\Gamma_{1g} \rightarrow {}^1\Gamma_{4u}$ --the plane form, ${}^1\Gamma_{4u}$, then going over to a perpendicular ${}^1\Gamma_2$ state.

- (3) R.S. Mulliken, "Electronic Structures of Polyatomic Molecules and Valence. IV. Electronic States, Quantum Theory of the Double Bond."

Phys. Revs., 43, 279-302 (1933).

In the previous paper, Mulliken used group theoretical notation for the various electronic states without giving any details of group theoretical methods. He did so in this paper, treating CH_2 in the C_{2v} group, plane ethylene in $V_h (=D_{2h})$, perpendicular ethylene in $V_d (=D_{2d})$, and intermediate ethylene in $V (=D_2)$. In the standard notation, the lowest spin-allowed transition in planar ethylene should be ${}^1A_{1g} \rightarrow {}^1B_{1u}$.

- (4) C.P. Snow and C.B. Allsopp, "Electronic Levels of Polyatomic Molecules. I. Some Levels of the C = C Double Bond." Trans. Far. Soc., 30, 93-99 (1934).

This represents the first attempt to correlate Mulliken's method of molecular orbitals with experiment. They observed the ethylene spectrum to have diffuse structure with band centers as shown in Table I-1. They assigned this transition as the allowed ${}^1A \rightarrow {}^1B$ ($\pi \rightarrow \pi^*$) as suggested by Mulliken. The weakness of the transition ($\log \epsilon = -1.0 \rightarrow 2.0$) was explained by the fact that the absorption maximum must lie in the Schumann region beyond the limits of their measurements.

- (5) G. Scheibe und H. Grieneisen, "Über die Lichtabsorption einiger Kohlenstoffverbindungen in Schumann - Ultraviolett."

Zeits. f. Physik Chemie, 25B, 52-56 (1934).

These workers reported the spectrum of ethylene vapor as having structural peaks at the wave-numbers given in Tables I-1 and I-3. They were experimentally limited to the region above $1650\text{\AA}$ and made no attempt at analysis of the spectrum.

- (6) E.J. Hilgendorff, "Die Absorptionsspektren von Blausäure, Hydrazin, Äthylen und Ammoniak in Schumann - Gebiet und von Hydrazin in Quarzultraviolett."

Zeits. f. Physik, 95, 781-788 (1935).

This reference seems quite qualitative and is included only for completeness.

- (7) W.C. Price and W.T. Tutte, "The Absorption Spectra of Ethylene, Deutero-ethylene and some Alkyl-substituted Ethylenes in the Vacuum Ultra-violet."

Proc. Roy. Soc. (London), 174, 207-220 (1940).

This paper represents a major contribution to our knowledge of the ethylene spectrum. It was observed photographically from $2000\text{\AA}$ to $1000\text{\AA}$ at a pressure of 0.01 mm in a pathlength of 2 meters. Absorption starts abruptly at $1745\text{\AA}$ and has a well-defined pattern of bands down to about $1600\text{\AA}$. This pattern then repeats itself with some modifications and smaller intensities starting at $1390\text{\AA}$, which is followed at $1290\text{\AA}$ by an even weaker set of bands. The authors

observed that such behavior is typical of a system of electronic bands converging to an ionization limit. They chose as ν_o 's those bands which undergo a small shift to shorter wavelengths in going from C_2H_4 to C_2D_4 and constructed the following Rydberg series:

$$\begin{aligned}\nu_o^n &= 84,750 - R/(n + 0.91)^2 \quad n = 2,3,4,\text{etc.} - C_2H_4 \\ \nu_o^n &= 84,850 - R/(n + 0.92)^2 \quad n = 2,3,4,\text{etc.} = C_2D_4\end{aligned}$$

Using these formulae they obtained the following comparison between observed and calculated frequencies:

<u>C₂H₄ series</u>		<u>C₂D₄ series</u>	
<u>Obs.</u>	<u>Calc.</u>	<u>Obs.</u>	<u>Calc.</u>
57,340	54,660	57,620	55,068
71,790	71,790	72,020	71,978
77,600	77,572	77,710	77,708
80,215	80,198	80,360	80,316
81,625	81,608	----	----

The deduced ionization potential from the series limit is 10.45 ev in good agreement with electron impact values (10.80 ± 0.05 ev). They interpreted the series as being due to $^1A_{1g} \rightarrow [x+x] ns a_{1g}, ^1B_{3u}$.

These band systems consist of doublets. The main spacing between doublets (about 1370 cm^{-1} in the $1700\text{\AA}$ pattern) was assigned as the totally symmetric CC stretch, $\nu_t^{(1)} \parallel \parallel$, which has a value of 1623 cm^{-1} in the ground state of ethylene. That the value of $\nu_t^{(1)} \parallel \parallel$ increases to 1450 cm^{-1} in the $1390\text{\AA}$ pattern and higher patterns was said to be due to the fact that the first Rydberg orbital is a little

more antibonding than subsequent ones.

The spacing between the doublets is about 470 cm^{-1} in C_2H_4 and 300 cm^{-1} in C_2D_4 for the first three members of the Rydberg series. On the basis of its isotopic ratio (1.57) it was assigned as a twisting of the two CH_2 groups (δ vibration). The authors observed two unexplained phenomena:

1. In the $1740\text{\AA}$ system both components of the doublets are equally strong; in the $1390\text{\AA}$ system and higher ones, the long wavelength component is very much weaker.

2. They also expressed puzzlement at the fact that only one quantum of this δ vibration is allowed to appear at a time.

Table I-3 shows their observed frequencies in the $1700\text{\AA}$ pattern for C_2H_4 and C_2D_4 , along with reported ν_0 's for the Rydberg series.

The frequencies at 58,340, 59,650, 60,930, and $62,195\text{ cm}^{-1}$ for C_2D_4 were said to correspond to a new type vibration of about 730 cm^{-1} . Two other much weaker Rydberg series, starting at $65,880\text{ cm}^{-1}$ and $69,640\text{ cm}^{-1}$, respectively were observed going to the same ionization limit.

The authors commented that the weaker system at longer wavelengths consisting of a progression having a mean frequency separation of 750 cm^{-1} is probably $^1\text{A}_{1g} \rightarrow [\text{x}+\text{x}, \text{b}_{3u}]^{-1} [\text{x}-\text{x}, \text{b}_{2g}]^1$, $^1\text{B}_{1u}$ in nature. Since this occurs from a planar ground state to a perpendicular excited state, they expect a long progression of twisting vibrations. This progression does seem to manifest itself as a long, continuous absorption having a maximum at $1630\text{\AA}$ and

appearing as a background to the discrete Rydberg system starting at $1700\text{\AA}$.

- (8) H. Sponer and E. Teller, "Electronic Spectra of Polyatomic Molecules."

Revs. Mod. Phys., 13, 76-170 (1941).

In Table E on page 138 of this reference, the comment is made that there is no satisfactory explanation for the system of doublets in the Rydberg series of ethylene.

- (9) R.S. Mulliken and C.A. Rieke, "Molecular Electronic Spectra, Dispersion and Polarization, The Theoretical Interpretation and Computation of Oscillator Strengths and Intensities."
"Reports on Progress in Physics," Phys. Soc. (London), 8, 231-273 (1941).

On page 249 in Table 2 of this reference the theoretical oscillator strength for the $N \rightarrow V$ transition in ethylene is reported to be about 0.30.

- (10) R.S. Mulliken, "Structure and Ultraviolet Spectra of Ethylene, Butadiene, and Their Alkyl Derivatives."

Revs. Mod. Phys., 14, 265-274 (1942).

Mulliken agreed with Price and Tuttle that the broad continuum in ethylene (peak at $1630\text{\AA}$) is the $N \rightarrow V$ and that the sharp superposed bands are $N \rightarrow R$. The frequency of C=C stretch in the N, or ground, state is 1623 cm^{-1} . The frequency should be reduced by the removal of an electron from the bonding π -MO, but not

much effected by the presence of an electron in the Rydberg orbital. The observed frequency 1375 cm^{-1} in state R agrees with this explanation. In state V there should be a strong additional reduction in ν because of an electron in the π^* antibonding orbital, agreeing with the observed frequency of about 800 cm^{-1} .

He agreed that the assignment of the doublet spacing on the $N \rightarrow R$ of 470 cm^{-1} as a twisting vibration ν_4 (Mulliken here refers to the twisting vibration as ν_7 but in later papers uses Herzberg's designation, ν_4) agrees with a planar equilibrium form of the R state with greatly reduced resistance to twisting. The frequency in state N is about 825 cm^{-1} . However, selection rules for a planar molecule demand that this 470 cm^{-1} must correspond to two quanta of ν_4 .

- (11) J.R. Platt and H.B. Klevens, "Spectroscopy of Organic Molecules in the Vacuum Ultraviolet."

Revs. Mod. Phys., 16, 182-223 (1944).

In Table II on page 205 of this reference is presented a summary of spectral data on ethylene and deuterio-ethylene.

- (12) R.S. Mulliken and C.C.J. Roothan, "The Twisting Frequency and the Barrier Height for Free Rotation in Ethylene."

Chem. Revs., 41, 219-231 (1947).

By use of the semiempirical LCAO MO method, variation of the energy of the ethylene molecule on changing the angle between methylene groups was computed for the states N, T, V, and Z of the molecule and the normal state I of the ethylene positive ion. The treatment

involves the six outer electrons and takes into account the phenomenon of hyperconjugation. The existence of hyperconjugation partially offsets the loss of bond strength in 90° twisted ethylene.

For state N they obtained a potential function which is almost parabolic with a small positive anharmonicity. They computed a ν_4 ranging between 648 and 892 cm^{-1} depending on parameters used. This agrees very well with the infrared value of 800 cm^{-1} . The parameters chosen could not account for the small value (235 cm^{-1} for C_2H_4 and 145 cm^{-1} for C_2D_4) of ν_4 observed in the R state (taken to be the same in state I). They stated that for a suitable choice of parameters the experimental ν_4 could be matched. They further predicted an isotope effect on ν_4 (C_2H_4 against C_2D_4) of $2^{\frac{1}{2}}$ which is smaller than the observed ultraviolet ratio. This they said could be explained by a very strong positive anharmonicity, a condition which also could be matched by a suitable choice of parameters.

(13) J.R. Platt, H.B. Klevens, and W.C. Price, "Absorption Intensities of Ethylenes and Acetylenes in the Vacuum Ultraviolet." J. Chem. Phys., 17, 466-469 (1948).

This represents the first attempt to measure the absolute intensity of the ethylene absorption. Using a hydrogen arc source and photographic detection, they could not go beyond $1550\text{\AA}$. Below this wavelength they estimated the intensity from reproductions of Price's previous work which indicated that the intensity goes nearly to zero at $1400\text{\AA}$. For the $\text{N} \rightarrow \text{V}$ transition they reported the absorption maximum at $\lambda_{\text{max}} = 1625\text{\AA}$ ($\nu_{\text{max}} = 61500$) with $\epsilon_{\text{max}} = 15,000$ and a width

of $5,200\text{ cm}^{-1}$. The integrated area yielded an f-value of 0.34 ± 0.15 which agrees well with the theoretical value of Mulliken and Rieke.

They were able to measure only the first two doublets of the Rydberg and found the second pair to be about 0.8 as intense as the first. For the first they report $\lambda_{\text{max}} = 1743\text{\AA}$, $\nu_{\text{max}} = 57360$, $\epsilon_{\text{max}} = 5,500$, and width = 230 cm^{-1} . For the second, $\lambda_{\text{max}} = 1729\text{\AA}$, $\nu_{\text{max}} = 57840\text{ cm}^{-1}$, $\epsilon_{\text{max}} = 3,000$ and width = 230 cm^{-1} . The other three doublets were sketched in by comparison with Price's reproductions. They estimated that the total f-value of the group of five is three or four times the f-value of the first doublet, or about 0.03 ± 0.01 .

(14) D.P. Craig, "Polar Structures in the Theory of Conjugated Molecules. I. Identification of the Ethylene π -electron States."

Proc. Roy. Soc. (London), A200, 272-283 (1950).

At this point in the history some confusion existed as to whether the structured bands at the onset of absorption were part of the $N \rightarrow V$ progression or a separate electronic transition. The latter seemed analogous to the case of alkyl substituted ethylenes where a separate transition definitely occurs at lower energy than the $N \rightarrow V$. Snow and Allsopp assigned it as the $N \rightarrow T$ transition associated with the $N \rightarrow V$. Mulliken conceded that this assignment might be correct.

Using a valence-bond treatment and an augmented basis set containing polar structures as well as the ordinary non-polar one, Craig assigned the weak bands ($\sim 2000\text{\AA}$) as being ${}^1A_g \rightarrow {}^1A_g$, i.e. the double excitation $(\pi)^2 \rightarrow (\pi^*)^2$. The broad band peaking at

$1630\text{\AA}$ was taken to be $^1A_g \rightarrow ^1B_{1u}$ ($\pi \rightarrow \pi^*$).

- (15) P.G. Wilkinson and H.L. Johnston, "The Absorption Spectra of Methane, Carbon Dioxide, Water Vapor, and Ethylene in the Vacuum Ultraviolet."

J. Chem. Phys., 18, 190-193 (1950).

Ethylene was photographed in absorption on six plates from 1430 to $2000\text{\AA}$ at pressures from 0.02 to 0.4 mm. The broad continuum has a maximum value of absorption coefficient α of about 800 at $1614\text{\AA}$. This compares with a value of $\alpha = 1600$ at $1625\text{\AA}$ as reported by Platt, Khevers, and Price. They calculate for the $N \rightarrow V$ transition an oscillator strength of 0.30. Adjacent to the maximum they reported strong bands at 1652, 1665, 1689, 1729, and $1744\text{\AA}$.

- (16) W.E. Moffitt, "The Ultra-Violet Spectrum of Ethylene."

Proc. Roy. Soc. (London), A63, 1292 (1950).

Using a modified ASMO theory, Moffitt predicted a $^1B_{1u} - ^3B_{1u}$ splitting in ethylene of 1.1 ± 0.3 ev. He further found the excited 1A_g state of Craig to be at least 7 ev above the $^1B_{1u}$ state. Thus he agreed with Snow and Allsopp that the weak diffuse absorption at $\sim 2000\text{\AA}$ is $^1A_g \rightarrow ^3B_{1u}$, the broad continuum (peak at $1630\text{\AA}$) is the $^1A_g \rightarrow ^1B_{1u}$.

- (17) C. Reid, "Observation of Discrete Bands in the Near Ultraviolet Absorption Spectrum of Liquid Ethylene."

J. Chem. Phys., 18, 1299-1300 (1950).

The absorption spectrum of liquid ethylene at 120°K was run

in the range 2000 to 4000Å. With a path of 1.25 meters the continuous absorption at 2000Å was seen to extend to about 2600Å. Between 2600 and 4000Å in a pathlength of 2.5 meters bands were observed at frequencies given in Table I-4. They have an average spacing of 995 cm^{-1} similar to the spacing in the region of 2000Å, but of much lower intensity ($\alpha = 10^{-4}$).

Reid assigned this transition as the $T \leftarrow N$ which is both spin forbidden and strongly Franck-Condon forbidden in the region observed. The phosphorescence could not be observed in the region from 3000Å to 10,000Å. He suggested such emission would probably lie in the infra-red beyond the photographic region.

He noted that another possible assignment would be $V \leftarrow N$ where the V state is in the stable perpendicular form. Such a transition is highly Franck-Condon forbidden.

(18) A.D. Walsh, "The Electronic Orbitals, Shapes, and Spectra of Polyatomic Molecules. Part IX. Hexatomic Molecules: Ethylene."

J. Chem. Soc. (London), 1953, 2325-2329.

Walsh suggested that the first excited state of ethylene (triplet or singlet) should have (i) a pyramidal arrangement of the bonds about each C atom, (ii) one CH_2 twisted relative to the other through 90° about the C-C bond, and (iii) each C atom possibly slightly out of the mirror plane that bisects the HCH angle of the other CH_2 group. He confirms that the lowest energy singlet-singlet transition is $----(b_{3u})(b_{2g}), {}^1B_{1u} \leftarrow ----(b_{3u})^2, {}^1A_{1g}$. In light of

his expected shape of the $^1B_{1u}$ state he expects the following vibrations might appear in the transition:

- (i) the C-C valence vibration, $\nu_2^{a_g}$ (1623 cm^{-1} in the ground state).
- (ii) the $\text{CH}_2\text{-CH}_2$ twisting vibration, $\nu_4^{a_u}$ (1027 cm^{-1} in the ground state, previously taken as 800 cm^{-1} by Mulliken and others).
- (iii) one or both of the out-of-plane bending vibrations, $\nu_7^{b_{1u}}$ and $\nu_8^{b_{2g}}$ (949 and 943 cm^{-1}).
- (iv) one or both of the in-plane deformation vibrations, $\nu_{10}^{b_{2u}}$ and $\nu_6^{b_{1g}}$ (995 and $1050(?)\text{ cm}^{-1}$).
- (v) one or both of the CH_2 deformation vibrations, ν_3 and ν_{12} .
- (vi) one or both of the CH stretching vibrations, ν_1 and ν_{11} .

He concludes that ν_2 and ν_4 are most likely, but all the above are possible.

(19) M. Zelikoff and K. Watanabe, "Absorption Coefficients of Ethylene in the Vacuum Ultraviolet."

J. Opt. Soc. Am., 43, 756-759 (1954).

These authors presented a well-resolved spectrum of ethylene in which they used a photoelectric method of detection for determining intensities. They observed the absorption from 2000 to $1065\text{\AA}$ and divided the spectrum into three regions: A($1375\text{-}2000\text{\AA}$), B($1090\text{-}1360\text{\AA}$), and C($<1090\text{\AA}$). Their entire spectrum is shown in Figure I-1.

Region A contains the onset of absorption ($1940\text{\AA}$) containing structured peaks down to $1770\text{\AA}$ (Frequencies given in Table I-1). This absorption extends to $1375\text{\AA}$ as a broad continuum with a maximum

at $1620\text{\AA}$. The spacings of the bands in the region $1940\text{-}1770\text{\AA}$ are 800, 750, 790, 820, 730, and 750 cm^{-1} . Integrating over the limits $\nu = 50,000\text{ cm}^{-1}$ to $\nu = 72,730\text{ cm}^{-1}$ yields an f -value of 0.34 in good agreement with other values reported for the $N \rightarrow V$ transition.

Region A also contains the sharp Rydberg doublets, the positions of which are given in Table I-3. They agree well with those of Price and Tutte and contain six previously unreported members. The intensities of these peaks were found to vary very little as pressure was varied from 0.023 mm to 0.46 mm. The agreement is not good when absorption coefficients are compared with previous photographically determined ones. See Table I-5.

Region B contains a second continuum ($f \sim 0.30$) with the remaining members of the Rydberg series. It is noted that long wavelength members of the doublets in the $1744\text{\AA}$ system are more intense than short wavelength members, whereas those appearing at $1392\text{\AA}$ have their relative intensities reversed. The remaining systems at 1289, 1247, and $1225\text{\AA}$ again resemble the $1744\text{\AA}$ system. The spacing between doublets of 470 cm^{-1} is maintained in all five systems.

Region C contains the ionization continuum. The long wavelength limit appears to be $\sim 1180\text{\AA}$ or 10.45 ev.

(20) L.C. Jones, Jr., and L.W. Taylor, "Far Ultraviolet Absorption Spectra of Unsaturated and Aromatic Hydrocarbons."

Analytical Chemistry, 27, 228-237 (1955).

These authors reported intensities using a photoelectric detector (Table I-5). On comparison with the work of Zelikoff and Watanabe, they find good agreement in observed wavelengths but poor agreement in molar absorptivities, their being about 12% higher.

(21) P.G. Wilkinson and R.S. Mulliken, "Far Ultraviolet Spectra of Ethylene and Ethylene-d₄."

J. Chem. Phys., 23, 1895-1907 (1955).

This reinvestigation of the absorption of ethylene and ethylene-d₄ was done on a Harrison 21-foot vacuum spectrograph in the region 1500⁰Å to 2050⁰Å. It represents the standard reference (along with the work of Price and Tutte) on ethylene's absorption. Great care was taken in establishing that the purity was high (>99.95%) so that any observed peaks were ethylenic.

Figure I-2 shows their spectrum of the doublet Rydbergs in the range 1500 to 1750⁰Å and Tables I-1 and I-2 include their observed frequencies. They used the notation Rv_2, v_4 where v_2 = number of quanta of the stretching vibration, v_4 = number of quanta of twisting vibrations. They observed the following:

1. Whereas the identification of the $Rv_{2,0}$ bands as a progression of the C=C stretching vibration seems certain from isotopic effects, the identification of the doublet spacing as

$2\nu_4$ is not as certain. In fact, the ratio of the doublet spacing (C_2H_4 to C_2D_4) is much larger than for a pure harmonic torsional oscillator.

2. They reported for the first time red shoulders (d's in Figure I-2) which are ascribed as excitation to $4\nu_4$. Isotopic ratios tend to negate any assignment other than this one.

3. A small splitting ($24-65\text{ cm}^{-1}$) occurs in the second member of each doublet (S's in Table I-2) and is probably partial resolution of P and R rotational branches.

4. The intensity of $R_{00} \leftarrow N$ is stronger than $R_{02} \leftarrow N$ in C_2H_4 but the reverse is true in C_2D_4 . Such is also the case for $R_{10} \leftarrow N$ and $R_{12} \leftarrow N$, but the two members are about equally intense for higher states of ν_2 .

The attempt to fit observed values of ν_4 in the Rydberg states to those calculated for a torsional oscillator-rotator using a potential function of the form $V = \frac{1}{2}V_0 (1 + \cos 2\theta)$ yields only rough agreement. The anomalous isotope effect and intensities in the $R \leftarrow N$ twisting bands are said to be due to perturbation of the R state levels by V state levels and/or departure from the simple cosine form.

The broad diffuse bands from 2069 to $1750\text{\AA}$ (Figure I-3) are again ascribed to part of the $V \leftarrow N$ peaking at $1620\text{\AA}$. Observed frequencies and spacings are included in Table I-1. Spacings of the main peaks, ascribed to ν_2 , were fitted to empirical equations

which locate the 0,0 band at about $2500\text{\AA}$. The newly observed fine structure in C_2D_4 is attributed to torsional oscillation being allowed to appear as single quanta since the V state is bent and probably staggered.

- (22) V.J. Hammond and W.C. Price, "Oscillator Strengths of the Vacuum Ultra-violet Absorption Bands of Benzene and Ethylene." Trans. Far. Soc., 51, 605-610 (1955).

Table I-5 presents their values of molar extinction coefficients as compared with literature values. They calculated $f = 0.29$ for the $V \leftarrow N$ transition and $f = 0.33$ for the combined $V \leftarrow N$ and $R \leftarrow N$ transitions.

- (23) P.G. Wilkinson, "Absorption Spectra of Ethylene and Ethylene- d_4 in the Vacuum Ultraviolet. II." Can. J. Phys., 34, 643-652 (1956).

Herein is presented a detailed spectrum of the absorption from $1300\text{\AA}$ to $1500\text{\AA}$ photographed in the first order of a 21-foot vacuum spectrograph using a krypton continuum as a source. Observed frequencies are shown in Table I-5 and the densitometer tracings are shown in Figure I-4. These data represent six Rydberg transitions belonging to four Rydberg series, all converging to the same ionization limit (10.45 eV).

The series were named $nR \leftarrow N$, $nR' \leftarrow N$, $nR'' \leftarrow N$ and $nR''' \leftarrow N$. Wilkinson concluded that the $nR \leftarrow N$ transition cannot be of symmetry $B_{1u} \leftarrow A_g$ (z allowed) since it is perturbed very little by the

underlying $V \leftarrow N$ of the same symmetry. It is therefore either $B_{2u} \leftarrow A_g$ (y polarized) or $B_{3u} \leftarrow A_g$ (x polarized) since it seems strong enough to consider as allowed. He concluded that the $3R''' \leftarrow N$ is $B_{1u} \leftarrow A_g$ since it should, but does not, appear in the region 1600 - 1700 Å. It must mix strongly with $V(B_{1u})$ and become very diffuse.

Wilkinson admitted his assignments are contingent on the following conditions:

1. The first transition should be the strongest in each band system. This condition is true only for the 1740 Å and 1500 Å systems.

2. Short wavelength isotope shift on deuteration should be constant for each system. This is true for all except the 1370 Å system.

3. One should observe expected vibrational transitions. This condition is met for the ν_2 vibration. However, the assignment of $2\nu_4$ for the doublet splitting still suffers anomalies in isotopic ratios and intensities. Since this can be explained only by assuming an unusual shape for the true potential barrier, he concluded that the stable equilibrium configuration in the Rydberg states is not of D_{2h} symmetry but is bent or staggered in some fashion.

(24) R.S. Mulliken, "Conjugation and Hyperconjugation: A Survey with Emphasis on Isovalent Hyperconjugation."

Tetrahedron, 5, 253-274 (1959).

Mulliken noted that the spectroscopic data on Rydberg states in C_2H_4 and C_2D_4 (which are essentially states of the positive

ethylene ion plus an electron in a large diffuse orbital) show features impossible to reconcile with a planar $C_2H_4^+$ structure. Indeed, the results of his computation reported here indicate that the ion (and thus the Rydberg state) is bent. He noted that the alternate interpretation of spectroscopic data involving a low-frequency out-of-plane bending in the upper state cannot be excluded but seems less likely.

(25) D.F. Evans, "Magnetic Perturbation of Singlet-Triplet Transitions.

Part IV. Unsaturated Compounds."

J. Chem. Soc., 1960, 1735-1745.

Using the technique of singlet-triplet absorption enhancement by oxygen, Evans reported for C_2H_4 and C_2D_4 a regular series of rather broad bands in the region $3500 - 2800\text{\AA}$ having an average separation of about 1000 cm^{-1} and tending to a maximum at about $2700\text{\AA}$. On the basis of isotopic ratios and similarity to the spacings observed by Reid (See Table I 4) he concludes the spacings on this $T \leftarrow N$ transition are due to C C stretch.

Investigation of pure ethylene at 50 atmospheres pressure indicates no evidence for any transition other than $V \leftarrow N$ in the region 2200 to $2000\text{\AA}$.

(26) R.S. Mulliken, "Lowest Triplet States of Ethylene."

J. Chem. Phys., 33, 1596-1597 (1960).

In this reference Mulliken agreed with Evans and Reid that the bands with maximum intensity at 4.6 eV ($2700\text{\AA}$) are indeed the $T \leftarrow N$

transition in agreement with SCF LCAO-MO calculations. He also predicted a small energy separation between the R and T_R states. He says that the Rydberg state is probably of $\cdots(\pi x + \pi x)(3s)$, $^1B_{3u}$ symmetry.

(27) A. Kuppermann and L.M. Raff, "Determination of Electronic Energy Levels of Molecules by Low-Energy Electron Impact Spectroscopy."

J. Chem. Phys., 37, 2497-2498 (1962).

(27a) A. Kuppermann and L.M. Raff, "Electron Impact Spectroscopy."

Disc. Far. Soc., 35, 30-42 (1963).

(27b) A. Kuppermann and L.M. Raff, "Difference Between Low-Energy Electron Impact Spectra at 0° and at Large Scattering Angle."

J. Chem. Phys., 39, 1607-1608 (1963).

These papers describe a new spectroscopic technique, electron impact spectroscopy, in which selection rules for transitions are greatly relaxed and optically forbidden electronic transitions can usually be detected as clearly as optically allowed ones in a fairly routine manner. These authors observed peaks that agree well with optical results. However, they reported an additional resonance peak at 6.5 eV ($\sim 2080\text{\AA}$) which they initially assumed to be $T_R \leftarrow N$ as Mulliken had predicted. However, they found that the energy dependence of the excitation cross section indicates that the transition is not a triplet but is spin allowed.

(28) R.S. Berry, "Analog of $n \rightarrow \pi^*$ Transitions in Mono-Olefins."

J. Chem. Phys., 38, 1934-1938 (1963).

The work of Kuppermann and Raff again indicated that a separate transition at about $2080\text{\AA}$, or 6.5 ev, exists for ethylene. Snow and Allsopp had once assigned it as $T \leftarrow N$ and Mulliken now called it $T_R \leftarrow N$. This prompted Berry to a new, rather ingenious assignment. Reasoning by analogy with formaldehyde which has a low-lying $n \rightarrow \pi^*$, he assigned the 6.5 ev band as $\sigma \rightarrow \pi^*$, the σ being the highest filled CH bonding orbital. It is bonding between carbons and adjacent hydrogens, antibonding between olefinic carbons, and antibonding between geminate hydrogens. His ideas were prompted also by the fact that mono-olefins exhibit two closely spaced filled orbitals from ionization threshold data. He further described this σ orbital as being π'_y , i.e., antibonding between the two in-plane p_y orbitals making it b_{1g} in D_{2h} symmetry. His coordinate frame has the x-axis directed along the double bond, the z-axis out of the molecular plane. The electronic transition is thus $(b_{1g})^2 \rightarrow (b_{1g})(b_{2g})$ or $A_g \rightarrow B_{3g}$ which is symmetry forbidden. (In Mulliken's coordinate frame it would be $(b_{3g})^2 \rightarrow (b_{3g})(b_{2g})$ or $A_g \rightarrow B_{1g}$). He speculated that it becomes vibronically allowed for the a_u twisting mode (1027 cm^{-1}) and the b_{2g} and b_{1u} hydrogen out-of-plane bending modes (943 and 949.2 cm^{-1}). Allowedness now becomes dependent on the population of the first excited vibrational state, explaining why Snow and Allsopp report the transition at room temperature whereas Reid at low temperatures did not.

- (29) J.A. Simpson and S.R. Mielczarek, "Determinations of Electronic Energy Levels of Molecules by Low-Energy Electron-Impact Spectroscopy."
J. Chem. Phys., 39, 1606-1607 (1963).
- (29a) M.I. Al-Joboury and D.W. Turner, "Molecular Photoelectron Spectroscopy. Part II. A Summary of Ionization Potentials."
J. Chem. Soc., 1964, 4434-4441.
- (29b) E.N. Lassettre and S.A. Francis, "Inelastic Scattering of 390-V Electrons by Helium, Hydrogen, Methane, Ethane, Cyclohexane, Ethylene and Water."
J. Chem. Phys., 40, 1208-1217 (1964).
- (29c) C.R. Bowman and W.D. Miller, "Excitation of Methane, Ethane, Ethylene, Propylene, Acetylene, Propyne, and 1-Butyne by Low-energy Electron Beams."
J. Chem. Phys., 42, 681-686 (1965).
- (29d) J. Geiger und K. Wittmaack, "Hochauflösende Elektronenstrasspektrometrie des Elektronen- und Schwingungsspektrums von Äthylene."
Z. Naturforsch., 20A, 628-629 (1965).

These authors all reported the absence of any peak at 6.5 eV despite improvement in the techniques of electron impact spectroscopy. In Figure I-1 is reproduced the electron impact spectrum of ethylene under high resolution reported by Geiger and Wittmaack compared

with the optical absorption spectrum of Zelikoff and Watanabe.

- (30) L. Burnelle, "Geometry of the Low-lying Excited States of Ethylene and Butadiene."

J. Chem. Phys., 43, S29 (1965).

On the basis of the stereospecificity characteristic of the electrophilic additions to double bonds, and on the basis of MO calculations, the author concluded that the T state of ethylene is bent and also has a "flapped" configuration of the CH₂ groups as Walsh had previously predicted. The computed stabilization due to flapping is considerable, the minimum of the energy surface lying about 1 ev above that of the ground state. However, for the V state, flapping was found to cause an increase in energy.

- (31) K.J. Ross and E.N. Lassettre, "Intensity Distribution in the Energy-Loss Spectrum of Ethylene."

J. Chem. Phys., 44, 4633-4635 (1966).

The high resolution electron-impact spectrum of ethylene obtained at 200-V electron kinetic energies was reported and compared to the work of Geiger and Wittmaack at 33-KV electron kinetic energies. Excellent agreement resulted except for the appearance at 7.45 V of an apparently forbidden quadrupole transition. A slight increase in intensity had been noted in the electron-impact spectrum of Simpson and Mielczarek in the region of 7.45 V. Recalling the assignments made by Craig, this transition was assigned as the $A_{1g} \rightarrow (b_{2g})^2$, A_{1g} two-electron quadrupole transition.

(32) R.R. Hart and M.B. Robin, "Expanded Gaussian Orbitals and the Electronic States of Ethylene."

Theoret. chim. Acta (Berlin), 3, 375-377 (1965).

These authors described the use of Gaussian-type basis orbitals (GTO's) for SCF treatments of electronic and molecular structure. Using ethylene as a test case, they predicted, for bases ranging from 16 to 36 GTO's, the $\pi \rightarrow \pi^*$ triplet and singlet excitations to remain in the intervals 3.78 ± 0.32 ev and 10.28 ± 0.70 ev, compared to the observed energies of 4.8 and 7.6 ev. A large configuration interaction calculation involving several hundred excited configurations affected the predicted energies only slightly. It thus appears that a small GTO basis yields spectral predictions very similar to those of more extended calculations.

However, they found that one should use GTO basis functions more expanded in space in order to improve spectral predictions. They selected for orbital exponents the following: C s-type - 9.00, 0.32, 0.35; C p-type - 0.80, 0.08; H s-type - 0.17. The computations then yielded 4.67 ev and 7.96 ev for the $\pi \rightarrow \pi^*$ triplet and singlet excitation energies, a much improved agreement with experiment. In addition, the $\text{CH} \rightarrow \text{CH}^*$ and $\pi \rightarrow \text{CH}^*$ excitations dropped from 16 ev. and 12 ev to 10 ev and 7 ev, the $\text{CH} \rightarrow \pi^*$ transition of Berry remaining rather stationary at about 8 ev. They thus concluded that these three transitions are all candidates for assignment in the vacuum ultraviolet spectrum.

(33) M.B. Robin, R.R. Hart, and N.A. Kuebler, "Assignment of the Ultraviolet Mystery Band of Olefins."

J. Chem. Phys., 44, 1803-1811 (1965).

Here is first coined the name "mystery band" for the transition which definitely occurs in alkyl-substituted olefins in the range 5-6 eV and might exist in ethylene at 6.5 eV. On the basis of their GTO calculation using basis functions more expanded in space, these workers assigned the lowest transition as an allowed $\pi \rightarrow \text{CH}^*$, being about 0.5 eV below the $\text{N} \rightarrow \text{V}$ whereas the $\text{CH} \rightarrow \pi^*$ is about 1 eV above the $\text{N} \rightarrow \text{V}$. The CH^* orbital is antibonding between all the carbons and hydrogens but strongly $\text{sp}\sigma$ bonding between the two carbon atoms. It is of a_g symmetry in their and Mulliken's coordinate frames. (They have the z-axis along the double bond, the y-axis perpendicular to the molecular plane).

Their augmented Gaussian calculation predicts a transition moment of $0.29\text{e}\overset{\circ}{\text{A}}$ in ethylene. They compare this with the measured moment $0.1\text{--}0.25\text{e}\overset{\circ}{\text{A}}$ in substituted ethylene. They pointed out that this is not much larger than the moment expected for the forbidden $\text{CH} \rightarrow \pi^*$ of Berry on stealing intensity by a vibronic mechanism ($\sim 0.1\text{e}\overset{\circ}{\text{A}}$).

They noted that for $\pi \rightarrow \text{ns}$ Rydberg transitions, the terminating orbitals have the same symmetry, a_g , as the $\pi \rightarrow \text{CH}^*$ (${}^1A_g \rightarrow {}^1B_{2u}$). Thus the upper orbital may contain both valence-shell and Rydberg orbitals in any ratio, the distinction between Rydberg

and valence-shell being meaningful only if the ratio is extreme. They thus repeated the augmented GTO calculation with the addition of four s-type orbitals centered at the molecular midpoint and having the exponents 0.00208, 0.00052, 0.00013, and 0.0000325. They found the CH* orbital to be made up of roughly half valence-shell C-C σ bonding and C-H σ antibonding and half Rydberg orbitals of exponents 0.00208 and 0.00052. However, the distinction between these orbital types is blurred by the fact that there is considerable overlap between the components of the valence-shell CH* MO and the lowest s-type Rydberg Gaussian.

The authors discuss the fact that the idea of σ - π separability, the basis of π -electron theories, seems a less substantial approximation in light of these results.

(34) H. Berthod, "Comment on the Ultraviolet Mystery Band of Olefins."

J. Chem. Phys., 45, 1859-1860 (1966).

Herein is reported the results of an SCF calculation on ethylene with Slater orbitals. The orbital ordering above the ground state configuration was found to be two CH* orbitals as the lowest empty orbitals, followed by the π^* . The first transition obtained is $\pi \rightarrow \text{CH}^*$ symmetry forbidden, the second is $\pi \rightarrow \text{CH}^*$ (${}^1\text{A}_g \rightarrow {}^1\text{A}_u$) symmetry allowed at 6.3 eV. The CH $\rightarrow \pi^*$ transition of Berry is well above the $\pi \rightarrow \pi^*$. The difference in symmetry of this $\pi \rightarrow \text{CH}^*$ band and that of Robin, Hart and Kuebler is said

due to a different distribution of the empty orbitals.

- (35) A. Lubezky and R. Kopelman, "Electronic Spectrum of Ethylene Single Crystal; Search for the Olefin Mystery Band."
J. Chem. Phys., 45, 2526-2528 (1966).

These researchers grew ethylene single crystals and observed their spectra in the range 2000 to 2500 $\text{\AA}$ to consist of a number of bands quite analagous to the $N \rightarrow V$ transition in the vapor phase. There appeared no additional transitions such as $\pi \rightarrow CH^*$ or $CH \rightarrow \pi^*$ despite relaxed selection rules in the crystalline state. They concluded that if the mystery band exists at all in ethylene its excited state is likely to either a triplet state or a Rydberg state or a combination of both. They reported two peaks on the $N \rightarrow V$ at 2079 and 2044 $\text{\AA}$ which correlate well with 2069 and 2035 $\text{\AA}$ peaks previously reported in the vapor, shifted in the solid by about 250 cm^{-1} .

- (36) J.P. Doering, "Low-Energy, Large Angle Electron-Impact Spectrum of Ethylene."
J. Chem. Phys., 46, 1194-1196 (1966).

On measuring the high-resoltuion electron-impact spectrum of ethylene at low primary energies (35, 50 and 70 ev), excellent agreement was found with the optical spectrum. The most intense peak at about 8 ev corresponds to the combined $N \rightarrow V$ and $N \rightarrow R$; a peak at 4.6 ev to the $N \rightarrow T$. There was no observed mystery transition at 6.5 ev.

- (37) R. McDiarmid and E. Charney, "Far-Ultraviolet Spectrum of Ethylene and Ethylene-d₄."

J. Chem. Phys., 47, 1517-1524 (1967).

The frequencies given in Table I-1 and I-2 were reported for the $V \leftarrow N$ transition of C_2H_4 and C_2D_4 . By varying the temperature from $-78^\circ C$ to $100^\circ C$, they determined that one progression is a hot one (denoted by H in the tables) having about the same spacings as the primary progression. The strongest observed bands were found to fit the empirical expressions: C_2H_4 , $\nu = 46697 + 807\nu$; C_2D_4 , $\nu = 46948 + 547\nu$. On the basis of the ground state being planar and the V state bent, they assumed that the torsional mode ν_4 is the most likely assignment for the observed spacings. In fact, in D_2 symmetry, the highest subgroup contained in D_{2h} and D_{2d} , ν_4 is an a_1 mode and can appear as single quanta. The isotopic ratio 0.68 compares well with 0.707 of the ground state. Therefore, the observed frequencies (807 cm^{-1} for C_2H_4 , 547 cm^{-1} for C_2D_4) are concluded to be torsional frequencies. A frequency of 150 cm^{-1} in C_2D_4 was observed but not interpreted. An analysis of the torsional progression shows the torsional potential of the V state to be parabolic, i.e., $V = V_0\theta^2$.

- (38) T.H. Dunning and V. McCoy, "Nonempirical Calculations on Excited States: The Ethylene Molecule."

J. Chem. Phys., 47, 1735-1747 (1967).

On the basis of nonempirical calculations they concluded that for the lowest excited singlet state of ethylene ($^1B_{3u}$ in their

coordinate frame which has the x-axis along the double bond and the z-axis out of plane, ${}^1B_{1u}$ in Mulliken's system) the coupling between the π electron and σ electrons is significant. The excitation energy decreases from 11.98 eV to 10.17 eV and the oscillator strength from 1.03 to 0.73. This coupling has little effect on the triplet.

They reported two excited states, ${}^1B_{2g}$ at 10.47 eV and ${}^1B_{3g}$ at 10.46 eV, in the same region of the spectrum as the ${}^1B_{3u}$. In Mulliken's coordinate frame, these correspond to ${}^1B_{2g}$ and ${}^1B_{1g}$ states.

- (39) J.P. Doering and A.J. Williams III, "Low-Energy, Large Angle Electron Impact Spectra: Helium, Nitrogen, Ethylene, and Benzene."

J. Chem. Phys., 47, 4180-4185 (1967).

The 6.5 eV ethylene mystery band was not observed at energies as low as 10.9 eV. Presence of the $N \rightarrow T$ at 4.4 eV was confirmed.

- (40) U. Kaldor and I. Shavitt, "LCAO-SCF Computations for Ethylene."

J. Chem. Phys., 48, 191-203 (1968).

This article presents an excellent review on the subject of electronic transitions in ethylene. A rather comprehensive survey of all the pertinent computational papers on ethylene is included as well as a review of the experimental history.

They carried out LCAO-SCF calculations with a minimal Slater basis for the ethylene molecule and its positive and negative ions. They found that the errors introduced by neglecting σ - π exchange are roughly proportional to the number of π electrons in each state and are significant for the determination of energy differences involving changes in the number of these electrons. Their results caused them to favor the opinion that the mystery band of substituted ethylenes corresponds to the sharp Rydberg at 7.11 eV in ethylene, with this level having some valence-shell $\pi \rightarrow \text{CH}^*$ character. This seems a more logical assignment than corresponding them to an unproven 6.4 eV band.

It was found that ionic levels are degenerate in a perpendicular configuration and show a Jahn-Teller splitting. They expect similar behavior for the Rydberg $\pi \rightarrow \text{ns}$ states.

(41) A.-J. Merer and L. Schoonveld, "Nonplanarity of the First Rydberg State of Ethylene."

J. Chem. Phys., 48, 522-523 (1968).

They investigated the $1744\text{\AA}$ transition in absorption at high temperatures up to 450°C . Spectra were photographed in the first order of a 21-foot concave grating spectrograph. New bands which appear at high temperature are the ν_4 (1-1) bands of C_2H_4 and C_2D_4 and the ν_4 (3-1) band of C_2D_4 . These new bands plus those observed at room temperature and the ground-state torsional frequencies (assumed to be 1023 and 726 cm^{-1}) give the energies

of upper-state torsional levels up to $\nu'_4 = 4$ for C_2H_4 and C_2D_4 , with the exception of $\nu'_4 = 3$ for C_2H_4 . The irregularity of these torsional levels prompted them to suggest the involvement of a double-minimum potential function. They fitted the data to a potential function of the form $V = \frac{1}{2}V_0(1-\cos 2\gamma) + \frac{1}{2}V_4(1-\cos 4\gamma) + \dots$. They conclude that the Rydberg state is nonplanar, twisted at $\sim 26^\circ$, the barrier to inversion through the planar form being low, and that the molecule becomes effectively planar on excitation of one or two quanta of the torsional vibration.

(42) M.B. Robin, H. Basch, N.A. Kuebler, B.E. Kaplan, and J. Meinwald, "Assignments in the Ultraviolet Spectra of Olefins."

J. Chem. Phys., 48, 5037-5047 (1968).

Previous calculations involving Gaussian basis sets have led to the $\pi \rightarrow \pi^*$, which is known to be valence-shell, being contaminated with big-orbital Rydberg character. In this paper they used an indirect SCF approximation which circumvents this difficulty and shows clearly which states are valence-shell and which are Rydberg. Their Gaussian basis when translated into Slater orbitals is equivalent to a best-atom double zeta (BADZ) basis.

They find the $\pi \rightarrow \pi^*$ and the two lowest $\sigma \rightarrow \pi^*$ transitions to be valence-shell whereas the four lowest $\pi \rightarrow \sigma^*$ excitations and the lowest $\sigma \rightarrow \sigma^*$ are of principal quantum number 3. Table I-7

gives their reported values with and without inclusion of single-zeta 3s and 3p orbitals. They concluded that the lowest transitions in ethylene and simple olefins should be Rydberg $\pi \rightarrow \sigma^*$ in nature, the $\sigma \rightarrow \pi$'s being valence-shell and lying above the $\pi \rightarrow \pi^*$.

(43) J.F. Ogilvie, "Structural Deductions from the Vibronic Spectra of Ethene and Ethene-d₄."

J. Chem. Phys., 49, 474-475 (1968).

Ogilvie, using the data of McDiarmid and Charney, averaged all the frequencies (primary and hot) and obtained $795 \pm 59 \text{ cm}^{-1}$ for C₂H₄ and $547 \pm 40 \text{ cm}^{-1}$ for C₂D₄. The resultant isotopic ratio is then 0.688 ± 0.071 . In view of this large standard deviation, the out-of-plane bending mode becomes a candidate for assignment, having a ground state isotopic ratio of 0.756. If the molecule were to distort extremely in the manner of ν_7 , then the effect on the π^* state would be to diminish the repulsion due to the occupied π^* orbitals as suggested by Walsh. In this large distortion the molecule would resemble an eclipsed ethane molecule with two hydrogens removed. The axes of the two CH₂ groups would be neither collinear nor parallel. ν_7 then becomes allowed, being a_1 in the C_{2v} point group. It was then concluded that the unexplained frequency of 150 cm^{-1} could be the torsional ν_4 vibration. However, ν_4 is not totally symmetric under C_{2v} indicating the molecule may be slightly staggered.

(44) M. Yaris, A. Moscovitz, and R.S. Berry, "Low-lying Excited States of Mono-olefins."

J. Chem. Phys., 49, 3150-3160 (1968).

On the basis of semiempirical calculations of energies, oscillator strengths and rotational strengths, they concluded that there exists a minimum of three low-lying singlet states in ethylene and simple olefins. These are:

1. a ${}^1B_{xu}(\pi_z \rightarrow \pi_z^*)$ responsible for the strong, broad absorption.
2. a ${}^1B_{zu}(\pi_z \rightarrow \sigma^*)$ 3s Rydberg responsible for the band with $\epsilon = 1000$ in alkyl substituted olefins and corresponding to the sharp Rydberg at $1744\overset{0}{\text{\AA}}$ in ethylene.
3. a ${}^1B_{yg}(\pi_z \rightarrow \pi_y^*)$ Rydberg-like state accounting for the low-lying electric quadrapole-allowed transition observed by Ross and Lassettre in electron-impact and these authors in optical rotatory dispersion. In normal group theoretical notation and using the coordinate frame of Mulliken, these states are: (1) ${}^1A_g \rightarrow {}^1B_{1u}$, (2) ${}^1A_g \rightarrow {}^1B_{3u}$ and (3) ${}^1A_g \rightarrow {}^1B_{1g}$. The calculated energies of (1) and (3) are shown in Table I-7. Also shown is the $\pi_y({}^1b_{zg}) \rightarrow \pi_z^*$, ($\sigma \rightarrow \pi^*$) at 10.91 ev.

(45) A.J. Merer and R.S. Mulliken, "Ultraviolet Spectra and Excited States of Ethylene and Its Alkyl Derivatives."

To be published.

This article, which Professor Mulliken was kind enough to

provide us prior to publication, is an excellent review of the subject and does much to clear the confusion resulting from apparently erroneous experimental work (the "shoulder" at about $2000\text{\AA}$ reported by Snow and Allsopp and the peak at 6.5 eV preported by Kuppermann and Raff). He also comments that confusion exists because of appearance in the literature of computations done in various coordinate frames, leading to various group theoretical symbols for the same states. He suggest the coordinate frame for ethylene recommended by the Joint Commission on Spectroscopy of the IAU and the IUPAP, i.e., the x-axis taken as perpendicular to the molecular plane, the z-axis through the two carbon atoms.

He further comments on the confusion resulting from Robin, Hart and Kuebler's failure to recognize the $\pi \rightarrow \text{CH}^*$ as being identical with $\pi \rightarrow \text{ns}$, a situation they recognized in their later publication. He also comments on their mistake in thinking Berry was assigning $\text{CH} \rightarrow \pi^*$ for the $\text{R} \leftarrow \text{N}$ ($\epsilon = 500\text{--}1000$) systems in alkyl-substituted ethylenes when he was actually referring to much weaker bands ($\epsilon = 0.1$ to 1, see Chapter II) in these compounds. This latter mistake, however, seems a natural one as Berry was not altogether clear on this point in his initial publication on the subject.

We should like to make the further comment that it seems a great mistake to do semi-empirical calculations on ethylene and then refer the results to transitions in larger olefins, or, even worse, to

refer them to bands such as the 6.5 eV transition in ethylene which is unconfirmed and, according to the overwhelming experimental evidence, non-existent.

- (46) A.J. Merer and R.S. Mulliken, "Vibrational Structure of the $\pi^* - \pi$ Electronic Transition of Ethylene." J. Chem. Phys., 50, 1026-1027 (1969).

These authors first review the previous assignments given the $V \leftarrow N$ progression: ν_2' by Wilkinson and Mulliken, ν_4' by McDiarmid and Charney, and ν_{12}' by Oglivie. They state that Oglivie numbers his vibration ν_7 because he has taken the z-axis as perpendicular to the plane of the molecule. This seems confusing since Oglivie describes his vibration as one which in the extreme yields a geometry similar to eclipsed ethane with two hydrogens missing. This is indeed the situation resulting from a large out-of-plane bending mode ν_7 , regardless of coordinate system chosen. However, ν_7 becomes b_1 in C_{2v} symmetry using Mulliken's coordinate frame, whereas ν_{12} becomes a_1 in this situation, the requirement needed for vibronic allowedness in Oglivie's assignment.

They conclude that both ν_2 and ν_4 contribute to the spectrum. They use an essentially sinusoidal potential for the twisting mode and they alter the C-C distance to keep up with the expected extension of bond length in going from a more twisted to a more planar V state. By so doing, their calculation yields results very similar to the

observed $V \leftarrow N$, producing the intensity distribution in the transition almost exactly. They state that the parabolic potential function of McDiarmid and Charney is physically unreal and yields reasonable answers only because they neglected the expected stretching of the C-C bond.

(47) R. McDiarmid, "Vibrational Intensity Progression in the $V \leftarrow N$ Transition of Ethylene."

J. Chem. Phys., 50, 1794-1800 (1969).

Herein is reported the results of a calculation treating the ethylene molecule as a one dimensional oscillator and examining two choices of the potential function V in the Schrödinger equation: the sinusoidal choice of Mulliken, $V = \frac{1}{2}V_0(1-\cos 2\theta)$ and a parabolic potential, $V = V_0\theta^2$. The observed intensities are found to agree better with the latter choice. They also conclude that the bonds on each carbon atom are trigonal and not distorted toward tetrahedral. This seems to preclude the suggestion of Walsh that the carbon atoms lie off the minimum axis of inertia. The oscillator strength is estimated to be ~ 0.1 , in good agreement with predicted values of 0.3. They state that there is no evidence for the extreme extension of the C-C bond other than Mulliken's analogy with O_2 .

Summary: The transitions which experimentally do exist in ethylene absorption are the following:

(a) A singlet-triplet transition at ~ 4.4 ev, generally

agreed to be $T \leftarrow N$.

(b) A broad continuum (maximum at $1620\text{\AA}$) having an oscillator strength of about 0.3, generally agreed to be $V \leftarrow N$.

(c) A sharp series of doublets starting abruptly at $1744\text{\AA}$ and having an f-value of ~ 0.03 , generally assigned as $R(3s) \leftarrow N$.

(d) Higher members of this Rydberg series and other Rydberg series extending out to an ionization continuum at about 10.5 eV.

(e) Optical rotatory dispersion measurements of Berry and electron-impact measurements of Ross and Lessettre indicate an electric dipole forbidden, electric quadrupole allowed transition at about 7.45 eV, assigned by Berry as $\pi \rightarrow {}^1b_{2u}$.

(f) The spectrum should demonstrate one further peak, $T_R \leftarrow N$, which has not as yet been observed.

The 6.5 eV mystery band according to overwhelming experimental evidence does not exist.

In Table I-8, we give the three coordinate frames chosen by various workers and show the correspondence of the various symmetry elements of D_{2h} . This allows easy conversion of notations from one frame to another. For example, the $\pi \rightarrow \pi^*$ transition in ethylene is ${}^1A_g \rightarrow {}^1B_{1u}$ ($b_{2u} \rightarrow b_{3g}$) in frame I, ${}^1A_g \rightarrow {}^1B_{1u}$ ($b_{3u} \rightarrow b_{2g}$) in frame II, and ${}^1A_g \rightarrow {}^1B_{3u}$ ($b_{1u} \rightarrow b_{2g}$) in frame III.

In Table I-9 are listed frequencies reported for the fundamental vibrational modes of ethylene in the ground state and how these vibrations transform in D_{2h} for the three coordinate frames of Table I-8.

TABLE I-1

ABSORPTION BANDS IN THE $V \leftarrow N$ TRANSITION OF C_2H_4

McDiarmid and Charney*			Wilkinson and Mulliken		Snow and Allsopp	Scheibe and Grieneison	Zelikoff and Watanabe
$\nu(\text{cm}^{-1})$	$\Delta\nu^\dagger$	$\Delta\nu_{P-H}^\ddagger$	$\nu(\text{cm}^{-1})$	$\Delta\nu^\dagger$	$\nu(\text{cm}^{-1})$	$\nu(\text{cm}^{-1})$	$\nu(\text{cm}^{-1})$
46223 ^H							
46475	898	252					
47214 ^H							
47373	958	169					
48058 ^H							
48331	817	273	48333	817	48330		
49148	783		49140	836	49210		
49658 ^H							
49931	787	273	49976	768	50000		
50489 ^H							
50718	861	229	50744	858	50760	50610	
51579	848		51602	889	51680	51690	51600
52065 ^H							
52427	796	358	52491	667		52500	52400
52886 ^H							
53123	817	237	53158	816		53240	53150

Table I-1 (Continued)

McDiarmid and Charney*			Wilkinson and Mulliken		Snow and Allsopp	Scheibe and Grieneison	Zelikoff and Watanabe
$\nu(\text{cm}^{-1})$	$\Delta\nu^\dagger$	$\Delta\nu_{\text{P-H}}^\ddagger$	$\nu(\text{cm}^{-1})$	$\Delta\nu^\dagger$	$\nu(\text{cm}^{-1})$	$\nu(\text{cm}^{-1})$	$\nu(\text{cm}^{-1})$
53697 ^H							
53941	814		53974	805		54000	53940
54397 ^H							
54755	759	358	54779	763		54800	54760
55514	789		55542	755		55560	55490
56303			56297	775		56270	56240
			57072			56960	

* We have omitted a frequency of 49433 cm^{-1} which the authors say does not fit any series.

H--refers to frequencies belonging to a hot progression. All other frequencies refer to members of a primary progression.

[†] $\Delta\nu$ refers to spacings between frequencies of the primary progression, assigned as ν_4 by McDiarmid and Charney, ν_2 by Wilkinson and Mulliken (later as a combination of ν_2 and ν_4).

[‡] $\Delta\nu_{\text{P-H}}$ refers to spacings between primary and hot peaks.

TABLE I-2

ABSORPTION BANDS IN THE $V \leftarrow N$ TRANSITION OF C_2D_4

McDiarmid and Charney						Wilkinson and Mulliken		
$\nu(\text{cm}^{-1})$	$\Delta_1 \nu_2$	$\Delta_2 \nu_2$	$\Delta \nu_{1-2}$	$\Delta \nu_2^H$	$\Delta \nu_{P-H}$	$\nu(\text{cm}^{-1})$	$\Delta_1 \nu_2$	$\Delta_1 \nu_4$
51681 ^H				551	178			
51859	547		165			51929	664	546
52024						52047		
52232 ^H		1070		529	174			
52406	559					52593	732	
52751 ^H				574	214			
52965	585		129			52806		188
52751 ^H						52994		177
53094		596				53171		154
53325 ^H				557	225	53325	774	
53550	540		140			53504		214
53690		545				53718		211
53882 ^H				560	208	53929		170
54090	535		135			54099	678	
54225		553				54247		172
54442 ^H				528	183	54419		195
54625	530		153			54614		163
54778		533				54777	709	
54970 ^H				521	185	54991		182
55155	565		156			55173		313
55311		583				55486	714	
55491 ^H				547	229			
55720	535		174			55709		175
55894		500				55884		151
56038 ^H				566	217	56035		165
56255	530		139			56200	741	
56394						56418		137
56604 ^H					181	56555		386
56785						56941		
57007 ^a								

a. First Rydberg transition from a vibrationally excited ground state.

TABLE I-3
ABSORPTION BANDS IN THE R ← N TRANSITION OF C₂H₄ AND C₂D₄ (cm⁻¹)

Wilkinson and Mulliken			Price and Tuttle		Schiebe and Grieneison	Platt, Kleven and Price	Zelikoff and Watanabe
Upper State*	C ₂ H ₄	C ₂ D ₄	C ₂ H ₄	C ₂ D ₄	C ₂ H ₄	C ₂ H ₄	C ₂ H ₄
R ₀₀	57336.0	57620.8	57340	57620	57320	57340	57340
R ₀₂	57807.6s	57903.0s	57815	57910	57790	57840	57800
R ₀₂	57858.0s	57927.0s					
R ₀₄	58420d	58333.4d		58340			
R ₁₀	58706.3	58915.5	58715	58910	58610		58720
R ₁₂	59167.2s	59190.7s	59185	59200	59160	59210	59180
R ₁₂	59231.0s	59218.0s					
R ₁₄	59904.7d	59637.3d		59650			
R ₂₀	60055.4	60199.3	60070	60190	60010	60060	60070
R ₂₂	60513.2	60473.6	60530	60480	60490	60533	60530
R ₂₄	61226d	60918d		60930			61220
R ₃₀	61379.1	61466.2		61460			
R ₃₂	61838.6	61739.0		61750			61860
R ₃₄	62547d	62212d		62195			62540
R ₄₀	62689.5	62705.7					
R ₄₂	63151.8	62976.6					63070
R ₄₄	63879d	63455d					63820

* R refers to the state as Rydberg in nature. The first subscript refers to the number of quanta of ν_2 , the second to the number of quanta of ν_4 .

TABLE I-4

ABSORPTION BANDS IN THE T ← N TRANSITION (cm⁻¹)

[After D.F. Evans, J. Chem. Soc. (1960)]

C_2H_4			C_2D_4
Evans		Reid	Evans
O_2 , high pressure	O_2 , low pressure	liquid C_2H_4	O_2 , high pressure
28700			28940
29720		29802	29950
30760	30770	30758	30880
31800	31810	31729	31910
32860	32800	32710	33050
33840	33780	33698	33800
34700	34750	34686	34720
35640	35660	35610	35590
36600	36600	36583	36500
		37540	
		38476	

TABLE I-5

MOLAR EXTINCTION COEFFICIENTS (ϵ) OF THE RYDBERG DOUBLETS

$\lambda(\text{\AA})$	Platt, Klevens and Price	Wilkinson and Johnston	Zelikoff and Watanabe	Hammond and Price	Jones and Taylor
1744	4900	4400	13500	15500	16800
1730	2900	4600	10400	13000	11200
1704	6300	5400	14400	16300	17100
1650	9700	5800	11900	10200	
1625	15100	7300	7800	10400	
1600	14600	7300	8000	10000	
1575	11700	6800	5900	7800	
1550	8300	4900	6300	5600	
1525		3900	5200		
1500		2900	4900	2900	
1475		2200	3900		
1450		1600	2900	920	

TABLE I-6

ABSORPTION BANDS OF ETHYLENE AND ETHYLENE-d₄

d--diffuse; dd--very diffuse

Intensities are estimates of absorption coefficients

[After P.G. Wilkinson, Can. J. Phys., 34 (1956)]

Ethylene			Ethylene-d ₄		
Intensity (cm ⁻¹)	Wavenumber (cm ⁻¹)	Transition	Intensity (cm ⁻¹)	Wavenumber (cm ⁻¹)	Transition
500	66607	3R' ₀₀	500	6693	3R' ₀₀
200d	67077	3R' ₀₂	50dd	66952	3R' ₀₂
100d	67918	3R' ₁₀	100d	67911	3R' ₁₀
1000d	69516	3R'' ₀₀	1000	69656	3R'' ₀₀
300d	70035	3R'' ₀₂	300	69987	3R'' ₀₂
330d	70745	3R'' ₀₄	50	70533	3R'' ₀₄
310d	70888	3R'' ₁₀	350	70977	3R'' ₁₀
320d	71445	3R'' ₁₂	300	71309	3R'' ₁₂
			600	71804	3R'' ₁₄
2000	71788	3R ₀₀	900	72047	3R ₀₀
500	71951	a	1000	72122	a
1770d	72191	3R ₀₂	2000	72296	3R ₀₂
1800d	72286	3R'' ₂₀			3R'' ₂₀
		3R'' ₁₄			
100d	72788	3R'' ₂₂	950	72546	3R'' ₂₂
		3R ₀₄	800	72766	3R ₀₄
1000	73011	4R''' ₀₀	850	73007	4R''' ₀₀
1200	73239	3R ₁₀			
1300	73350	4R''' ₀₂	900	73260	4R''' ₀₂
1300	73493	a			
			1100	73433	3R ₁₀
1450	73667	3R ₁₂	1300	73662	3R ₁₂
					3R'' ₃₀
1200	73749	3R'' ₃₀			

Table I-6(Continued)

Ethylene			Ethylene-d ₄		
Intensity (cm ⁻¹)	Wavenumber (cm ⁻¹)	Transition	Intensity (cm ⁻¹)	Wavenumber (cm ⁻¹)	Transition
500	74266	3R'' ₃₂	800	73875	3R'' ₃₂
		3R'' ₁₄	800	74143	3R'' ₁₄
900	74471	4R''' ₁₀	850	74356	4R''' ₁₀
			900	74630	4R''' ₁₂
800d	74615	3R'' ₂₀	950	74739	3R'' ₂₀
1000	74854	4R''' ₁₂			
500	75511	4R' ₀₀	500d	75670	4R' ₀₀
600	75730	a			
600	76060	4R' ₀₂	600d	76040	4R' ₀₂
			600d	76380	4R' ₀₄
600	76733	4R'' ₀₀	600d	76854	4R'' ₀₀
		4R' ₁₀			4R' ₁₀
100d	77196	4R'' ₀₂			
200	77609	4R'' ₀₀			
50	77760				
180	77923	4R' ₂₀ 4R'' ₁₀			
0d	78029	4R' ₂₂ 4R'' ₁₂			

a. May be members of a fifth (nR'''-A) Rydberg series.

TABLE I-7

COMPUTED LOW-LYING TRANSITIONS OF ETHYLENE

[After Robin, et al., J. Chem. Phys., 48 (1968) and Berry, et al., J. Chem. Phys., 49 (1968)]

Transition Symmetry in Mulliken's coord. frame	Robin, et al.				Berry, et al. [†]			Observed Energy (ev)
	Basis Excitation*	BADZ		BADZ+3s,3p		Upper State	Orbital Excitation	
		E(ev)	f	E(ev)	f			
$1A_g \rightarrow 1B_{3u}$	$1A_g \rightarrow 1B_{2u} (\pi \rightarrow 3s+3s)$			7.55	0.026			7.1
$1A_g \rightarrow 1B_{1g}$ ($b_{3u} \rightarrow b_{2u}$)	$1A_g \rightarrow 1B_{1g} (\pi \rightarrow 3p_x + 3p_x)$			8.39	0.000	$1B_{xg}$	$\pi_z \rightarrow \pi_y^* (1B_{yu})$ ($\pi_y^* = p_y + p_y$)	8.31
$1A_g \rightarrow 1B_{2g}$	$1A_g \rightarrow 1B_{3g} (\pi \rightarrow 3s-3s)$			8.42	0.000			
$1A_g \rightarrow 1B_{3u}$	$1A_g \rightarrow 1B_{2u} (\pi \rightarrow 3p_z - 3p_z)$			9.03	0.089			8.3
$1A_g \rightarrow 1B_{1u}$ ($b_{3u} \rightarrow b_{2g}$)	$1A_g \rightarrow 1B_{1u} (\pi \rightarrow \pi^*)$	9.40	0.307			$1B_{xu}$	$\pi_z (1b_{2u}) \rightarrow \pi_y^* (1b_{yg})$	7.81
$1A_g \rightarrow 1B_{1g}$ ($b_{3g} \rightarrow b_{2g}$)	$1A_g \rightarrow 1B_{1g} (1b_{2g} \rightarrow \pi^*)$	9.60	0.000			$1B_{xg}$	$\pi_y (1b_{zg}) \rightarrow \pi_z^*$	10.91
$1A_g \rightarrow 1B_{2g}$	$1A_g \rightarrow 1B_{3g} (3a_g \rightarrow \pi^*)$	11.01	0.000					
$1A_g \rightarrow 1B_{2g}$	$1A_g \rightarrow 1B_{3g} (\pi \rightarrow 3b_{1u})$	11.06	0.000					
$1A_g \rightarrow 1B_{3u}$	$1A_g \rightarrow 1B_{2u} (\pi \rightarrow 4a_g)$	11.14	0.009					

* See item I-42 for explanation of terms.

[†] See item I-44 for explanation of terms.

TABLE I-8

COORDINATE FRAMES IN D_{2h}

Coordinate Frame	Axis Perpendicular to Molecular Plane	Axis along Double Bond	Irreducible Representations								Used by
			A_g	B_{1g}	B_{2g}	B_{3g}	A_u	B_{1u}	B_{2u}	B_{3u}	
I	y	z	A_g	B_{1g}	B_{2g}	B_{3g}	A_u	B_{1u}	B_{2u}	B_{3u}	Robin
II	x	z	A_g	B_{1g}	B_{3g}	B_{2g}	A_u	B_{1u}	B_{3u}	B_{2u}	Mulliken, Craig, Walsh
III	z	x	A_g	B_{3g}	B_{1g}	B_{2g}	A_u	B_{3u}	B_{1u}	B_{2u}	Kaldor & Shavitt, Berry, Dunning & McCoy

TABLE I-9

CONSENSUS^a OF FREQUENCY ASSIGNMENTS FOR THE FUNDAMENTAL
MODES OF ETHYLENE (D_{2h})

Vibrational Mode ^b	Active	C_2H_4 (cm^{-1})	C_2D_4 (cm^{-1})	Isotopic Ratio $\frac{D}{H}$	Symmetry		
					Frame I	Frame II	Frame III
ν_1	R	3019	2251	0.746	a_g	a_g	a_g
ν_2	R	1623	1515	0.933	a_g	a_g	a_g
ν_3	R	1342	981	0.731	a_g	a_g	a_g
ν_4	---	1027	726	0.707	a_u	a_u	a_u
ν_5	R	3075	2304	0.749	b_{2g}	b_{3g}	b_{1g}
ν_6	R	1236 (or 1050)	1009 (or 883)	0.816 (or 0.841)	b_{2g}	b_{3g}	b_{1g}
ν_7	IR	949	720	0.759	b_{2u}	b_{3u}	b_{1u}
ν_8	R	943	780	0.827	b_{3g}	b_{2g}	b_{2g}
ν_9	IR	3106	2345	0.755	b_{3u}	b_{2u}	b_{2u}
ν_{10}	IR	810 (or 995)	586 (or 712)	0.723 (or 0.716)	b_{3u}	b_{2u}	b_{2u}
ν_{11}	IR	2990	2200	0.736	b_{1u}	b_{1u}	b_{3u}
ν_{12}	IR	1444	1080	0.748	b_{1u}	b_{1u}	b_{3u}

- a. Consensus is taken from the assignments of:
W.S. Gallaway and E.F. Barker, J. Chem. Phys., 10, 88-97 (1942).
G.H. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules",
D. Van Nostrand, 1945, p.326.
R.L. Arnett and B.L. Crawford, Jr., J. Chem. Phys., 18, 118-126
(1950).
C. Breecher and R.S. Halford, J. Chem. Phys., 35, 1109-1117 (1961).
W.L. Smith and I.M. Mills, J. Chem. Phys., 40, 2095-2109 (1964).
S. Kaufman, D.B. Hall, and J.J. Kaufman, J. Mol. Spectry., 16,
264-277 (1965).
- b. For vector description of these vibrational modes see G.H. Herzberg,
"Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand,
1945, p.107.

Figure I-1

Vacuum UV Absorption of Ethylene
[After Geiger and Wittmaack, Z. Naturforsch, 20A (1965)]

Figure I-2

Doublets of the $1740\overset{\circ}{\text{Å}}$ Rydberg System
 [After Wilkinson and Mulliken, J. Chem. Phys., 23 (1955)]

Figure I-3

V ← N Absorption Bands of C_2H_4 and C_2D_4

[After Wilkinson and Mulliken, J. Chem. Phys., 23, 1895 (1955)]

Figure I-4 .

Absorption Bands of C_2H_4 and C_2D_4 in the Region 1500-1300Å

[After Wilkinson, Can. J. Phys., 34, 643 (1956)]

CHAPTER II

AN ANNOTATED BIBLIOGRAPHY OF THE ELECTRONIC STRUCTURE AND ULTRAVIOLET ABSORPTION SPECTRA OF ALKYL SUBSTITUTED ETHYLENES

This bibliographical history will deal mainly with the methyl-substituted ethylenes since they display adequately the transitions occurring in the ultraviolet absorption spectra of simple mono-olefins. Cyclohexene and cyclopentene demonstrate that cyclic olefins display the same transitions.

To avoid confusion as to what bands are being referred to in the individual papers, we initially reproduce the absorption spectra (in the various phases in which reported) of the methyl-substituted ethylenes and these two cyclic olefins--Figures I-1 and I-8.

The spectra are in general more diffuse and less sharply structured than that of ethylene, obviating any complete spectral analyses. Therefore, we shall not tabulate reported frequencies from the literature as was done in Chapter I for ethylene.

Figure II-1

Propylene Spectrum (Vapor)

[After Samson, Marmo and Watanabe, J. Chem. Phys., 36, 783 (1962)]

Figure II-2

Isobutene Spectrum (Vapor)

[After Gary and Pickett, J. Chem. Phys., 22, 599 (1954)]

Figure II-3

cis-Butene-2 Spectrum (Vapor)

[After Gary and Pickett, J. Chem. Phys., 22, 599 (1954)]

Figure II-4

trans-Butene-2 Spectrum (Vapor)

[After Gary and Pickett, J. Chem. Phys., 22, 599 (1954)]

Figure II-5

Trimethylethylene Spectra

(A--Vapor, B--Liquid and Solution, C--Solution and glass at 77°K)

A--after Robin, Hart and
Kuebler, J. Chem. Phys.,
44, 1803 (1966)

B--after Carr and
Walter, J.
Chem. Phys.,
4, 756 (1936)

C--after Potts, J. Chem.
Phys., 23, 65 (1955)

Figure II-6
Tetramethylethylene Spectra
(A--Vapor, B--Liquid and Solution,
C--, Solution and Glass at 77°K)

Figure II-7
Cyclopentene Spectrum
(Vapor)

[after Pickett, Muntz and McPherson, J. Am. Chem. Soc.,
73, 4862 (1951)]

Figure II-8
Cyclohexene
(A--Vapor, B--Liquid and Solution, C--Solution and glass at 77°K)

- (1) J. Stark, W. Steubing, C.J. Enklaar und P. Lipp, "Die Ultravioletten Absorptionsbanden der Wechselseitigen Bindung von Kohlenstoffatomen. I. Methodik, Äthylenbindung." Jahrbuch der Radioaktivität und Elektronik, 10, 139-174 (1913).

- (1a) J. Stark und P. Lipp, "Einfluss der innermolekularen Relativbewegung auf die Intensität der Absorption und Fluoreszenz von Valenzelektronen." Zeit. f. Physik. Chemie, A86, 36-41 (1914).

These two references present very qualitative absorption spectra of isobutene, trimethylethylene, and n-hexane-2 in the vapor phase. They show the onset of absorption to lie in the range 230-210 millimicrons. This weak absorption then rises up the side of a stronger transition which has an inflection between 206 and 209 millimicrons. The maximum of the weak absorption band was estimated to be at about 180 millimicrons.

- (2) A. Lüthy, "Absorptionsspektrum in Ultravioletten von ungesättigten Verbindungen. Dampfspektren von Acrolein, Crotonaldehyd und Glyoxal." Zeits. f. Physik. Chemie, A107, 285-304 (1923).

Herein is reported the solution spectrum of trimethylethylene in hexane. The onset of absorption was reported to be a weak band

with its maximum between 2340 and 2350Å. The absorption then rises rapidly to about 1935Å (the lowest wavelength they report). Their curve also shows an inflection at about 2100Å.

(3) R.S. Mulliken, "Electronic Structures of Polyatomic Molecules and Valence. II. Quantum Theory of the Double Bond." Phys. Rev., 41, 751-758 (1932).

(3a) R.S. Mulliken, "Electronic Structures of Polyatomic Molecules and Valence. IV. Electronic States, Quantum Theory of the Double Bond." Phys. Rev., 43, 279-302 (1933).

Mulliken extended his treatment of planar and bent ethylene (See Chapter I-2&3) to ethylene derivatives of the form $R_1R_2C = CR_3R_4$ since they show qualitatively the same spectral behavior as ethylene. He interpreted the first strong transition ($\sim 2000\text{\AA}$) as being from the planar π level to the first excited π^* level, and suggested that its shift to longer wavelengths was probably due to the excited state being more nearly normal than in ethylene. The weaker absorption at 2300 to 2100Å was tentatively attributed to the corresponding triplet. He further stated that the stronger absorption at shorter wavelengths was probably an extension of the $\pi \rightarrow \pi^*$. His interpretation of the structure of olefins thus accounts for the conversion of cis into trans isomers and vice versa on absorption of ultraviolet light.

- (4) G. Scheibe, F. Povenz, und C.F. Linström, "Über die Lichtabsorption einiger Kohlenstoffverbindungen im Schumann-Ultraviolett."

Z. fur. Physik. Chemie, B20, 283-304 (1933).

They reported only that trimethylethylene shows a continuous absorption with no marked maxima, increasing in intensity from 45000 to 53000 cm^{-1} .

- (5) C.P. Snow and C.B. Allsopp, "Electronic Levels of Polyatomic Molecules. I. Some Levels of the C=C Double Bond." Trans. Far. Soc., 30, 93-99 (1934).

These workers reported the absorption spectra of cyclohexene and trimethylethylene in cyclohexene. Their data agrees with the previously reported olefin spectra, both absorptions being characterized by an intense maximum ($\log \epsilon = 4.0$) at about 1850Å and a weaker band between 2300 and 2900Å which is $\sim 10^{-4}$ times as strong. They agreed with Mulliken that the strong absorption is $^1A \rightarrow ^1B$ ($\pi \rightarrow \pi^*$), and also assign the weaker absorption as the corresponding $^1A \rightarrow ^3B$.

- (6) E.P. Carr and H. Stücklen, "Die Absorptionsspektren einiger Kohlenwasserstoffverbindungen im Schumann-Violett."

Z. fur Physik. Chemie, B25, 57-70 (1934).

This is the first in a series of papers by these workers and their colleagues which report spectra of olefins in the vacuum

ultraviolet region. Herein is reported the vapor spectra of n-heptene-1, n-pentene-1, n-pentene-2, and trimethylethylene. For the latter, they observed a broad, intense transition below $1530\text{\AA}$, a broad band with maximum at $1740\text{\AA}$ (57500 cm^{-1}), and two weaker ones at 2066 and $2171\text{\AA}$ (48403 and 46062 cm^{-1}).

(7) M.L. Sherril and G.F. Walter, "Preparation and Physical Constants of 2-Methylbutene-1."

J. Am. Chem. Soc., 58, 742-745 (1936).

They observed that the absorption curves for trimethylethylene, 2-methylbutene-1, 1-pentene, and 2-pentene in the pure liquid and in hexane solutions are all very similar. The step-out in absorption (i.e., weaker band) is shown by the pentenes in the region $42000\text{--}45000\text{ cm}^{-1}$. The position of this weak band appears to be dependent on the number of alkyl groups (and to a lesser extent on the arrangement of alkyl groups) around the double bond--being at longer wavelengths the greater the number of alkyl groups.

(8) E.P. Carr and M.K. Walker, "The Ultraviolet Absorption Spectra of Simple Hydrocarbons."

J. Chem. Phys., 4, 751-755 (1936).

The absorption spectra of n-heptene-3 and tetramethylethylene were reported in the liquid and hexane solution phases between 4000 and $2100\text{\AA}$. For n-heptene-3 they observed a step-out in absorption extending from 35200 cm^{-1} to approximately 39000 cm^{-1} corresponding

to a weak absorption, another step-out between 42000 and 46000 cm^{-1} due to a band of much higher intensity, and a final rise in absorption which continues to 47200 cm^{-1} .

Absorption begins in tetramethylethylene with a weak band ($\log \epsilon = -1.0$) from 30200 to 39000 cm^{-1} . Intensity then rises sharply to about 43400 cm^{-1} ($\log \epsilon = 3.0$) at which point three narrow bands are observed. These correspond to the first three peaks in a series of six narrow bands observed in the vapor phase.

Comparison of their spectra with earlier work reveals a progressive shift toward the visible as the hydrogen atoms of ethylene are replaced by alkyl groups. They also noted the similarity between the spectra of different hydrocarbons having the same configuration with respect to the double bond.

(9) E.P. Carr and G.F. Walter, "The Ultraviolet Absorption Spectra of Simple Hydrocarbons. II. In Liquid and Solution Phase."

J. Chem. Phys., 4, 756-760 (1936).

This paper reports the solution spectra in hexane of twelve olefinic hydrocarbons between 300 and 2100 $\text{\AA}$. They noted that the beginning of absorption ($\log \epsilon = -2.0$) seems characteristic of the number of alkyl groups bound to the carbon atoms of the double bond and is only very slightly affected by the nature of the alkyl groups. The weak absorption bands in the quartz region are

summarized as follows:

<u>Configuration</u>	<u>Frequency (cm⁻¹)</u>
RHC = CH ₂	38000 - 39000
RHC = CHR	34500 - 35800
R ₂ C = CH ₂	35000 - 36400
R ₂ C = CHR	32000 - 32800
R ₂ C = CR ₂	30,000

(10) E.P. Carr and H. Stüchli, "The Ultraviolet Absorption Spectra of Simple Hydrocarbons. III. In Vapor Phase in the Schumann Region."

J. Chem. Phys., 4, 760-768 (1936).

The vapor spectra of fourteen ethylenic hydrocarbons are presented for the range 2300 - 1500Å. Once again it is observed that the number of alkyl groups, not the nature of the alkyl group, determines the position of the first band in this region. Whether two alkyl groups are bound symmetrically or unsymmetrically causes only a slight difference in the wave number. The absolute intensity of this band was not reported, but it is stronger than the initial bands in the quartz region. Its position in the various alkyl

derivatives is summarized as follows:

<u>Configuration</u>	<u>Frequency (cm⁻¹)</u>
RHC = CH ₂	~53000
RHC = CHR	48000 - 49000
R ₂ C = CH ₂	49000 - 50000
R ₂ C = CHR	~46500
R ₂ C = CR ₂	~43100

They plotted the frequency of this absorption band versus the number of alkyl groups, obtaining a nearly straight line extrapolating to the transition in ethylene (zero alkyl groups) at 1744 $\overset{\circ}{\text{A}}$. They thus concluded that if this first transition is $^1\text{A} \rightarrow ^1\text{B}$ as assigned by Snow and Allsopp, then the 1744 $\overset{\circ}{\text{A}}$ peak in ethylene must be similarly assigned. They also concluded that the assignment by Snow and Allsopp of $^1\text{A} \rightarrow ^3\text{B}$ for the very weak bands in the quartz region is correct.

They stated that the first transition in the Schumann region appears to be overlapped by higher electronic transitions in most of the molecules studied. They could find no consistent frequency separations, the bands being too diffuse. Thus, no vibrational analysis was possible. In most cases the maxima were separated by 1200 - 1500 cm⁻¹ which is of the same order as the C=C stretching frequency in ethylene (1350 cm⁻¹).

- (11) A.A. Ashdown, L. Harris and R.T. Armstrong, "The Ultraviolet Absorption of Pure Cyclopropane and Propylene; Their Preparation and Boiling Points."

J. Am. Chem. Soc., 58, 850-852 (1936).

These workers looked at absorption of liquid propylene (-78°C) in a quartz cell with 1.5 cm pathlength. They were able to view only the onset of absorption in the neighborhood of $2400\text{\AA}$.

- (12) E.P. Carr and H. Stücklen, "The Ultraviolet Absorption Spectra of the Isomers of Butene-2 and Pentene-2."

J. Am. Chem. Soc., 59, 2138-2141 (1937).

This paper reports a great similarity in the structured absorption of cis-butene-2 and cyclohexene vapors ($47000 - 54000\text{ cm}^{-1}$), whereas the structure in the trans-butene-2 is different. The separation of the strongest peaks in cis-butene-2 is 1510 cm^{-1} ; in trans-butene-2, 1570 cm^{-1} . This compares with the ground state frequencies (Raman active) for the C=C stretch of 1658 cm^{-1} and 1674 cm^{-1} for the cis and trans forms, respectively. For cyclohexene the ultraviolet spacing is 1485 cm^{-1} compared with the ground state frequency 1646 cm^{-1} . This closely parallels the values of cis-butene-2.

- (13) E.P. Carr and H. Stücklen, "The Ultraviolet Absorption of Simple Hydrocarbons. IV. Unsaturated Cyclic Hydrocarbons in the Schumann Region."

J. Chem. Phys., 6, 55-61 (1938).

This paper presents the vapor absorption spectra of cyclohexene and cyclopentene in the region 2300 to 1650 $\text{\AA}$. They again note the similarity between the absorption of cyclohexene and that of cis-butene-2, both having spacings expected for a C=C stretching frequency. However, the cyclopentene absorption in the Schumann region is different from all the other olefins. The beginning of absorption is at 47600 cm^{-1} in accord with the other olefins. However, the spectrum in this region consists of a series of about twenty equally spaced narrow bands, the average separation of which is 130 cm^{-1} .

Quite clearly marked band separations of 1520 and 2470 cm^{-1} occur in the higher electronic level which begins at about 53000 cm^{-1} . These they compare with Raman values of 1610 cm^{-1} and a group of lines at 2846, 2902, 2947 and 3060 cm^{-1} .

- (14) E.P. Carr and H. Stücklen, "An Electronic Transition of the Rydberg Series Type in the Absorption Spectra of Hydrocarbons."

J. Chem. Phys., 7, 631 (1939).

The position of the diffuse bands of moderate intensity in the region between 43000 and 53000 cm^{-1} , when plotted versus the

number of alkyl groups, yields a nearly straight line. This line extrapolates to a value of $57,320 \text{ cm}^{-1}$ ($1744\overset{0}{\text{\AA}}$) in ethylene as measured by Price and Tutte (See Chapter I-7). It was identified as the first member of a Rydberg series. These authors thus concluded that the first absorptions in the Schumann region were Rydberg in nature, and were superimposed on the beginning of a continuous band of high intensity ($\nu_{\text{max}} \approx 57000 \text{ cm}^{-1}$ in most olefins). This band they assigned as $N \rightarrow V$ ($^1A \rightarrow ^1B$).

(15) W.C. Price and W.T. Tutte, "The Absorption Spectra of Ethylene, deutero-Ethylene, and Some Alkyl-Substitued Ethylenes in the Vacuum Ultra-violet."

Proc. Roy. Soc. (London), 174, 207-220 (1940).

These authors noted that the diminution in the heat of hydrogenation with increasing alkyl substitution parallels the red shift in the spectrum. However, the shift in the bands is considerably less than the diminution in ionization potential. This indicates the upper state is becoming increasingly antibonding with the alkyl substitution. Ionization potentials were computed from Rydberg series limits in the vacuum ultraviolet absorption. They obtained 10.45 ev for ethylene, 9.6 ev for propylene, 9.2 ev for tran-butene-2, 8.75 ev for trimethylethylene, and 8.3 ev for tetramethylethylene.

- (16) H. Sponer and E. Teller, "Electronic Spectra of Polyatomic Molecules."

Revs. Mod. Phys., 13, 138-141 (1941).

Table E of this reference summarizes the spectral data on olefinic hydrocarbons to this date.

- (17) R.S. Mulliken, "Structure and Ultraviolet Spectra of Ethylene, Butadiene, and Their Alkyl Derivatives."

Revs. Mod. Phys., 14, 265-274 (1942).

Mulliken noted that the $N \rightarrow R$ band in ethylene ($1745\text{\AA}$) is progressively red-shifted when methyl groups are successively substituted for the four hydrogens, becoming much lower in energy than the $N \rightarrow V$. At the same time the $N \rightarrow V$ red-shifts, but less rapidly ($\lambda_{\text{max}} = 1630\text{\AA}$ in ethylene, $1730\text{\AA}$ in propylene, and $1870\text{\AA}$ in tetramethylethylene). He designated the various molecular electronic structures as

$$N: ---(\text{xx})^2 ; V: ---(\text{xx})(\text{x}\bar{\text{x}}) ; R: ---(\text{xx})(\text{r}),$$

where (xx) refers to the bonding π -MO, ($\text{x}\bar{\text{x}}$) to the antibonding π^* -MO, and r is a Rydberg orbital, perhaps essentially a 3s orbital centered around the midpoint of the double bond. He stated that the triplet level which corresponds to V may be the upper level of the very weak absorption in liquid and solution phases at longer wavelengths, as had been assigned by Snow and Allsopp.

He estimated the orbit of the electron in r to be at least $3\text{\AA}$ so that it would spend most of its time well outside the H atoms in ethylene. However, collision of the r electron with methyl groups could account for the diffuseness of the $N \rightarrow R$ bands in the ethylenic derivations.

Since ionization potentials reflect the term value of the xx -MO and since both $N \rightarrow V$ and $N \rightarrow R$ transitions occur from this MO, he was able to calculate term values for $x\bar{x}$ and r from observed transition energies. It was seen that the $x\bar{x}$ term value decreases with methyl substitution, whereas the effect is small for the r -MO.

On the basis of an LCAO-MO calculation on propylene, he concluded that the decrease in the xx and $x\bar{x}$ term values with increased methylation is due mainly to charge transfer. This involves the accumulation of negative charge on the central carbon atoms at the expense of the more electropositive CH_3 groups. A small portion of the decrease was accounted for by hyperconjugation between the $\text{C}=\text{C}$ double bond and the CH_3 groups.

He thus concluded that the red-shift in the $N \rightarrow R$ on alkyl substitution is due mainly to charge transfer; the red-shift of the $N \rightarrow V$ can be explained by hyperconjugation.

(18) J.R. Platt and H.B. Klevens, "Spectroscopy of Organic Molecules in the Vacuum Ultraviolet."

Revs. Mod. Phys., 16, 182-223 (1944).

This reference summarizes the assignments given the various

electronic transitions in olefins. Table III on page 205 reviews to this date all the spectral data on compounds containing unconjugated double bonds.

(19) E.P. Carr, "Electronic Transitions in the Simple Unsaturated Hydrocarbons."

Chem. Revs., 41, 293-299 (1947).

Carr found on reviewing the spectra of cyclic dienes that the structure in their first, very weak absorption is similar to the structure of their $N \rightarrow R$ band. By analogy with this system, she concluded that the initial weak bands in mono-olefins ($38000 - 30000 \text{ cm}^{-1}$) were also Rydberg in nature. The low intensity in comparison with the Rydberg transition could be explained if this long-wavelength transition were $N \rightarrow T_R$. Thus, the energy difference between the $N \rightarrow R$ and $N \rightarrow T_R$ should evaluate the difference between two electronic states of the carbon atom in the unsaturated hydrocarbon molecule. Since the weak bands are structureless in the mono-olefins, and since the $N \rightarrow R$ transitions are diffusely structured, no reference point for finding this energy difference could be arrived at in these compounds.

(20) J.R. Platt, H.B. Klevens, and W.C. Price, "Absorption Intensities of Ethylenes and Acetylenes in the Vacuum Ultraviolet."

J. Chem. Phys., 17, 466-469 (1949).

This represents the first attempt at determining absolute

intensities of transitions in mono-olefins. Their detection method was photographic and involved a plate calibration technique. They reported molar extinction coefficients for isomeric octenes and for cyclohexene measured in hexane solutions. For the latter they reported $\epsilon_{\text{max}} = 6600$ at $\nu_{\text{max}} = 54900 \text{ cm}^{-1}$ for the $N \rightarrow V$, the transition having a band width of 8100 cm^{-1} . This yielded an f-value of 0.23 ± 0.05 .

- (21) L.W. Pickett, M. Muntz and E.M. McPherson, "Vacuum Ultraviolet Absorption Spectra of Cyclic Compounds. I. Cyclohexane, Cyclohexene, Cyclopentane, Cyclopentene and Benzene." J. Am. Chem. Soc., 73, 4862-4865 (1951).

This reference presents photographically determined intensity measurements on cyclopentene and cyclohexene, using the compounds as flowing vapors to minimize photodecomposition. They did not report frequencies of absorption since their values agree with previous ones of Carr and Stücklen. However, they plot molar extinction coefficient versus wavenumber and calculate the following oscillator strengths:

<u>Substance</u>	<u>Wavenumber (cm^{-1})</u>	<u>f-value</u>
Cyclohexene	45600 - 51200	0.01
	51200 - 58100	0.19
	58100 - 64300	0.20
Cyclopentene	47600 - 50000	0.004
	50000 - 64000	0.32

They observed that the spacing on the initial peak in cyclopentene of 130 cm^{-1} represents vibrations of the ring. A spacing of 1485 cm^{-1} in cyclohexene probably corresponds to the double bond stretching frequency of 1650 cm^{-1} observed in the ground state through Raman and infrared measurements.

(22) J.T. Gary and L.W. Pickettt, "The Far Ultraviolet Absorption Spectra of the Isomeric Butenes."

J. Chem. Phys., 22, 599-602 (1954).

A photographic vapor absorption study of four isomeric butenes yielded the following f-values in the range 45000 to 64000 cm^{-1} : butene-1, 0.39; cis-butene-2, 0.59; trans-butene-2, 0.32; and isobutene, 0.39. The position of the first Rydberg band was found to be 53390 cm^{-1} for butene-1, 49750 cm^{-1} for isobutene, 49470 cm^{-1} for trans-butene-2, and 48400 cm^{-1} for cis-butene-2. This supports earlier findings that the position depends on the number of alkyl groups substituted on double-bonded carbons.

However, the position of maximum absorption exhibits no such rule. Isobutene exhibited maximum absorption at 53100 cm^{-1} , trans-butene-2 at 56270 cm^{-1} ; but butene-1 and cis-butene-2 showed highest molar extinction coefficients at 57100 and 57000 cm^{-1} , respectively, although the band center appeared to be perhaps 200 cm^{-1} larger.

They noted that these positions depend on the molecular shape and seem related to the ground state dipole moment vector.

Butene-1 and cis-butene-2 have dipole moments perpendicular to the double bond and are at relatively high energies. trans-Butene-2 has a zero dipole moment and lies at a lower energy. Isobutene, having a dipole moment along the double bond, has its maximum at a still lower energy.

No vibrational analysis was possible although all the spectra show prominently a separation near 1500 cm^{-1} which is certainly due to C=C stretch. It was noted that these bands in cis-butene-2 are especially sharpened on cooling the vapor to -80°C .

(23) D. Semenow, A.J. Harrison, and E.P. Carr, "Absorption Intensities of the Isomeric Pentenes in the Vacuum Ultraviolet."

J. Chem. Phys., 22, 638-642 (1954).

A photographic study of the absolute absorption intensities of isomeric pentene vapors in the range $45000 - 65000\text{ cm}^{-1}$ yielded the following results.

<u>Compound</u>	<u>Maximum of N $\rightarrow$ V</u>		<u>First N $\rightarrow$ R Band</u>	
	<u>ev</u>	<u>log ϵ</u>	<u>ev</u>	<u>log ϵ</u>
1-pentene	7.01	4.19	6.57	3.59
3-methyl-1-butene	7.03	4.12	6.53	3.39
cis-2-pentene	7.01	4.22	6.05	2.93
trans-2-pentene	6.88	4.13	6.17	3.10
2-methyl-1-butene	6.60	4.05	6.17	3.42
trimethylethylene	7.01	4.02	5.65	2.16

This table reveals that the position of the $N \rightarrow V$ maximum does not depend on the number of alkyl substituents. Thus it cannot be explained on the basis of hyperconjugation as Mulliken has supposed. It seems to depend more strongly on the molecular shape as previously reported for isomeric butenes. The position of the $N \rightarrow R$ band again appears to depend only on the number of alkyl substituents.

Their reported f-values are:

<u>Compound</u>	<u>Wavenumber (cm^{-1})</u>	<u>f-value</u>
cis-2-pentene	53360 - 61700	0.45
trimethylethylene	50690 - 63850	0.44
1-pentene	54000 - 60730	0.38
3-methyl-1-butene	54250 - 62850	0.38
trans-2-pentene	52880 - 59750	0.32
2-methyl-1-butene	51200 - 58350	0.26

(24) J.T. Gary and L.W. Pickett, "The Far Ultraviolet Absorption Spectra of Selected Isomeric Hexenes."

J. Chem. Phys., 22, 1266-2167 (1954).

It was again found that the maximum of the $N \rightarrow V$ depended not on the number of alkyl substituents, but on the dipole moment vector of the molecule. Trimethylethylene, having a zero vector, shows a band maximum at 53500 cm^{-1} ($f=0.33$). Hexane-1 and cis-3-hexene, having a moment perpendicular to the double bond, have

absorption maxima at 55900 ($f=0.48$) and 56110 ($f=0.34$), respectively.

2,3-Dimethyl-1-butene, with a vector along the double bond, absorbs at lower energies with $\nu_{\max} = 53,200 \text{ cm}^{-1}$ ($f=0.40$).

- (25) W.J. Potts, Jr., "Low-Temperature Absorption Spectra of Selected Olefins in the Farther Ultraviolet Region."
J. Chem. Phys., 23, 65-72 (1955).

The absorption spectra of tetramethylethylene, trimethylethylene, cyclohexene, and hexene-1 were observed in solutions of 3-methylpentane-isopentane at room temperature, and in a rigid hydrocarbon glass (six parts isopentane, 3 parts 3-methylpentane) at 77°K. The structured $N \rightarrow R$ bands are not found in these spectra, presumably because the large Rydberg orbital is greatly perturbed by solvent molecules. Instead a "red shoulder" appears on the $N \rightarrow V$ transition at room temperature, but not at low temperature. This is explained as resulting from the fact that the potential curves for twist about the double bond in the ground and excited states have slopes of opposite sign.

A weaker absorption, partially masked at room temperature by the tail of the "red shoulder" on the $N \rightarrow V$, is clearly seen at 77°K in the region 40000 - 48000 cm^{-1} . It is assigned as $N \rightarrow T$ on the basis of its analogy to the $N \rightarrow V$ transition in position, extinction coefficient and oscillator strength. The following

data is presented for this $N \rightarrow T(?)$ transition:

<u>Molecule</u>	<u>Tetramethylethylene</u>	<u>Trimethylethylene</u>	<u>Cyclohexene</u>	<u>Hexene-1</u>
Center of $N \rightarrow T$	43800 cm^{-1}	44200 cm^{-1}	44000 cm^{-1}	46400 cm^{-1}
Average ϵ	2.5 ± 0.5	0.6 ± 0.1	1.0 ± 0.2	0.2 ± 0.1
f-number	$4.2 \pm 1.0 \times 10^{-5}$	$1.0 \pm 0.5 \times 10^{-5}$	$2.7 \pm 0.8 \times 10^{-5}$	$0.26 \pm 0.1 \times 10^{-5}$

Also presented is the following data on the $N \rightarrow V$ transition:

<u>Molecule</u>	<u>Tetramethylethylene</u>		<u>Trimethylethylene</u>		<u>Cyclohexene</u>		<u>Hexene-1</u>	
Temperature	298°K	77°K	298°K	77°K	298°K	77°K	298°K	77°K
$\nu_{\text{max}} (\pm 500 \text{ cm}^{-1})$	52250	53750	53000	54000	54750	55500	56000	56500
ϵ_{max}	10000 (± 700)	10500 (± 900)	5800 (± 700)	5600 (± 900)	6800 (± 700)	6800 (± 900)	6300 (± 700)	5400 (± 900)
f-number	0.45 (± 0.10)		0.34 (± 0.09)		0.38 (± 0.09)		0.29 (± 0.08)	

Potts looked for emission from tetramethylethylene, but found none. He suggested that cyclohexene might be a more likely candidate to phosphoresce since it cannot lose excitation by radiationlessly twisting without breaking a C-C bond.

(26) S. Stokes and L.W. Pickettt, "Absorption of Bicycloheptane and Bicycloheptene in the Vacuum Ultraviolet."

J. Chem. Phys., 23, 258-260 (1955)

The vapor spectrum of bicycloheptene (norbornene) was reported in the region 45000 to 65000 cm^{-1} . It is different from the absorption

of other olefins in that two quite distinct and equally intense bands appear instead of the normal $N \rightarrow R$ structured peak overlapped by the stronger $N \rightarrow V$. The first observed absorption has its maximum at 51125 cm^{-1} , the second at $59,715 \text{ cm}^{-1}$. Both have an oscillator strength of 0.15.

(27) L.C. Jones, Jr. and L.W. Taylor, "Far Ultraviolet Absorption Spectra of Unsaturated and Aromatic Hydrocarbons." Analytical Chemistry, 27, 228-237 (1955).

These authors present the absorption spectra of 69 hydrocarbons in the range 1700 to $2300\text{\AA}$. They determined intensities photoelectrically and compared them with the previous photographically determined values. They reported:

<u>Compound</u>	<u>State</u>	<u>Wavelength ($\text{\AA}$)</u>	<u>Molar Absorptivity</u>
Propylene	V	~ 1730	$\sim 11,500$
cis-2-Butene	V	1740	16,000
trans-2-Butene	V	1780	13,000
Isobutene	V	1882	11,300
Trimethylethylene	V	1775	11,000
Tetramethylethylene	V	1870	15,600
Cyclopentene	V	1828	13,600
Cyclohexene	V	1755	8,000

In general, their intensity data is about 12% higher than the previous photographic values reported.

- (28) B.B. Loeffler, E. Eberlin, and L.W. Pickett, "Far Ultraviolet Absorption Spectra of Small Ring Hydrocarbons." J. Chem. Phys., 28, 345-347 (1958).

These workers reported the molar extinction coefficients for the far ultraviolet absorption of cyclobutene, 1-methylcyclobutene, and methylenecyclobutane. For the $N \rightarrow V$ transition they reported the following:

<u>Compound</u>	<u>Wavenumber range (cm^{-1})</u>	<u>Band Max (cm^{-1})</u>	<u>f</u>
cyclobutene	51000 - 61150	56700	0.28
methylenecyclobutane	47500 - 56900	57000	0.29
1-methylcyclobutene	48500 - 58450	56500	0.29

Once again they observed that the position of the $N \rightarrow R$ transition seems dependent only on the number of alkyl groups attached to the double bond, whether cyclic or acyclic. The $N \rightarrow V$ band maximum appears to depend strongly on the dipole moment vector of the molecule as previously reported in acyclic mono-olefins.

- (29) J.A.R. Samson, F.F. Marmo, and K. Watanabe, "Absorption and Photoionization Coefficients of Propylene and Butene-1 in the Vacuum Ultraviolet." J. Chem. Phys., 36, 783-786 (1962).

Absorption and photoionization coefficients of propylene vapor were measured photoelectrically in the region 1050 - 2000 $\text{\AA}$. Two Rydberg series were observed in propylene yielding series limits of 9.74 and 9.80 ev. Photoionization curves yielded ionization

potentials of 9.73 and 9.80 ev.

(30) R.S. Berry, Analog of $n \rightarrow \pi^*$ Transitions in Mono-olefins."

J. Chem. Phys., 38, 1934-1938 (1964).

Reasoning by analogy with the $n \rightarrow \pi^*$ transition of formaldehyde, Berry assigned a transition of 6.5 ev in ethylene as $\sigma \rightarrow \pi^*$. Later experimental evidence indicates such a transition does not exist (see Chapter I-28). This transition, he said, corresponded to the weak absorption in alkylated ethylenes at $2300\text{\AA}$ (sometimes $2500\text{\AA}$) to the onset of stronger absorption around $2100\text{\AA}$. It seems he was referring to the weak absorption observed in liquid and solution phases in the quartz region. However, this transition begins at $\lambda \approx 3300\text{\AA}$ in tetramethylethylene. His reference to the fact that some structure has been observed on these bands in the vapor phase seems to indicate he was referring to the $N \rightarrow R$ band. It seems natural that some confusion would develop later as to exactly which band he was calling $\sigma \rightarrow \pi^*$.

(31) D.F. Evans, "Effect of Nitrogen Under Pressure on the

Rydberg Spectra of Polyatomic Molecules; the Nature of the Long-wavelength Olefin Band."

Proc. Roy. Soc. (London), 1963, 378-379.

Evans, thinking Berry had assigned as $\sigma \rightarrow \pi^*$ the bands previously thought to be $\pi \rightarrow R$, obtained the vapor spectra of

cyclohexene and tetramethylethylene in the presence of 133 atmospheres of nitrogen. The effect of such a high pressure of inert gas was to cause broadening and a washing out of structure in the region 2400 - 2100 $\text{\AA}$. This is the effect one would expect if the upper state of the transition is a large Rydberg orbital, probably 3s.

(32) M.B. Robin, R.R. Hart, and N.A. Kuebler, "Assignment of the Mystery Band of Olefins."

J. Chem. Phys., 44, 1803-1811 (1966).

These authors also misunderstood Berry's assignment and gave the name "mystery band" to the structured absorption in the region 2300 - 2100 $\text{\AA}$. They assigned it as an anti-Berry $\pi \rightarrow \sigma^*$ transition on the basis of a Gaussian-AO computation on ethylene (See Chapter I-33). Because their basis set was Gaussian, they were unable to distinguish well between valence-shell and Rydberg character in their σ^* -MO. They assumed it was mainly CH* antibonding with considerable ns Rydberg character. This prompted them to a discussion of whether the commonly held idea of σ - π separability is a valid one.

(33) P.A. Clark, "Electronic Transitions in Methyl-Substituted Ethylenes."

J. Chem. Phys., 48, 4795-4796 (1968).

Clark performed CNDO-MO computations on the series of methyl-substituted ethylenes, but did not include the 3s-AO in her basis-set. The shift in predicted energies for the $\pi \rightarrow \sigma^*$ transition

on increased methylation approximately paralleled the observed shift for the $R \leftarrow N$ bands. However, absolute values were in poor agreement. She noted that one would expect the $\pi \rightarrow \sigma^*$ (valence-shell) and $\pi \rightarrow$ Rydberg excitation energies to have the same slope when plotted versus the number of alkyl groups.

- (34) M.B. Robin, H. Basch, N.A. Kuebler, B.E. Kaplan and J. Meinwald, "Assignments in the Ultraviolet Spectra of Olefins." J. Chem. Phys., 48, 5037-5047 (1968).

These authors were able to distinguish between valence-shell and Rydberg contributions to their MO's of ethylene by using an indirect SCF calculation in a Gaussian basis (See Chapter I-42). They determined that the low-lying $\pi \rightarrow \sigma^*$ excitations are Rydberg in nature; the low-lying $\sigma \rightarrow \pi^*$ excitations strictly valence shell. They thus agree with the original assignment of Carr and Stüchlen, $N \rightarrow R(3s)$, for the absorption just below the $N \rightarrow V$ in simple olefins.

They further report the vapor absorption spectrum of tricyclo[3.3.0.0]oct-3-ene (TCO) to have three distinct electronic transitions below the $\pi \rightarrow \pi^*$, with band maxima at about 48000, 55000, and 64000 cm^{-1} . All three peaks have quite sharp vibrational structure. The second and third transitions disappear in the spectrum of a polycrystalline TCO film, leaving the lowest transition (~ 48000) clearly observable. This lowest transition appears to be valence-shell in character, either $\sigma \rightarrow \pi^*$ or $\pi \rightarrow \sigma^*$.

They conclude that in simple olefins, Rydberg $\pi \rightarrow \sigma^*$ excitations will be lowest, but in more strained olefins, a low-lying valence-shell transition is nearly degenerate with, or falls below, the lowest Rydberg.

- (35) M. Yaris, A. Moscovitz, and R.S. Berry, "Low-Lying Excited States of Mono-olefins."

J. Chem. Phys., 49, 3150-3160 (1968).

This reference presents computations on ethylene and trans-cyclo-octene (See Chapter I-44). The authors report that three low-lying transitions are needed to explain experimental data:

- a. $\pi \rightarrow \pi^*$ - responsible for the strong, olefinic absorption ($\epsilon \sim 10^4$).
- b. $\pi \rightarrow 3s$ Rydberg - responsible for the olefin band with $\epsilon \approx 10^3$.
- c. $\pi \rightarrow \sigma^*$, 3p Rydberg - accounting for a low-lying electric quadrupole-allowed transition observed in the optical rotatory properties of the twisted double bond.

- (36) A.J. Merer and R.S. Mulliken, "Ultraviolet Spectra and Excited States of Ethylene and Its Alkyl Derivatives."

To be published.

Professor Mulliken's review of the subject is an excellent one. He comments on the confusion which has resulted from Robin's misinterpretation of Berry's original assignment. See Chapter I-45 for further comments.

SUMMARY: The electronic transitions which have been experimentally observed in alkyl substituted ethylenes and cyclic olefins are the following:

a. A broad, intense absorption in the range 6.5 - 7.5 ev with an f-value of ~ 0.30 ($\epsilon = 10^4$). This is generally assigned as the $N \rightarrow V$ (lowest $\pi \rightarrow \pi^*$) transition.

b. A moderately intense, diffusely structured band in the range 5 - 7 ev with an f-value of ~ 0.01 ($\epsilon = 10^3$). This appears to be $N \rightarrow R(3s)$ as originally assigned by Carr and Stüchlen.

c. A very weak, structureless band ($\log \epsilon = -2.0$) observable only in the liquid phase at 4 - 5 ev. This is thought to be triplet in nature and was assigned as $N \rightarrow T$ by Carr and Potts. Mulliken feels it could possibly be $N \rightarrow T_R$.

d. An electric-dipole forbidden, electric-quadrupole allowed transition in the region 6 - 6.5 ev for a twisted double bond. This was assigned by Berry as $\pi \rightarrow \sigma^*(3p)$ Rydberg.

e. Sharp Rydberg series at higher energies, as yet unassigned.

The spectra should exhibit two singlet-triplet bands, the $N \rightarrow T$ and the $N \rightarrow T_R$. The weak absorption at 4 - 5 ev may correspond to one of these two possibilities. No emission has yet been observed from simple olefins to confirm the triplet nature of this weak band.

It has been shown by Robin that more complicated mono-olefins, especially those having much σ -strain, exhibit transitions to the red or the $N \rightarrow V$ which include both Rydberg and valence-shell types.

The shifts that are observable on appending methyl groups to ethylene are as follows:

a. The ionization potential shifts from 10.5 ev in ethylene to 8.3 ev in tetramethylethylene. This, says Mulliken and Price, is due to negative charge transfer from the methyls to the double-bonded carbons.

b. The $N \rightarrow R$ transition is red-shifted from 7.1 ev to ~ 5.4 ev with increased methylation. This shift seems dependent only on the number of alkyl substituents and not on their nature or arrangement about the double bond. It, too, is thought to result from the charge transfer mechanism.

c. The $N \rightarrow V$ transition is red-shifted less than the $N \rightarrow R$ on methylation, from 7.6 ev in ethylene to ~ 6.5 ev in tetramethylethylene. Mulliken says this is explicable completely on the basis of hyperconjugation. Carr, Gary and Pickett, however, in studying isomeric butenes, pentenes and hexenes, find the transition energy to depend on the molecular geometry and dipole moment of the molecule.

d. The weak bands in the liquid may or may not correspond to the $N \rightarrow T$ at ~ 4.4 ev in ethylene. They shift from 4.8 ev in olefins of the form $RHC = CH_2$ to 3.7 ev in olefins of the form $R_2C = CR_2$.

CHAPTER III

COMPUTATIONS

(A) Description of the Computational Methods: These one-electron calculations were done on the ground state configurations of the various molecules within the framework of the Mulliken-Wolfsberg-Helmholz method. This section gives only a brief description of the method which has been described in detail elsewhere¹⁻⁸ and applied to a variety of systems, mainly inorganics. It is our contention that much confusion has developed because semiempirical calculations have been done on ethylene and the results extrapolated to larger olefins. We feel that the results of a computation on one molecule serve only as a suggestion for assignments in that one molecule, these assignments being subject to experimental verification.

It is our further contention that a semiempirical investigation of trends in a series of mono-olefinic compounds, involving the same approximations throughout the series, might have more meaning and should be helpful in fixing definite assignments to observed transitions. The first series we chose to investigate is the same one studied by Clark^{II-33}--the methyl substituted ethylenes. This choice seems a logical one since more spectroscopic data exist in the literature for this series of mono-olefins: than for any other. These data demonstrate quite clearly the existence of transitions lower in energy than the $\pi \rightarrow \pi^*$. It is known that as one increases the number of methyl groups in the series, the $\pi \rightarrow \pi^*$ is red-shifted

due to hyperconjugation as first explained by Mulliken^{II-17}. If the computations can quantitatively duplicate this shift, then one can certainly put more trust in any other shifts predicted for increased methylation. Also reported are some initial computations on cyclic mono-olefins and cycloalkylidene--cycloalkanes which are not completed as of this writing.

In order to briefly describe the computational methods and, at the same time, give credit to the persons having written the various programs utilized, we present the following description of these programs:

ZEVC55--This program was written by A.T. Armstrong. It employs as basis orbitals Clementi-type AO's and minimizes energy utilizing the variational method as performed on a linear combination of these AO's. In our computations we chose as our basis set the 2s, 2p, and 3s orbitals of carbon (also the 3p's in one case for ethylene) and the 1s orbital on hydrogen. Coulomb integrals (H_{ii}) were approximated as the atomic valence state ionization potentials (VSIP). However, pi-type atomic functions are further parametrized by an adjustment of the VSIP term, i.e. a multiplicative factor⁸ of 0.8, which has been found to nicely reproduce the ionization potential and first transition energy in benzene, was applied. Resonance integrals (H_{ij}) were approximated by the method of Cusachs⁹,

$$H_{ij} = (2 - |S_{ij}|)(H_{ii} + H_{jj})S_{ij}/2$$

Overlaps were evaluated using the Clementi double-zeta set of AO's.¹⁰ Having no previous rules to guide us in the selection of a single orbital exponent for the virtual 3s function, we have varied it from 0.10 to 0.65 in the ethylene molecule. Two values, 0.30 and 0.483 (obtained from Slater's rules on promotion of a 2p electron into the 3s level) were employed for the computations on the molecular series. All computations involved an iteration to charge convergence utilizing a Mulliken population analysis.

TRIEL--This program was written by L.C. Cusachs to compute approximate transition moments (electric dipole, magnetic dipole, and electric quadrupole) and oscillator strengths. It employs energies and Löwdin molecular orbitals as obtained from ZEVC55. Although the eigenvectors are cast into the Löwdin MO form¹¹, it treats the AO's as still being centered on the nuclei. It thus evaluates all one-center terms and neglects all two-center ones. Such an approximation has been shown by Cusachs¹² to give rather reliable results. The program incorporates Slater-type AO's in computing transition moments, whereas we have employed coefficients from Löwdin orbitals obtained using Clementi-type AO's. The orbital exponents used for these Slater AO's were obtained from Slater's rules or from the program described next. As mentioned before, ξ_{3s} was varied from 0.10 to 0.65 for ethylene.

OAOS--This program was written by L.C. Cusachs¹³. It generates an effective single Slater-type orbital (STO) exponent which mimics the self-overlap of SCF functions at various interatomic separations.

SOC 1--This program was written by L.G. Vanquickenborne to evaluate singlet-triplet mixing as given by $\langle S | \mathcal{H}' | T \rangle$ where $\mathcal{H}'$ represents the one-electron spin-orbit coupling interaction of the two molecular orbitals^{2,14,15}. Only one-center terms are included in the calculation which utilizes Löwdin MO's and energies from ZEVC55 and dipole transition moments from TRIEL to compute $S_0 \rightarrow T_1$ transition moments and phosphorescence lifetimes.

VESCF--This program was written by J.V. Russell and performs a VESCF^{16,17} (variable electronegativity self-consistent field) calculation on pi-electron systems, using orbital populations as obtained from ZEVC55.

CI--This program, by J.V. Russell, employs output from VESCF and performs a configuration interaction calculation using SCF wavefunctions, yielding energies and oscillator strengths of $S_0 \rightarrow T_1$, $\pi \rightarrow \pi^*$ transitions.

SDIPOL--This program, written by L.C. Cusachs, uses orbital populations outputted from ZEVC55 to compute static dipole moments.

(B) Computational Results: Ethylene

At the time these computations were begun, we were unaware of the coordinate frame recommended by Mulliken and chose frame I of Table I-8, i.e. the z-axis along the double bond and the y-axis out of the molecular plane. Thus, our group theoretical notation agrees with that of Robin and is easily converted to the other coordinate frames using Table I-8. We used 1.34 $\text{\AA}$ for the C=C distance, 1.07 $\text{\AA}$ for the C-H distance and 118 $^\circ$ for the HCH angle.

Selection of a proper orbital exponent (ξ) for the virtual 3s orbital presented an initial difficulty. Slater's rules give $\xi_{3s} = 0.20$ for a 3s orbital with six electrons in the second valence shell. They yield 0.483 if one promotes a 2p electron to the 3s level. The OAOS program indicated that an orbital exponent of 0.30 would best mimic SCF overlaps, but could provide no information regarding a virtual orbital. We decided to vary ξ_{3s} from 0.10 to 0.65 to see what effect this has on the computations.

The results of this variation in ξ_{3s} are shown in Figure III-1, in which we plot MO energies versus ξ_{3s} . For values of $\xi_{3s} = 0.10$ to 0.45, the ordering of MO's is the same, having $b_{3g}(\pi^*)$ as the lowest unfilled MO, the $a_g(R(3s))$ next, and the $b_{1u}(R^*(3s,2s))^\dagger$ third.

[†]It has occurred to us that the name "antisymmetric" might better apply in describing this $R^*(3s,2s)$ orbital. Mulliken (II-17) has stated that the Rydberg orbital may be thought of as a large diffuse atomic-like orbital centered in the middle of the double bond. This is indeed where Robin (I-33) situated his Gaussian representation of the virtual 3s. This does not allow for the possibility of "symmetric" 3s+3s (referred to as "bonding" in the text) or "antisymmetric" 3s-3s ("antibonding" in the text). We feel that the "bonding-antibonding" nomenclature used in the text is justified since our H_{ii} terms for the 3s's are finite: $H_{ii}(3s) = -3.4$ ev as compared with $H_{ii}(2s) = -20.6$ ev.

Figure III-1

Ethylene MO Diagram, Varying ξ_{3s}

At $\xi_{3s} = 0.483$, the $R^*(3s,2s)$ falls below the π^* and $R(3s)$ levels, and this order remains the same for the three lowest unfilled MO's as ξ_{3s} is increased to 0.65. The highest filled σ orbital, b_{2g} , is about 1.1 eV below the π level. Tables III-1 and III-2 give the ordering of MO's and predicted energies for the values $\xi_{3s} = 0.483$ and 0.300, respectively, along with their composition in terms of AO's. Table III-3 gives the energies predicted for the two low-lying transitions, along with their percentage Rydberg character. These results suggest that both the $\pi \rightarrow R(3s)$ and the $\pi \rightarrow R^*(3s,2s)$ lie in the range of, and possibly below, the $\pi \rightarrow \pi^*$. The $R(3s)$ orbital seems to be mostly Rydberg 3s in nature; the $R^*(3s,2s)$ appears to be about half Rydberg 3s, half valence-shell. The $\sigma \rightarrow \pi^*$ transition of Berry appears to be valence-shell in nature and does not vary with changing ξ_{3s} , lying about 1 eV above the $\pi \rightarrow \pi^*$. The $\pi \rightarrow \pi^*$ is at 7.12 eV and, being valence-shell, is also invariant.

These results do not however make any easier the selection of a proper ξ_{3s} . The value of 0.483 seems a logical choice on the basis of Slater's rules. We examined the output AO populations obtained from the calculations and, using Slater's rules, calculated the output ξ_{3s} on a carbon center if the $2p\pi$ population is omitted and an electron is considered as being in the virtual 3s orbital. The results are shown in Table III-4. It appears that a value of about 0.32 is consistently arrived at by this means. Since we had

TABLE III-1
MO'S OF ETHYLENE USING $\xi_{3s} = 0.483$

Common Notation	MO	Energy (ev)	Symmetry (Frame I)	Composition
σ π $R^*(3s, 2s)$ π^* $R(3s)$	1	-24.44	$(a_g)^2$	$\sigma(2s, 2p_z, CH)$
	2	-17.87	$(b_{1u})^2$	$\sigma^*(2s, 2p_z), \sigma(CH)$
	3	-15.25	$(b_{3u})^2$	$\sigma(2p_x), \sigma^*(CH)$
	4	-13.03	$(a_g)^2$	$\sigma(2p_z, CH)$
	5	-12.04	$(b_{2g})^2$	$\sigma^*(2p_x), \sigma(CH)$
	6	-10.89	$(b_{2u})^2$	$\pi(2p_y)$
	7	- 4.08	$(b_{1u})^0$	$\sigma^*(3s, 2s, 2p_z, C(2s)H), \sigma(C(3s)H)$
	8	- 3.78	$(b_{3g})^0$	$\pi^*(2p_y)$
	9	- 3.43	$(a_g)^0$	$\sigma(3s, 2p_z, 2s, C(3s)H), \sigma^*(C(2s)H)$
	10	7.76	$(b_{3u})^0$	$\sigma(2p_x), \sigma^*(CH)$
	11	12.15	$(a_g)^0$	$\sigma(2s, 2p_z, 3s), \sigma^*(CH)$
	12	15.03	$(b_{2g})^0$	$\sigma^*(2p_x, CH)$
	13	15.20	$(b_{1u})^0$	$\sigma^*(2p_z, 3s, 2s, CH)$
	14	55.57	$(b_{1u})^0$	$\sigma^*(2s, 2p_z, 3s), \sigma(CH)$

Transition	Symmetry	$\Delta E(\text{ev})$
$n \rightarrow \pi^*$	${}^1A_g \rightarrow {}^1B_{1g}; (b_{2g})^2 \rightarrow (b_{2g})(b_{3g})$	8.26
$\pi \rightarrow \pi^*$	${}^1A_g \rightarrow {}^1B_{1u}; (b_{2u})^2 \rightarrow (b_{2u})(b_{3g})$	7.11
$\pi \rightarrow R(3s)$	${}^1A_g \rightarrow {}^1B_{2u}; (b_{2u})^2 \rightarrow (b_{2u})(a_g)$	7.46
$\pi \rightarrow R^*(3s, 2s)$	${}^1A_g \rightarrow {}^1B_{3g}; (b_{2u})^2 \rightarrow (b_{2u})(b_{1u})$	6.81

TABLE III-2
MO'S OF ETHYLENE USING $\xi_{3s} = 0.300$

Common Notation	MO	Energy (ev)	Symmetry (Frame I)	Composition
	1	-24.41	$(a_g)^2$	$\sigma(2s, 2p_z, CH)$
	2	-17.87	$(b_{1u})^2$	$\sigma^*(2s, 2p_z), \sigma(CH)$
	3	-15.25	$(b_{3u})^2$	$\sigma(2p_x), \sigma^*(CH)$
	4	-13.03	$(a_g)^2$	$\sigma(2p_z, CH)$
σ	5	-12.03	$(b_{2g})^2$	$\sigma^*(2p_x), \sigma(CH)$
π	6	-10.90	$(b_{2u})^2$	$\pi(2p_y)$
π^*	7	- 3.78	$(b_{3g})^0$	$\pi^*(2p_y)$
$R(3s)$	8	- 3.46	$(a_g)^0$	$\sigma(3s, 2p_z, 2s, C(3s)H), \sigma(C(2s)H)$
$R^*(3s, 2s)$	9	0.60	$(b_{1u})^0$	$\sigma^*(3s, 2s, 2p_z, C(2s)H), \sigma(C(3s)H)$
	10	7.75	$(b_{3u})^0$	$\sigma(2p_x), \sigma^*(CH)$
	11	9.02	$(a_g)^0$	$\sigma(2s, 2p_z, 3s), \sigma^*(CH)$
	12	10.11	$(b_{1u})^0$	$\sigma^*(2p_z, 3s, 2s, CH)$
	13	15.02	$(b_{2g})^0$	$\sigma^*(2p_x, CH)$
	14	33.69	$(b_{1u})^0$	$\sigma^*(2s, 2p_z, 3s), \sigma(CH)$

Transition	Symmetry	$\Delta E(\text{ev})$
$n \rightarrow \pi^*$	${}^1A_g \rightarrow {}^1B_{1g}; (b_{2g})^2 \rightarrow (b_{2g})(b_{3g})$	8.25
$\pi \rightarrow \pi^*$	${}^1A_g \rightarrow {}^1B_{1u}; (b_{2u})^2 \rightarrow (b_{2u})(b_{3g})$	7.12
$\pi \rightarrow R(3s)$	${}^1A_g \rightarrow {}^1B_{2u}; (b_{2u})^2 \rightarrow (b_{2u})(a_g)$	7.44
$\pi \rightarrow R^*(3s, 2s)$	${}^1A_g \rightarrow {}^1B_{3g}; (b_{2u})^2 \rightarrow (b_{2u})(b_{1u})$	11.50

TABLE III-3

ETHYLENE: EFFECT OF VARYING ξ_{3s}

ξ_{3s}	$\Delta E(\text{ev}), \pi \rightarrow R(3s)$	% Rydberg	$\Delta E(\text{ev}), \pi \rightarrow R^*(3s, 2s)$	% Rydberg
0.10	7.49	99.97	11.13	99.57
0.15	7.45	99.83	11.81	98.59
0.20	7.46	99.29	12.64	91.42
0.25	7.45	98.20	12.59	70.47
0.30	7.44	96.49	11.50	54.81
0.35	7.44	94.37	10.06	47.90
0.40	7.44	91.96	8.66	45.32
0.45	7.45	89.57	7.46	44.82
0.483	7.47	87.99	7.12	45.22
0.50	7.48	87.23	7.12	45.54
0.55	7.50	85.07	7.12	46.93
0.60	7.53	83.10	7.12	48.69
0.65	7.55	81.36	7.12	50.62

TABLE III-4

ETHYLENE: COMPARISON OF INPUT AND OUTPUT ξ_{3s} 's

Input ξ_{3s}	Output ξ_{3s}^*
0.10	0.318
0.15	0.318
0.20	0.318
0.25	0.318
0.30	0.319
0.35	0.319
0.40	0.321
0.45	0.323
0.483	0.323
0.50	0.325
0.55	0.327
0.60	0.329
0.65	0.331

*Using AO population outputted from ZEV55, and Slater's rules.

begun the computations using a value near 0.32 (i.e., 0.300), we decided to retain it in later calculations on methyl-substituted ethylenes. We also carried out all calculations on this series with $\xi_{3s} = 0.483$.

The results of transition moment calculations for ethylene are shown in Table III-5 for $\xi_{3s} = 0.300$ and Table III-6 for $\xi_{3s} = 0.483$. In both cases, $\xi_{2px} = \xi_{2py} = \xi_{2pz} = 1.625$ (from Slater's rules). These tables present a rather surprising result. Although the computation predicts an f-value of 0.280 for the $\pi \rightarrow \pi^*$, which agrees well with the experimental value of 0.30, it fails to predict the observed values of 0.03 for the sharp $\pi \rightarrow R(3s)$. The predicted value is an order of magnitude too small when $\xi_{3s} = 0.483$ is used, and two orders of magnitude too small when $\xi_{3s} = 0.300$ is used. We have been informed by Mulliken in a private communication that he feels this computed value is too low, and that the $\pi \rightarrow R(3s)$ transition dipole moment should be about the same as that for the $3p_y \rightarrow 4s$ transition in the united sulfur atom. A hand calculation of this atomic transition moment using single Slater AO's yields a transition moment length of $0.0405\text{\AA}$ (using $\xi_{4s} = 0.243$, $\xi_{3py} = 1.817$ from Slater's rules). This corresponds to an f-value of 1.068×10^{-3} which is still an order of magnitude too small. It does agree well with the oscillator strength predicted for the ethylene molecule using $\xi_{3s} = 0.483$, and provides another reason for using this value

TABLE III-5

COMPUTED INTENSITIES FOR ETHYLENE, $\epsilon_{3s} = 0.300$

Transition	f_{total}	f_{ED}	$\vec{R}_{\text{ED}}(\text{\AA})$	f_{MD}	$\vec{R}_{\text{MD}}(\text{\AA}^2)$	f_{EQ}	$\vec{R}_{\text{EQ}}(\text{\AA}^2)$	$\Delta E(\text{e.v.})$
$\sigma \rightarrow \pi^*$	8.24×10^{-6}	0.0	0.0	6.72×10^{-6}	0.6705	1.52×10^{-6}	0.2133	8.25
$\pi \rightarrow \pi^*$	0.280	0.280	0.6700	0.0	0.0	0.0	0.0	7.12
$\pi \rightarrow R(3s)$	1.08×10^{-4}	1.08×10^{-4}	0.01287	0.0	0.0	0.0	0.0	7.44
$\pi \rightarrow R^*(3s, 2s)$	2.27×10^{-8}	0.0	0.0	1.85×10^{-8}	0.02138	4.17×10^{-9}	0.00680	11.50

TABLE III-6

COMPUTED INTENSITIES FOR ETHYLENE, $\xi_{3s} = 0.483$

Transition	f_{total}	f_{ED}	$\vec{R}_{\text{ED}}(\text{\AA})$	f_{MD}	$\vec{R}_{\text{MD}}(\text{\AA}^2)$	f_{EQ}	$\vec{R}_{\text{EQ}}(\text{\AA}^2)$	$\Delta E(\text{e.v.})$
$\sigma \rightarrow \pi^*$	8.25×10^{-6}	0.0	0.0	6.73×10^{-6}	0.6703	1.52×10^{-6}	0.2132	8.26
$\pi \rightarrow \pi^*$	0.280	0.280	0.6700	0.0	0.0	0.0	0.0	7.12
$\pi \rightarrow R(3s)$	3.02×10^{-3}	3.02×10^{-3}	0.06797	0.0	0.0	0.0	0.0	7.46
$\pi \rightarrow R^*(3s, 2s)$	3.36×10^{-9}	0.0	0.0	2.74×10^{-9}	0.01806	6.17×10^{-10}	0.00574	6.81

in computations on the alkyl substituted ethylenes.

Table III-5 and III-6 also reveal that the computed f-value for the $\pi \rightarrow R^*$ (3s,2s) is very small ($\sim 10^{-8}$). This is expected since the transition is electric dipole forbidden and gains only a small amount of allowedness through electric quadrupole and magnetic dipole contributions as shown. The electric quadrupole and magnetic dipole oscillator strengths are evaluated approximately from the respective transition moments, as described in Kauzmann¹⁸, as a ratio to the corresponding electric dipole oscillator strength.¹⁹ The formulas used were

$$f_{ED} = [1.085 \times 10^{-5}] [\Delta E (\text{cm}^{-1})] [\vec{R}_{ED} (\text{\AA})]^2$$

$$f_{EQ} \approx [1.13 \times 10^{-19}] [\Delta E (\text{cm}^{-1})]^3 [R_{EQ} (\text{\AA}^2)]^2$$

$$f_{MD} \approx [5.15 \times 10^{-20}] [\Delta E (\text{cm}^{-1})]^3 [R_{MD} (\text{\AA}^2)]^2$$

It is also seen that the electric dipole forbidden $\sigma \rightarrow \pi^*$ transition of Berry does gain some allowedness ($f \approx 8 \times 10^{-6}$) through magnetic dipole ($f_{MD} \approx 6.7 \times 10^{-6}$) and electric quadrupole ($f_{EQ} \approx 1.5 \times 10^{-6}$) contributions.

One further MWH calculation was done on ethylene in which we included the 3p orbitals. We used $\xi_{3s} = \xi_{3p_x} = \xi_{3p_y} = \xi_{3p_z} = 0.300$. Tables III-7 and III-8 show these results for the lowest transitions, with and without the 0.8 adjustment factor applied to the $3p\pi$

TABLE III-7

EFFECT OF INCLUDING 3p's IN ETHYLENE (NO ADJUSTMENT OF VSIP)

Transition	$\Delta E(\text{e.v.})$	Composition of Lower MO	Composition of Upper MO	f_{ED}
$\pi \rightarrow \pi^*$	5.51	99.94% $2p_y$	79.94% $2p_y$, 20.06% $3p_y$	0.168
$\sigma \rightarrow \pi^*$	6.68	45.03% $2p_x$, 54.40% CH	79.94% $2p_y$, 20.06% $3p_y$	0.0
$\pi \rightarrow R^*(3p_z)$	7.36	99.94% $2p_y$	88.66% $3p_z^*$, 4.15% $2s^*$, 5.00% $3s^*$	0.0
$\pi \rightarrow R(3s)$	7.42	99.94% $2p_y$	96.38% $3s$	3.82×10^{-3}
$\pi \rightarrow R(3p_x)$	8.35	99.94% $2p_y$	96.13% $3p_x$	0.0
$\pi \rightarrow R(3p_y)$	8.58	99.94% $2p_y$	99.94% $3p_y$	0.0

TABLE III-8

EFFECT OF INCLUDING 3p's IN ETHYLENE ($H_{ii}(3p_y) \times 0.8$)

Transition	$\Delta E(\text{e.v.})$	Composition of Lower MO		Composition of Upper MO	f_{ED}
$\pi \rightarrow \pi^*$	6.52	99.94% $2p_y$		95.00% $2p_y$, 5.00% $3p_y$	0.240
$\pi \rightarrow R^*(3p_z)$	7.36	99.94% $2p_y$		88.66% $3p_z^*$, 4.15% $2s^*$, 5.00% $3s^*$	0.0
$\pi \rightarrow R(3s)$	7.42	99.94% $2p_y$		96.38% $3s$	3.76×10^{-3}
$\sigma \rightarrow \pi^*$	7.69	45.03% $2p_x$,	54.40% CH	95.00% $2p_y$, 5.00% $3p_y$	0.0
$\pi \rightarrow R(3p_x)$	8.35	99.94% $2p_y$		96.13% $3p_x$	0.0
$\pi \rightarrow R(3p_y)$	8.81	99.94% $2p_y$		99.94% $3p_y$	0.0

Coulomb term. We first note that without the 0.8 VSIP factor the $\pi(2p_y)$ is very contaminated with $\pi(3p_y)$; with the factor it is less contaminated (95% $2p_y$). We tend to trust the results more with the factor included since the $\sigma \rightarrow \pi^*$ of Berry then occurs at 7.69 eV in good agreement with the experimental value of 7.45 eV. The $R^*(3s, 2s)$ is now replaced by an orbital of the same symmetry, $R^*(3p_z, 2s, 3s)$. As expected, only the $\pi \rightarrow \pi^*$ and $\pi \rightarrow R(3s)$ transitions are symmetry allowed, f-values for the others all being zero.

In fact, all Rydberg transitions from the π level are forbidden in D_{2h} symmetry until we reach the $\pi \rightarrow R^*(3p_y)$, which is the $\pi(2p_y) \rightarrow \pi^*(3p_y)$ transition. We presume this is the transition responsible for the second broad continuum in the region 1300 to 1500 Å. Yet, Price and Tuttle observe two weak Rydberg series starting about 1518 and 1436 Å and having quantum defects of 0.4 and 0.7, respectively, indicating they are to a p orbital. These two series go to the same ionization potential as the $\pi \rightarrow R(3s)$ series indicating they are transitions from the π level. Wilkinson found that there are four series including the $\pi \rightarrow R(3s)$. We were thus posed with the problem of how the three forbidden series, although weak, could have any intensity. One obvious way would be via a vibronic stealing mechanism since they are in every case above underlying continuous absorption from the $\pi \rightarrow \pi^*$ or the $\pi \rightarrow \pi^*(3p_y)$. Examination of the symmetries involved showed this could occur by various modes in D_{2h} .

The possibilities for such an occurrence are shown in Table III-9 which shows the vibrations, rotations, and combinations which can couple with various transitions. Stealing is allowed from the ${}^1A_g \rightarrow {}^1B_{1u}$ ($\pi \rightarrow \pi^*$) transition whenever the transition, plus coupling, becomes z-polarized.

It is possible that allowedness arises not by this mechanism, but as a result of excited states being of symmetry other than D_{2h} . However, we were intrigued by the possibility that our computed f-values for the $\pi \rightarrow R(3s)$ might be reliable and that it, also, gains its observed intensity by this mechanism. Might the $\pi \rightarrow R(3s)$ on coupling with one quantum of ν_8 steal intensity from the $\pi \rightarrow \pi^*$? We reasoned by analogy with benzene in which the first transition (symmetry forbidden) steals intensity from the first allowed transition. Albrecht²⁰ has treated this situation in benzene and arrived at an empirical vibronic coupling matrix element of 0.27 ev. His equation is

$$f_A = \left(\frac{E_A}{E_B}\right) (f_B) \left(\frac{H_{VC}}{\Delta E}\right)^2,$$

where f_A = oscillator strength gained by transition A on stealing intensity from transition B.

f_B = oscillator strength of transition B.

E_A and E_B = energies of transitions A and B in ev.

TABLE III-9

VIBRATIONS, ROTATIONS, OR COMBINATIONS^a WHICH CAN COUPLE IN D_{2h}

Symmetry	Transition	x-polarized	y-polarized	z-polarized ^b
${}^1A_g \rightarrow {}^1B_{1u}$	$\pi \rightarrow \pi^*$	$R_y, R_y + a$ ($a_g = \nu_1, \nu_2, \text{ or } \nu_3$) $R_z + \nu_8$ ν_5, ν_6	$R_x, R_x + a$ ($a_g = \nu_1, \nu_2, \text{ or } \nu_3$) $R_z + \nu_5 \text{ or } \nu_6$ ν_8	ν_1, ν_2, ν_3 $R_y + \nu_5 \text{ or } \nu_6$
${}^1A_g \rightarrow {}^1E_{2u}$	$\pi \rightarrow R(3s)$	$R_z, R_z + a$ ($a_g = \nu_1, \nu_2, \text{ or } \nu_3$) $R_y + \nu_8$	$\nu_1, \nu_2, \text{ or } \nu_3$ $R_y + \nu_5 \text{ or } \nu_6$ $R_x + \nu_8$	R_x ν_8 $R_z + \nu_5 \text{ or } \nu_6$
${}^1A_g \rightarrow {}^1B_{3g}$	$\pi \rightarrow R^*(3s, 2s)$ $\pi \rightarrow R^*(3p_z, 2s, 3s)$	ν_4 $R_z + \nu_{11} \text{ or } \nu_{12}$ $R_y + \nu_7$ $R_x + \nu_9 \text{ or } \nu_{10}$	$\nu_{11} \text{ or } \nu_{12}$ $R_z + \nu_4$ $R_x + \nu_7$ $R_y + \nu_9, \nu_{10}$	ν_7 $R_y + \nu_4$ $R_x + \nu_{11} \text{ or } \nu_{12}$ $R_z + \nu_9 \text{ or } \nu_{10}$
${}^1A_g \rightarrow {}^1B_{1g}$	$\pi \rightarrow R(3p_x)$	ν_7 $R_y + \nu_4$ $R_x + \nu_{11} \text{ or } \nu_{12}$ $R_z + \nu_9 \text{ or } \nu_{10}$	$\nu_9 \text{ or } \nu_{10}$ $R_y + \nu_{11} \text{ or } \nu_{12}$ $R_z + \nu_7$ $R_x + \nu_4$	ν_4 $R_z + \nu_{11} \text{ or } \nu_{12}$ $R_y + \nu_7$ $R_x + \nu_9 \text{ or } \nu_{10}$
${}^1A_g \rightarrow {}^1A_g$	$\pi \rightarrow R(3p_y)$	$\nu_9 \text{ or } \nu_{10}$ $R_x + \nu_4$ $R_y + \nu_{11} \text{ or } \nu_{12}$ $R_z + \nu_7$	ν_7 $R_y + \nu_4$ $R_x + \nu_{11} \text{ or } \nu_{12}$ $R_z + \nu_9 \text{ or } \nu_{10}$	$\nu_{11} \text{ or } \nu_{12}$ $R_z + \nu_4$ $R_x + \nu_7$ $R_y + \nu_9 \text{ or } \nu_{10}$

TABLE III-9 (Continued)

Footnotes

- a. The obvious combination of two quanta of any vibration or rotation, which is always totally symmetric, is not included in the table.
- b. All couplings which lead to z-polarization also enable the transition to steal intensity from the $\pi \rightarrow \pi^*$.

H_{vc} = vibronic coupling matrix element.

$\Delta E = E_A - E_B$ in ev.

We used the same matrix element as used in benzene, a value of 0.28 for the f-value of the $\pi \rightarrow \pi^*$ transition, and the experimentally observed energies 7.10 and 7.61 ev for the $\pi \rightarrow R(3s)$ and $\pi \rightarrow \pi^*$. This yielded $f(\pi \rightarrow R(3s)) = 0.075$. The mechanism thus provides plenty of intensity to account for the observed value. More will be said in the next section about its application to this transition in the alkyl substituted ethylenes.

The VESCF-CI calculation on ethylene yielded a manifold of singlets at -0.22, 7.32, and 11.66 ev. It predicts the $\pi \rightarrow \pi^*$ to be at 7.54 ev and have an f-value of 0.433, in good agreement with experiment. The $(\pi)^2 \rightarrow (\pi^*)^2$ transition of Craig is at 11.88 ev with zero intensity. It further predicts the $^3\pi^*$ to lie 4.34 ev above the ground state, in excellent agreement with Reid's reported 4.4 ev. Spin-orbit coupling calculations predict the oscillator strength of this transition to be 1.57×10^{-9} . No experimental f-value has been reported. However, Reid reports a maximum absorption coefficient of about 10^{-4} which corresponds to a molar extinction coefficient of about 10^{-3} . If we assumed the $\pi \rightarrow ^3\pi^*$ to be as broad as the $\pi \rightarrow \pi^*$ ($\epsilon = 10,000$, $f = 10^{-1}$), then we expect the $\pi \rightarrow ^3\pi^*$ to have an oscillator strength of about 10^{-8} . This is good agreement with our computed value.

(C) Computational Results on Methyl Substituted Ethylenes: These molecules were all treated as having planar carbon skeletons. We chose their skeletal plane as the xz-plane with the z-axis along the double bond, making the out-of-plane y-axis the pi-direction. All methyl hydrogens were placed in a staggered configuration (one up and two down or vice-versa). This is probably the most stable arrangement although it causes the molecules to deviate slightly from their proper symmetry point groups [D_{2h} for tetramethylethylene (TETME) and ethylene, C_{2v} for isobutene (ISOB) and cis-butene-2 (cis B), C_{2h} for trans-butene-2 (trans B), and C_s for trimethylethylene (TRIME) and propylene]. The molecules do, in fact, possess the symmetries cited because the methyl groups are free to rotate. We have taken all C=C double bond distances to be $1.34\text{\AA}$, C-C single bonds as $1.53\text{\AA}$, CH as $1.07\text{\AA}$ when the carbon is double bonded, and CH as $1.09\text{\AA}$ when the carbon is a methyl carbon.

We first performed MWH calculations on the series using a 3s orbital exponent of 0.300. The resulting MO energies along with their symmetries and percentage Rydberg characters are given in Table III-10. We use the symbol σ_B for the highest filled σ -orbital chosen by Berry in his $\sigma_B \rightarrow \pi^*$ assignment. It is antibonding in $2p_x$ and bonding between the carbons of the double bond and the methyl carbons.

TABLE III-10

MO'S PREDICTED FOR METHYL SUBSTITUTED ETHYLENES ($\xi_{3s} = 0.300$)

Molecule	MO	Symmetry	E(ev)	Percentage Rydberg Character
Ethylene(D_{2h})	σ_B	b_{2g}	-12.03	0.0
	π, N	b_{2u}	-10.90	0.0
	π^*, V	b_{3g}	- 3.78	0.0
	$R(3s)$	a_g	- 3.46	96.5
Propylene(C_s)	σ_B	a'	-11.74	0.0
	π, N	a''	-10.02	0.0
	$R(3s)$	a'	- 3.36	95.0
	π^*, V	a''	- 3.28	0.0
ISOB(C_{2v})	σ_B	b_1	-11.63	0.0
	π	b_2	- 9.38	0.0
	$R(3s)$	a_1	- 3.32	88.1
	π^*	b_2	- 2.76	0.0
cis B(C_{2v})	σ_B	b_1	-11.41	0.0
	π, N	b_2	- 9.43	0.0
	$R(3s)$	a_1	- 3.24	95.0
	π^*, V	a_2	- 2.76	0.0
trans B(C_{2h})	σ_B	a_g	-11.32	0.0
	π, N	a_u	- 9.34	0.0
	$R(3s)$	a_g	- 3.27	94.7
	π^*, V	b_g	- 2.90	0.0
TRIME (C_s)	σ_B	a'	-11.25	0.0
	π, N	a''	- 8.86	0.0
	$R(3s)$	a'	- 3.20	94.1
	π^*, V	a''	- 2.36	0.0
TETME (D_{2h})	σ_B	b_{2g}	-10.97	0.0
	π, N	b_{2u}	- 8.37	0.0
	$R(3s)$	a_g	- 3.08	94.4
	$\sigma^*(3s)$	b_{1u}	- 2.87	36.9
	π^*, V	b_{3u}	- 1.91	0.0

Tables III-11, 12, 13 and 14 give the calculated excitation energies of the low-lying transitions along with their symmetries and polarizations, and the computed ionization potentials. Included also are the reported experimental values. These results are plotted in Figures III-2 and III-3. Figure III-2 shows a remarkable agreement between calculation and experiment for the ionization potentials and the $N \rightarrow V$ excitation. Both are seen to shift regularly with increased methylation. The $N \rightarrow V$ energy is seen to vary a great deal among the three isomeric butenes as was first observed by Gary and Pickett. This variation is also predicted by the calculations as seen on the smaller graph inset in Figure III-2.

Inspection of the results failed to reveal the relative importance of the various effects (hyperconjugation, charge transfer, or molecular geometry) in determining the position of the $N \rightarrow V$ transition. Table III-15 shows the negative charge accumulated by the two double-bonded carbons and the dipole moment calculated on SDIPOL using outputted orbital populations from ZEVC55. Also included are the percentages of $1s_H$ in the π and π^* MO's. These should reflect the degree of hyperconjugation to some extent. However, since the molecular ground state is planar and the $(\pi)(\pi^*)$ state is bent (90°), these numbers cannot correctly tell the percentage of $1s_H$ character in the π^* -MO except for the single calculation done on 90° ethylene. The computed dipole moments do

TABLE III-11

$\sigma_B \rightarrow \pi^*$ EXCITATION ENERGIES IN METHYL SUBSTITUTED
ETHYLENES ($\xi_{3s} = 0.300$)

Molecule	Symmetry	Polarization	E(ev) Calculated
Ethylene	$(b_{2g})^2 \rightarrow (b_{2g})(b_{3g}); A_g \rightarrow B_{1g}$	F	8.25
Propylene	$(a')^2 \rightarrow (a')(a''); A' \rightarrow A''$	y	8.36
ISOB	$(b_1)^2 \rightarrow (b_1)(b_2); A_1 \rightarrow A_2$	F	8.27
cis B	$(b_1)^2 \rightarrow (b_1)(a_2); A_1 \rightarrow B_2$	y	8.65
trans B	$(a_g)^2 \rightarrow (a_g)(b_g); A_g \rightarrow B_g$	F	8.24
TRIME	$(a')^2 \rightarrow (a')(a''); A' \rightarrow A''$	y	8.89
TETME	$(b_{2g})^2 \rightarrow (b_{2g})(b_{3g}); A_g \rightarrow B_{1g}$	F	9.06

TABLE III-12

$\pi \rightarrow R(3s)$ EXCITATION ENERGIES IN METHYL SUBSTITUTED
ETHYLENE ($\xi_{3s} = 0.300$)

Molecule	Symmetry	Polarization	E(ev) calcd.	E(ev) exp.*
Ethylene	$(b_{2u})^2 \rightarrow (b_{2u})(a_g); A_g \rightarrow B_{2u}$	y	7.44	7.08 ^a
Propylene	$(a'')^2 \rightarrow (a'')(a'); A' \rightarrow A''$	y	6.66	6.53 ^a
ISOB	$(b_2)^2 \rightarrow (b_2)(a_1); A_1 \rightarrow B_2$	y	6.06	6.08 ^a , 6.15 ^b
cis B	$(b_2)^2 \rightarrow (b_2)(a_1); A_1 \rightarrow B_2$	y	6.19	6.08 ^a , 6.00 ^b
trans B	$(a_u)^2 \rightarrow (a_u)(a_g); A_g \rightarrow A_u$	y	6.07	6.08 ^a , 6.12 ^b
TRIME	$(a'')^2 \rightarrow (a'')(a'); A' \rightarrow A''$	y	5.66	5.75 ^a , 5.48 ^c
TETME	$(b_{2u})^2 \rightarrow (b_{2u})(a_g); A_g \rightarrow B_{2u}$	y	5.29	5.32 ^a , 5.43 ^c

* These experimental energies refer to the first band in the Schumann region ($\epsilon = 10^3$).

^a R.S. Mulliken, Rev. Mod. Phys., 14, 265 (1942).

^b Gary and Pickett, J. Chem. Phys., 22, 599 (1954).

^c Potts, J. Chem. Phys., 23, 65 (1955).

TABLE III-13

N → V EXCITATION IN METHYL SUBSTITUTED ETHYLENES ($\xi_{3s} = 0.300$)

Molecule	Symmetry	Polarization	E(ev) calcd.	E(ev) exp.*
Ethylene	$(b_{2u})^2 \rightarrow (b_{2u})(b_{3g}); A_g \rightarrow b_{1u}$	z	7.12	7.61 ^a
Propylene	$(a'')^2 \rightarrow (a'')(a''); A' \rightarrow A'$	x, z	6.74	7.17 ^b
ISOB	$(b_2)^2 \rightarrow (b_2)(b_2); A_1 \rightarrow A_1$	z	6.26	6.58 ^c
cis B	$(b_2)^2 \rightarrow (b_2)(a_2); A_1 \rightarrow B_1$	z	6.67	7.06 ^c
trans B	$(a_u)^2 \rightarrow (a_u)(b_g); A_g \rightarrow B_u$	x, z	6.44	6.97 ^c
TRIME	$(a'')^2 \rightarrow (a'')(a''); A' \rightarrow A'$	x, z	6.50	6.90 ^a , 6.57 ^d
TETME	$(b_{2u})^2 \rightarrow (b_{2u})(b_{3g}); A_g \rightarrow B_{1u}$	z	6.46	6.78 ^a , 6.47 ^d

*These experimental energies refer to the second, strong transition in the Schumann region ($\epsilon = 10^4$).

^aR.S. Mulliken, Rev. Mod. Phys., 14, 265 (1942).

^bG. Herzberg, "Electronic Spectra of Polyatomic Molecules", D. Van Nostrand Co., 1966, p.650.

^cGary and Pickett, J. Chem. Phys., 22, 599 (1954).

^dW.J. Potts, J. Chem. Phys., 23, 65 (1955).

TABLE III-14
IONIZATION POTENTIALS OF METHYL SUBSTITUTED
ETHYLENES ($\xi_{3s} = 0.300$)

Molecule	I.P.(ev), calcd.	I.P.(ev), exp.
Ethylene	10.90	10.5 ^a , 10.51 ^b , 10.45 ^c
Propylene	10.02	9.73, 9.73, 9.6
ISOB	9.38	8.95, 9.23, ----
cis B	9.43	9.13, 9.13, ----
trans B	9.34	9.24, 9.13, 9.2
TRIME	8.86	8.80, 8.68, 8.75
TETME	8.37	8.30, 8.30, 8.3

^aPrice, Bralsford, and Harris, Proc. Roy. Soc. (London), A258, 459 (1960).

^bD.W. Turner, Adv. Phys. Org. Chem., 4, 64 (1966).

^cPrice and Tutte, Proc. Roy. Soc. (London), 174, 207 (1940).

TABLE III-15

OUTPUT CHARGE, GROUND STATE DIPOLE MOMENTS, AND PERCENTAGE $1s_H$ CHARACTER IN THE π AND π^* MO's FOR METHYLSUBSTITUTED ETHYLENES ($\epsilon_{3s}=0.300$)

Molecule	Output Charge ^a		$\vec{D}$ (Debyes)	$\vec{D}_x$ (Debyes)	$\vec{D}_y$ (Debyes)	$\vec{D}_z$ (Debyes)	Percentage $1s_H$	
	C_1	C_2					π	π^*
Ethylene (Planar)	4.056	4.056	0.0	0.0	0.0	0.0	0.0	0.0
Ethylene (90°)	4.065	4.061	----	----	----	----	12.65	13.72
Propylene	4.089	4.023	2.31	1.92	-2.42	1.29	6.46	0.55
ISOB	4.121	3.992	0.44	-0.28	0.0	0.34	9.90	5.57
cis B	4.054	4.054	3.84	-3.84	0.0	-0.14	11.54	7.18
trans B	4.044	4.044	0.52	-0.28	0.0	-0.44	13.85	6.79
TRIME	4.078	4.015	2.22	-1.65	-1.42×10^{-3}	1.48	14.50	10.74
TETME	4.044	4.044	0.52	0.48	-0.21	0.0	21.68	13.74

^a C_1 and C_2 represent the two double-bonded carbons. The output charges are those outputted from ZEVC55. They represent the electronic charge on these two centers, and their differences from 4.000 indicate the charge accumulated by the double-bonded carbons from the methyl groups.

Figure III-2

Ionization Potentials and $N \rightarrow V$ Energies
in Methyl Substituted Ethylenes

Figure III-3

$N \rightarrow R(3s)$ and $\sigma \rightarrow \pi^*$ Energies in Methyl Substituted
Ethylenes

not agree well with what one expects from the molecular geometry. For example, tetramethylethylene should have a zero dipole moment but the calculations produce small moments in the x and y directions. This is due to methyl hydrogens being fixed rather than freely rotating.

In the case of the isomeric butenes where the effects of hyperconjugation and charge transfer from the methyls are more or less equal, the calculations predict that the $N \rightarrow V$ will lie at lower energies if the largest moment vector lies along the axis of polarization (z-axis for the $N \rightarrow V$). This agrees with the experimental findings of Gary and Pickett. The calculations also predict that the larger the dipole moment of the molecule (in the x and y directions), the larger is the $N \rightarrow V$ excitation energy (z-polarized). The predicted ordering for the $N \rightarrow V$ energy is thus cis-butene-2 > trans-butene-2 > isobutene. This is the order found experimentally.

In Figure III-2 we have plotted the calculated energies for both the $\sigma_B \rightarrow \pi^*$ transition of Berry and the $N \rightarrow R(3s)$ transitions of Carr and Stücklen and Mulliken. The latter shows remarkable agreement with the experimental values for the first absorption in the Schumann region, and clearly verifies the $N \rightarrow R(3s)$ assignment. We note that the calculated values agree with the experimental observation that the $N \rightarrow R(3s)$ energy varies little within the isomeric butenes, being seemingly dependent only on the number of

methyl groups.

Computed oscillator strengths for the $N \rightarrow V$ and $N \rightarrow R(3s)$ transitions are given in Tables III-16 and III-17, along with experimental values where reported. We notice first that calculations and experiment agree very well for the $N \rightarrow V$ intensities. Yet, we find the computed f-numbers to be smaller than the observed ones for the $N \rightarrow R(3s)$. They are about two orders of magnitude too small for ethylene and one order of magnitude too low for trimethylethylene and tetramethylethylene. It is further predicted that the intensity generally increases with increased methylation, whereas the experimental f-value for ethylene is 0.03 and that of tetramethylethylene is 0.01.

This apparent decrease in f-value with increased methylation, along with the discrepancy between predicted and observed intensities, again tempted us to investigate the vibronic stealing mechanism mentioned in Section III-B. Since the $N \rightarrow R(3s)$ is red-shifting with respect to the $N \rightarrow V$ on appending methyl groups, the vibronic stealing should decrease as one goes to the larger series members. Using the vibronic matrix element and equation of Albrecht (see Section III-B), we computed the f-values given in Table III-18. The mechanism of vibronic stealing from the $N \rightarrow V$ accounts nicely for the observed intensities and for the decrease in f-value as one goes from zero to four methyl groups.

TABLE III-16

CALCULATED f-NUMBERS* FOR THE N → V TRANSITION

($\xi_{3s} = 0.300$)

Molecule	f_{total}	f_{ED}	f_{MD}	f_{EQ}	$f_{\text{(experimental)}}$
Ethylene	0.280	0.280	0.0	0.0	0.34 ± 0.15^a , 0.29^b
Propylene	0.280	0.280	4.38×10^{-9}	2.18×10^{-8}	
ISOB	0.302	0.302	3.24×10^{-9}	2.62×10^{-8}	----
cis B	0.319	0.319	5.25×10^{-10}	8.92×10^{-10}	----
trans B	0.310	0.310	0.0	0.0	----
TRIME	0.327	0.327	4.54×10^{-10}	5.81×10^{-9}	0.34 ± 0.09^c , 0.33^d
TETME	0.332	0.332	1.51×10^{-10}	3.59×10^{-10}	

* ED = electric dipole, MD = magnetic dipole, EQ = electric quadrupole.

^aPlatt, Klevens, and Price, J. Chem. Phys., 17, 466 (1948).

^bHammond and Price, Trans. Far. Soc., 51, 605 (1955).

^cPotts, J. Chem. Phys., 23, 65 (1955).

^dSemenow, Harrison and Carr, J. Chem. Phys., 22, 638 (1954).

^eRobin, Hart, and Kuebler, J. Chem. Phys., 44, 1803 (1966).

TABLE III-17

CALCULATED f-NUMBERS FOR THE $N \rightarrow R(3s)$ TRANSITION

$(\xi_{3s} = 0.300)$

Molecule	f_{total}	f_{ED}	f_{MD}	f_{EQ}	$f_{\text{(experimental)}}$
Ethylene	1.08×10^{-4}	1.08×10^{-4}	0.0	0.0	$0.03 \pm 0.01^a, 0.04^b$
Propylene	2.16×10^{-4}	2.16×10^{-4}	4.82×10^{-8}	8.86×10^{-9}	----
ISOB	4.8×10^{-5}	4.8×10^{-5}	3.99×10^{-8}	7.67×10^{-9}	----
cis B	3.52×10^{-3}	3.52×10^{-3}	7.06×10^{-8}	1.38×10^{-8}	----
trans B	2.50×10^{-3}	2.50×10^{-3}	0.0	0.0	----
TRIME	9.90×10^{-4}	9.90×10^{-4}	1.94×10^{-8}	4.02×10^{-9}	$\sim 0.01^c$
TETME	1.20×10^{-3}	1.20×10^{-3}	1.05×10^{-11}	2.19×10^{-12}	$\sim 0.01^c$

^aPlatt, Klevens, and Price, J. Chem. Phys., 17, 466 (1940).

^bHammond and Price, Trans. Far. Soc., 51, 605 (1955).

^cApproximated from the molar extinction coefficients of 10^3 reported by several workers.

TABLE III-18

CALCULATION OF $f(N \rightarrow R(3s))$ BY VIBRONIC STEALING
FROM THE $N \rightarrow V$ TRANSITION

Molecule	$f(N \rightarrow R(3s))$
Ethylene	0.081
Propylene	0.047
ISOB	0.086
cis B	0.045
trans B	0.069
TRIME	0.012
TETME	0.014

As mentioned in Section III-B, Mulliken has informed us in a private communication that our computed oscillator strengths appear to be too low. He expects the f-number for the $N \rightarrow R(3s)$ of ethylene to be about the same as that calculated from the element $\langle 3p_y | y | 4s \rangle$ of the united sulfur atom. We have found that, using single Slater orbitals, this value agrees well with the f-number obtained using twice the carbon $\langle 2p_y | y | 3s \rangle$ element. If we assume the $N \rightarrow R(3s)$ transition to be pure C $2p_y \rightarrow 3s$ and multiply by the appropriate MO coefficients, we obtain the f-values given in Table III-19. They show the proper trend, decreasing with increasing methylation; but, again, they are two to three orders of magnitude too low. The vibronic stealing mechanism thus seems to be the only means by which we can explain the Rydberg intensities.

We next determined that rotation of the methyl groups had little effect on our MWH computations. Using propylene as a test case, we rotated the methyl group by 30° intervals until a configuration identical with the initial one was reached. The results (Table III-20) show there was little effect on the $N \rightarrow V$ and $N \rightarrow R(3s)$ transitions.

The MWH computations were repeated on these molecules using $\xi_{3s} = 0.483$. The resulting MO's and their energies are given in Table III-21. As was noted in the previous section, a new

TABLE III-19

CALCULATION OF $f\langle\pi|y|R(3s)\rangle$ IN METHYL SUBSTITUTED
ETHYLENES ASSUMING PURE $\langle 2p_y|y|3s\rangle$ TIMES
APPROPRIATE MO COEFFICIENTS

Molecule	$f\langle\pi y R(3s)\rangle$
Ethylene	1.85×10^{-3}
Propylene	5.40×10^{-4}
ISOB	2.03×10^{-4}
cis B	2.13×10^{-4}
trans B	2.24×10^{-4}
TRIME	1.14×10^{-4}
TETME	7.21×10^{-5}

TABLE III-20

EFFECT OF ROTATING THE METHYL GROUP IN PROPYLENE

$$(\xi_{3s} = 0.300)$$

Position	$E(N \rightarrow V)$ ev	$E(N \rightarrow R(3s))$ ev
1 = 5	6.62	6.49
2	6.81	6.57
3	6.62	6.49
4	6.45	6.43

TABLE III-21

MO'S PREDICTED FOR METHYL SUBSTITUTED ETHYLENES

($\xi_{3s} = 0.483$)

Molecule	MO	Symmetry	E(ev)	Percentage Rydberg
Ethylene	σ_B	b_{2g}	-12.04	0.0
	π, N	b_{2u}	-10.89	0.0
	$\sigma^*(3s, 2s)$	b_{1u}	- 4.08	45.2
	π^*, V	b_{3g}	- 3.78	0.0
	$R(3s)$	a_g	- 3.43	88.0
Propylene	σ_B	a'	-11.87	0.0
	π, N	a''	- 9.91	0.0
	$R^*(2s)$	a'	- 4.06	59.2
	π^*, V	a''	- 3.28	0.0
	$R(3s)$	a'	- 2.92	51.4
ISOB	σ_B	b_1	-11.69	0.0
	π, N	b_2	- 9.41	0.0
	$R(2s^*, 3s)$	b_1	- 3.84	71.6
	$R(3s)$	a_1	- 3.00	54.6
	π^*, V	b_2	- 2.78	0.0
cis B	σ_B	b_1	-11.40	0.0
	π, N	b_2	- 9.47	0.0
	$R^*(2s, 3s)$	b_1	- 3.89	64.75
	$\sigma(3s)$	a_1	- 3.60	31.21
	π^*, V	a_2	- 2.78	0.0
trans B	σ_B	a_g	-11.40	0.0
	π, N	a_u	- 9.34	0.0
	$R^*(2s)$	b_u	- 5.01	58.2
	$R(3s)$	a_g	- 3.12	73.2
	π^*, V	b_g	- 2.89	0.0

TABLE III-21 (Continued)

Molecule	MO	Symmetry	E(ev)	Percentage Rydberg
TRIME	σ_B	a'	-11.36	0.0
	π, N	a''	- 8.91	0.0
	$R^*(2s)$	a'	- 4.73	56.1
	$R(3s)$	a'	- 3.44	69.8
	π^*, V	a''	- 2.38	0.0

TETME	σ_B	b_{2g}	-11.03	0.0
	π, N	b_{2u}	- 8.49	0.0
	$\sigma^*(2s)$	b_{1u}	- 5.14	48.7
	$R(2p_x)$	b_{3u}	- 3.64	66.5
	$R(3s, 2s)$	a_g	- 3.10	74.7
	π^*, V	b_{3g}	- 1.94	0.0

low-lying MO now appears which is $R^*(3s,2s)$ in ethylene, i.e. an antibonding MO which is $\sigma^*(2s)$ and $\sigma^*(3s)$ between the double bonded carbons. We shall maintain the notation in which the information within the parentheses gives bonding and antibonding character between the carbons of the double bond. The symbol R will now be used to indicate more than 50% Rydberg character in the entire MO. The symbol σ will be used to indicate less than half Rydberg character. In this new notation the lowest unfilled MO in ethylene ($\xi_{3s} = 0.483$) becomes $\sigma^*(3s,2s)$ because it has 45.2% Rydberg character. The ionization potentials, and excitation energies for $\sigma_B \rightarrow \pi^*$, $N \rightarrow R(3s)$, and $N \rightarrow V$ are given in Tables III-22-25. They are all relatively unaffected by using $\xi_{3s} = 0.483$ instead of $\xi_{3s} = 0.300$.

However, a new trend now appears in the series. The $N \rightarrow \sigma^*(3s,2s)$ transition (Table III-26) now is the lowest transition in ethylene. It is seen to shift greatly with increased methylation, and in a regular manner. The composition is seen to change as the symmetry of the molecule changes. In fact, the orbital becomes $R^*(2s)$ for most of the molecules. From group theory it is the same MO throughout the series, being b_{1u} in both ethylene and tetramethylethylene--both of which are of D_{2h} symmetry. We shall refer to this new lowest-lying transition as simply $N \rightarrow R^*$.

Computed oscillator strengths for the three low-lying transitions are shown in Tables III-27-29. The $N \rightarrow V$ values are

TABLE III-22

$\sigma_B \rightarrow \pi^*$ EXCITATION ENERGIES IN METHYL SUBSTITUTED
ETHYLENES ($\xi_{3s} = 0.483$)

Molecule	Symmetry	Polarization	E(ev)
Ethylene	$A_g \rightarrow B_{1g}$		8.26
Propylene	$A' \rightarrow A''$	y	8.95
ISOB	$A_1 \rightarrow A_2$		8.91
cis B	$A_1 \rightarrow B_2$	y	8.26
trans B	$A_g \rightarrow B_g$		8.51
TRIME	$A' \rightarrow A''$	y	8.98
TETME	$A_g \rightarrow B_{1g}$		10.1

TABLE III-23

N → R(3s) EXCITATION ENERGIES IN METHYL SUBSTITUTED ETHYLENES($\xi_{3s} = 0.483$)

Molecule	Symmetry	Polarization	E(ev)
Ethylene	$A_g \rightarrow B_{2u}$	y	7.46
Propylene	$A' \rightarrow A''$	y	6.99
ISOB	$A_1 \rightarrow B_2$	y	6.41
cis B	$A_1 \rightarrow B_2$	y	5.87
trans B	$A_g \rightarrow A_u$	y	6.22
TRIME	$A' \rightarrow A''$	y	5.47
TETME	$A_g \rightarrow B_{2u}$	y	5.39

TABLE III-24

N → V EXCITATION ENERGIES IN METHYL SUBSTITUTED ETHYLENES($\xi_{3s} = 0.483$)

Molecule	Symmetry	Polarization	E(ev)
Ethylene	$A_g \rightarrow B_{1u}$	z	7.11
Propylene	$A' \rightarrow A'$	x,z	6.63
ISOB	$A_1 \rightarrow A_1$	z	6.63
cis B	$A_1 \rightarrow B_1$	z	6.69
trans B	$A_g \rightarrow B_u$	x,z	6.45
TRIME	$A' \rightarrow A'$	x,z	6.35
TETME	$A_g \rightarrow B_{1u}$	z	6.55

TABLE III-25

IONIZATION POTENTIALS OF METHYL SUBSTITUTED ETHYLENES

$$(\xi_{3s} = 0.483)$$

Molecule	I.P. (ev)
Ethylene	10.89
Propylene	9.91
ISOB	9.41
cis B	9.47
trans B	9.34
TRIME	8.91
TETME	8.49

TABLE III-26

N → R* EXCITATION ENERGIES IN METHYL SUBSTITUTED ETHYLENES

($E_{3s} = 0.483$)

Molecule	Symmetry	Polarization	E(ev)
Ethylene	$(b_{2u})^2 \rightarrow (b_{2u})(b_{1u}); A_g \rightarrow B_{3g}$	y	6.81
Propylene	$(a'')^2 \rightarrow (a'')(a'); A' \rightarrow A''$		5.85
ISOB	$(b_2)^2 \rightarrow (b_2)(b_1); A_1 \rightarrow A_2$		5.57
cis B	$(b_2)^2 \rightarrow (b_2)(b_1); A_1 \rightarrow A_2$		5.58
trans B	$(a_u)^2 \rightarrow (a_u)(b_u); A_g \rightarrow B_g$	y	4.33
TRIME	$(a'')^2 \rightarrow (a'')(a'); A' \rightarrow A''$		4.18
TETME	$(b_{2u})^2 \rightarrow (b_{2u})(b_{1u}); A_g \rightarrow B_{3g}$		3.35

TABLE III-27

COMPUTED f-NUMBERS FOR THE N → V TRANSITION IN METHYL
SUBSTITUTED ETHYLENES

$$(\underline{f}_{3s} = 0.483)$$

Molecule	f_{total}	f_{ED}	f_{MD}	f_{EQ}
Ethylene	0.280	0.280	0.0	0.0
Propylene	0.281	0.281	3.75×10^{-9}	2.13×10^{-8}
ISOB	0.301	0.301	1.15×10^{-9}	3.80×10^{-8}
cis B	0.322	0.322	2.66×10^{-10}	3.80×10^{-11}
trans B	0.299	0.299	0.0	0.0
TRIME	0.331	0.331	4.49×10^{-10}	5.59×10^{-9}
TETME	0.336	0.336	6.25×10^{-10}	4.90×10^{-10}

TABLE III-28

COMPUTED f-NUMBERS FOR THE $N \rightarrow R(3s)$ IN METHYL SUBSTITUED
ETHYLENES ($\xi_{3s} = 0.483$)

Molecule	f_{total}	f_{ED}	f_{MD}	f_{EQ}
Ethylene	3.02×10^{-3}	3.02×10^{-3}	0.0	0.0
Propylene	1.27×10^{-3}	1.27×10^{-3}	8.09×10^{-8}	1.20×10^{-8}
ISOB	4.38×10^{-3}	4.38×10^{-3}	6.35×10^{-8}	9.60×10^{-9}
cis B	3.64×10^{-3}	3.64×10^{-3}	2.24×10^{-9}	1.59×10^{-9}
trans B	1.65×10^{-2}	1.65×10^{-2}	0.0	0.0
TRIME	3.09×10^{-3}	3.09×10^{-3}	5.64×10^{-8}	1.02×10^{-8}
TETME	5.55×10^{-3}	5.55×10^{-3}	3.66×10^{-12}	2.68×10^{-12}

TABLE III-29
COMPUTED f-NUMBERS FOR THE N → R* TRANSITION
IN METHYL SUBSTITUTED ETHYLENES
($\xi_{3s} = 0.483$)

Molecule	f_{total}	f_{ED}	f_{MD}	f_{EQ}	$f_{\text{(experimental)}}$
Ethylene	3.36×10^{-9}	0.0	2.74×10^{-9}	6.16×10^{-10}	----
Propylene	3.07×10^{-3}	3.07×10^{-3}	7.92×10^{-10}	3.21×10^{-10}	----
ISOB	1.36×10^{-3}	1.36×10^{-3}	4.37×10^{-9}	9.67×10^{-10}	----
cis B	4.06×10^{-3}	4.06×10^{-3}	4.12×10^{-8}	8.08×10^{-9}	----
trans B	1.06×10^{-7}	1.01×10^{-7}	4.59×10^{-9}	1.14×10^{-9}	----
TRIME	5.14×10^{-4}	5.14×10^{-4}	1.39×10^{-8}	2.92×10^{-9}	$1.0 \pm 0.5 \times 10^{-5}^a$
TETME	6.09×10^{-4}	6.09×10^{-4}	6.68×10^{-10}	1.49×10^{-10}	$4.2 \pm 1.0 \times 10^{-5}^a$

^aThese refer to the oscillator strengths for the weak absorption in the quartz region as reported by Potts, J. Chem. Phys., 23, 65 (1955).

unaffected by the use of $\xi_{3s} = 0.483$, whereas the $N \rightarrow R(3s)$ values are increased. The computed intensities now are within reasonable agreement with experiment, being an order of magnitude too small for ethylene and about half the experimental value for the two largest members of the series. Having evoked the vibronic stealing mechanism before these results were obtained, we now wonder at its necessity. Yet, we cannot see why such a process cannot occur since it accounts so well for the intensities observed. It still seems a necessary assumption in the case of ethylene.

Table III-29 shows the $N \rightarrow R^*$ transitions to have the proper energy and intensity in trimethylethylene and tetramethylethylene to make it a candidate for the first weak transition in liquid olefins. Since the transition has been observed only in larger olefins which exist as liquids at room temperature, it would be interesting to see if they are greatly blue-shifted as methyl groups are removed. According to the computations, the transition should be very much weaker in trans-butene-2.

That this weakest transition observed in absorption is $N \rightarrow T$ or $N \rightarrow T_R$ are also possibilities. We have performed spin-orbit coupling computations on the series and obtained the results shown in Table III-30. The calculated oscillator strengths are much lower

TABLE III-30

SPIN-ORBIT COUPLING RESULTS FOR METHYL SUBSTITUTED ETHYLENES

Molecule	$f(N \rightarrow T)$	$f(N \rightarrow {}^3R(3s))$
Ethylene	1.57×10^{-9}	3.88×10^{-7}
Propylene	1.31×10^{-9}	2.22×10^{-6}
ISOB	1.35×10^{-8}	6.55×10^{-9}
cis B	9.93×10^{-10}	2.53×10^{-9}
trans B	1.04×10^{-9}	1.71×10^{-7}
TRIME	8.45×10^{-10}	1.75×10^{-8}
TETME	1.63×10^{-10}	1.40×10^{-9}

than those reported by Potts for trimethylethylene and tetramethylethylene. On the basis of this calculation it would appear that the low-energy transition in olefins is neither $N \rightarrow T$ nor $N \rightarrow T_R$. However, it is of course possible that the calculated values may be too low because of the one-center approximation. Also, the experimental values may be high owing to absorbed oxygen enhancement of the $S_0 \rightarrow T_1$ process. This would bring calculation and experiment more into line so that the $N \rightarrow T$ and $N \rightarrow T_R$ assignments are still possible.

Although the VESCF-CI programs can handle only planar pi-systems, we inputted the output charges from ZEVC55 and treated the methyl groups as in-plane hydrogens. We hoped this would give us some idea of how the $N \rightarrow T$ shifts with increased negative charge transfer from the methyls. The results are shown in Table III-31. The agreement with the small observed shift in the weakest olefin transition is quite good, again pointing to the $N \rightarrow T$ assignment. The choice between $N \rightarrow R^*$ or $N \rightarrow T$ (or $N \rightarrow T_R$) can be easily made by experimentally observing this transition in the methylated series. If it shifts greatly with decreased methylation it would appear to be $N \rightarrow R^*$. If the shift is small, it would likely be $N \rightarrow T$ (or $N \rightarrow T_R$). Rigorous degassing and/or flushing with N_2 should decrease its intensity if it is singlet $\rightarrow$ triplet, but have no effect on the $N \rightarrow R^*$.

TABLE III-31

VESCF-CI RESULTS FOR THE N $\rightarrow$ T TRANSITION OF METHYL
SUBSTITUTED ETHYLENES

Molecule	$E(S_0 \rightarrow T_1)$ ev
Ethylene	4.34
Propylene	4.30
ISOB	4.27
cis B	4.27
trans B	4.26
TRIME	4.24
TETME	4.23

(D) Computational Results on Methylenecycloalkanes, Cycloalkylidene-cycloalkanes, and Cyclic Mono-Olefins: Computations were done on these molecules to see what effect σ -strain has on the ordering of the MO energies. Methylenecycloalkanes are ring compounds with a methylene group double-bonded to a carbon of the ring. They are natural extensions of a series starting with ethylene and isobutene. The cycloalkylidenecycloalkanes are two rings joined by a double bond and are extensions of a series beginning with ethylene and tetramethylethylene. All were treated as planar ring systems. Table III-32 gives the MO's obtained for the methylene cycloalkanes using $\xi_{3s} = 0.300$. It is interesting to note that in methylenecyclopropane and methylenecyclopentane a low-lying MO, $\sigma^*(2p_x)$, is obtained which is mostly valence-shell in character. It lies above the $\pi \rightarrow \pi^*$ however in both cases. Methylenecyclopentane also exhibits a purely valence-shell, second π -MO— π' . Table III-33 reveals that the trends observed for the methyl substituted ethylenes are not so regular in these molecules. The ability of the three and five membered rings to enter into resonance and lower the $\pi \rightarrow \pi^*$ transition is very evident. The MO's which result when $\xi_{3s} = 0.483$ is used are shown in Table III-34. This leads to additional low-lying Rydberg orbitals.

The results for two cycloalkylidenecycloalkanes are shown in Table III-35 for $\xi_{3s} = 0.300$ and Table III-36 for $\xi_{3s} = 0.483$. Here again we encounter several low-lying orbitals which are either

TABLE III-32

LOW-LYING MO'S IN METHYLENECYCLOALKANES $(\xi_{3s} = 0.300)$

Molecule	MO	Symmetry (C_{2v})	E(ev)	Percentage Rydberg
Methylenecyclopropane	σ_B	b_1	-11.88	0.0
	π	b_2	-10.67	0.0
	π^*	b_2	- 5.33	0.0
	R(3s)	a_1	- 3.63	83.6
	$\sigma^*(2px)$	b_1	- 3.50	25.0
Methylenecyclobutane	σ_B	b_1	-10.87	0.0
	π	b_2	- 9.34	0.0
	R(3s)	a_1	- 3.18	94.7
	π^*	b_2	- 2.78	0.0
Methylenecyclopentane	σ_B	b_1	- 9.18	0.0
	π	b_2	- 8.93	0.0
	R(3s, 2pz)	a_1	- 3.36	73.8
	π^*	b_2	- 2.46	0.0
	R(3s, 2s*)	a_1	- 2.16	66.2
	π'	b_2	- 1.23	0.0
	$\sigma^*(2px)$	b_1	- 1.15	8.0

TABLE III-33

EXCITATION ENERGIES IN THE METHYLENECYCLOALKANES($\epsilon_{3s} = 0.300$)

Molecule	Transition	E(ev)
Ethylene	$\sigma_B \rightarrow \pi^*$	8.25
ISOB		8.87
Methylenecyclopropane		6.55
Methylenecyclobutane		8.09
Methylenecyclopentane		6.72

Ethylene	$N \rightarrow R(3s)$	7.45
ISOB		6.06
Methylenecyclopropane		7.04
Methylenecyclobutane		6.16
Methylenecyclopentane		5.57

Ethylene	$N \rightarrow V$	7.13
ISOB		6.62
Methylenecyclopropane		5.34
Methylenecyclobutane		6.56
Methylenecyclopentane		6.47

Ethylene	Ionization Potential	10.91
ISOB		9.38
Methylenecyclopropane		10.67
Methylenecyclobutane		9.34
Methylenecyclopentane		8.93

TABLE III-34

LOW-LYING MO's IN METHYLENECYCLOALKANES($\xi_{3s} = 0.483$)

Molecule	MO	E(ev)	Percentage Rydberg
Methylenecyclopropane	σ_B	-11.96	0.0
	π	-10.70	0.0
	$\sigma^*(2px)$	- 6.51	30.6
	π^*	- 5.33	0.0
	$\sigma(2s^*, 2p_z, 3s)$	- 4.83	43.2
	$R(3s, 2s^*)$	- 3.85	57.0
Methylenecyclobutane	σ_B	-11.05	0.0
	π	- 9.39	0.0
	$R(3s, 2s^*)$	- 4.24	55.1
	$R^*(2px)$	- 2.88	51.6
	π^*	- 2.80	0.0
	$R(2s^*, 3s)$	- 2.74	72.2
Methylenecyclopentane	σ_B	- 9.16	0.0
	π	- 9.02	0.0
	$\sigma(2s^*, 3s)$	- 5.32	43.0
	$\sigma^*(2px)$	- 4.57	15.4
	π^*	- 2.50	0.0
	$R(3s, 2s^*)$	- 1.99	77.4

TABLE III-35

LOW-LYING MO'S IN CYCLOALKYLIDENECYCLOALKANES($\xi_{3s} = 0.300$)

Molecule	MO	Symmetry (C_{2v})	E(ev)	Percentage Rydberg
Cyclopropylidenecyclopropane	σ_B	b_1	-11.77	0.0
	π	b_2	-10.30	0.0
	π^*	b_2	- 5.84	0.0
	$\sigma^*(2s)$	a_1	- 4.77	27.5
	$\sigma(2px)$	b_1	- 3.94	33.2
	$R(3s)$	a_1	- 3.60	83.3
	π'	b_2	- 3.22	0.0
	$\sigma^*(2px)$	b_1	- 3.20	6.0
Cyclobutylidenecyclobutane	σ_B	b_1	-10.35	0.0
	π	b_2	- 8.30	0.0
	$R(3s)$	a_1	- 3.23	91.7
	$\sigma^*(2s)$	a_1	- 3.22	10.8
	π^*	b_2	- 1.99	0.0
	$R^*(2s, 3s)$	a_1	- 1.43	77.1

TABLE III-36

LOW-LYING MO'S IN CYCLOALKYLIDENECYCLOALKANES

$$(\xi_{3s} = 0.483)$$

Molecule	MO	E(ev)	Percentage Rydberg
Cyclopropylidenecyclopropane	σ_B	-11.96	0.0
	π	-10.35	0.0
	$\sigma(2px)$	- 7.08	40.3
	$\sigma(2s)$	- 6.43	36.2
	$\sigma^*(2px)$	- 6.12	16.1
	π^*	- 5.84	0.0
	$R(2pz, 3s)$	- 3.80	50.3
	π'	- 3.21	0.0
	$\sigma(2px)$	- 2.66	0.0
Cyclobutylidenecyclobutane	σ_B	-10.56	0.0
	π	- 8.42	0.0
	$\sigma^*(2s)$	- 4.41	84.8
	$R(2px)$	- 3.92	62.3
	$\sigma(3s)$	- 3.15	35.6
	$R^*(3s, 2s)$	- 3.04	66.3
	$R(3s, 2pz)$	- 2.24	74.9
	π^*	- 2.04	0.0

valence-shell or Rydberg, or a mixture of the two.

Three cyclic mono-olefins--cyclopropene, cyclobutene and cyclopentene--were treated as having planar rings. The assumption of planarity is probably not a bad one. However, cyclopentene is known to have four carbons in plane and one carbon about 10° out of plane. The results using $\xi_{3s} = 0.300$ and $\xi_{3s} = 0.483$ are shown in Tables III-37 and 38. Here we encounter the unusual opportunity of having extensive pi-delocalization involving $p\pi$ orbitals of the ring, with the result that cyclobutene and cyclopentene exhibit several low-lying π -MO's. We denote them as π or π^* according to their bonding or antibonding character with respect to the double bond. The highest filled π -MO and the lowest unfilled π^* -MO are designated π and π^* as in the previous molecules. Any other π -type MO's are primed in our notation.

In cyclobutene the second-highest filled MO is not σ_B , but $\pi^{*'}(a_2)$ at -11.89ev. The highest filled π -MO is $\pi(b_2)$ at -10.33ev. All transitions between pi-MO's are allowed, being x-polarized if $A_1 \rightarrow A_1$ and y-polarized if $A_1 \rightarrow B_2$. This molecule could thus display three low-lying π, π transitions: $\pi^{*'} \rightarrow \pi^*$ ($A_1 \rightarrow A_1$) at 7.66ev, $\pi \rightarrow \pi'$ ($A_1 \rightarrow A_1$) at 7.05ev, and $\pi \rightarrow \pi^*$ ($A_1 \rightarrow B_2$) at 6.10ev. We would thus expect the absorption spectrum to exhibit a very broad absorption peak composed of these overlapping transitions. This agrees well with the spectrum reported

TABLE III-37

LOW-LYING MO'S IN CYCLIC MONO-OLEFINS($\xi_{3s} = 0.300$)

Molecule	MO	Symmetry (C_{2v})	E(ev)	Percentage Rydberg
Cyclopropene	σ_B	b_1	-12.13	0.0
	π	b_2	- 9.41	0.0
	π^*	a_2	- 3.88	0.0
	R(3s)	a_1	- 3.36	97.3
Cyclobutene	σ_B	b_1	-12.03	0.0
	$\pi^{*'} $	a_2	-11.89	0.0
	π	b_2	-10.33	0.0
	π^*	a_2	- 4.23	0.0
	R(3s)	a_1	- 3.65	84.7
	π'	b_2	- 3.28	0.0
	$\sigma^*(2s, 2px)$	b_1	- 3.24	14.6
Cyclopentene	σ_B	b_1	-12.15	0.0
	π'	b_2	-12.06	0.0
	π	b_2	- 9.50	0.0
	π^*	a_2	- 4.16	0.0
	R(3s)	a_1	- 3.64	76.8
	$\sigma^*(2s, 2px)$	b_1	- 2.34	18.6
	π''	b_2	- 2.14	0.0
	$\sigma(3s, 2s)$	a_1	- 1.42	25.9
	$\pi^{*'} $	a_2	- 0.31	0.0

TABLE III-38

LOW-LYING MO'S IN CYCLIC MONO-OLEFINS($\xi_{3s} = 0.483$)

Molecule	MO	Symmetry (C_{2v})	E(ev)	Percentage Rydberg
Cyclopropene	σ_B	b_1	-12.17	0.0
	π	b_2	- 9.42	0.0
	$\sigma^*(3s, 2s)$	b_1	- 4.58	38.6
	$\sigma(3s, 2s)$	a_1	- 4.32	29.1
	π^*	a_2	- 3.88	0.0
Cyclobutene	σ_B	b_1	-12.16	0.0
	$\pi^{*'} $	a_2	-11.87	0.0
	π	b_2	-10.38	0.0
	$\sigma^*(2s)$	b_1	- 6.36	15.5
	$\sigma(3s, 2s)$	a_1	- 4.57	40.4
	π^*	a_2	- 4.25	0.0
	π'	b_2	- 3.27	0.0
	$\sigma^*(3s, 2s)$	b_1	- 2.89	40.9
Cyclopentene	$R(3s, 2s)$	a_1	- 2.26	84.0
	σ_B	b_1	-12.23	0.0
	π'	b_2	-12.08	0.0
	π	b_2	- 9.51	0.0
	$\sigma(2pz, 2s,$ $2px, 3s)$	a_1	- 5.33	17.2
	$\sigma^*(2s)$	b_1	- 5.20	20.6
	π^*	a_2	- 4.18	0.0
	$R(3s, 2s)$	a_1	- 2.35	67.3
	π''	b_2	- 2.15	0.0
	$\sigma^*(3s, 2s)$	b_1	- 1.99	34.3
	$R(3s, 2s)$	a_1	- 1.50	71.9
	$\pi^{*'} $	a_2	- 0.31	0.0

by Loeffler, Eberlin and Pickett (see Chapter II-28) which shows continuous strong absorption in cyclobutene from 50,000 to 65,000 cm^{-1} .

The same is true of the spectrum of cyclopentene as reported by Pickett, Muntz and McPherson (see Chapter II-21). In this case the π, π transitions are separated enough so that a band maximum is observed at about 56,000 cm^{-1} , but the absorption is very strong from 50,000 to 65,000 cm^{-1} .

The computations again predict that σ -strain in the molecule produces low-lying σ and σ^* orbitals with varying degrees of Rydberg character.

CHAPTER IV
EXPERIMENTAL RESULTS

(A) Chemicals and Instrumentation: The olefins used in this study were available in research grades and were used without further purification. All were purchased from Phillip's Petroleum Company except tetramethylethylene which was obtained from Aldrich Chemical Company. The quoted purity specifications were as follows:

Ethylene--99.95 mole percent as determined by mass spectrometry.

Most probable impurities are ethane and methane.

Propylene--99.99 mole percent as determined by mass spectrometry.

Most probable impurity is propane.

Isobutene--99.95 mole percent; determined by GLC. Most probable impurity is butene-1.

cis-Butene-2--99.94 mole percent; determined by GLC and freezing point measurements. Most probable impurities are trans-butene-2 and 1,3-butadiene.

trans-Butene-2--99.63 mole percent; determined by GLC, freezing point measurements and infrared spectrum. Most probable impurity is butene-1 with a trace of n-butane.

Trimethylethylene--99.86 mole percent. No impurities could be determined by GLC analysis. Most probable impurities are cis-pentene-2, trans-pentene-2 and 2-methylbutene-2.

Tetramethylethylene-No purity specifications were given other than the designation "puriss" which Aldrich quotes as being 99.9 (plus) % pure.

Cyclohexene-99.94 mole percent; determined by GLC. Most probable impurity is cyclohexane.

Cyclopentene-99.99 mole percent; determined by GLC. Most probable impurity is cyclopentane.

The spectrum of ethylene shown in Figures IV-1,2 and 3 was obtained using a McPherson model 225 one-meter scanning monochromator equipped with the model 665 double beam attachment and model 781 ratio recording system. The source was a McPherson model 630 vacuum U.V. light source operated with a slow flow of hydrogen gas. Lithium fluoride windows were used in the light source and the 10 cm sample and reference cells.

The vapor spectra of the methyl substituted olefins, ethylene, cyclopentene and cyclohexene shown in Figures IV-4 through IV-13 were run on a Cary Model 15 recording spectrophotometer. A vacuum line was constructed at the instrument which allowed easy sampling and degassing of the olefins. Pressures as low as 10^{-4} mm were obtainable with a Welch 1402B vacuum pump. Pressures above 1 mm were measured with a "Speedivac" torr gauge manufactured by Edward's High Vacuum Ltd. Pressures below 1 mm were measured using

a Veeco Model DV-1M thermocouple gauge and Model RG-31X gauge control. This gauge was calibrated against a Vacustat McLeod gauge from Edward's High Vacuum Ltd. The sample cell was part of the vacuum system and could be isolated at a constant vapor pressure of the olefin being studied. Cells were obtained from Aminco in pathlengths of 0.1, 1, 10 and 100 mm. They were constructed of fused silica with far U.V. "ultrasil" windows.

The liquid olefin spectra in Figures IV-14 through IV-17 were run on the Cary 15. Cells were Sargent far U.V. silica with pathlengths of 1 mm and 1 cm. The isomeric butenes were collected in the sample cell at dry-ice temperatures. They were maintained as liquids by flowing N_2 vapor from liquid nitrogen through a specially constructed cell-holder.

(B) Experimental Results: Ethylene: The initial absorption in ethylene vapor, which is part of the broad $N \rightarrow V$ transition, is shown in Figure IV-1. Breaks in the curve correspond to decreases in concentration. The frequencies observed agree well with those reported by Wilkinson and Mulliken^{I-21} and McDiarmid and Charney^{I-37}. We are unable to say anything regarding which of the two assignments of the spacings is correct. The assignment by Wilkinson and Mulliken of the spacings as combinations of twisting and C=C stretching requires the assumption that the C=C bond length is greatly increased

Figure IV-1

Long-Wavelength Tail on the Ethylene $N \rightarrow V$ Transition

in the excited state. This seems very reasonable. However, McDiarmid^{I-47} has pointed out that there is no experimental evidence to verify this assumption. Their assignment of the spacings as being twisting vibrations fits the data if one assumes little or no increase in the double-bond length on going from the N state to the V state.

Figures IV-2 and IV-3 show the absorption of ethylene vapor in the range 52000 to 77000 cm^{-1} . Figure IV-2 shows the strong Rydberg doublets superposed on the broad $N \rightarrow V$ transition. Figure IV-3 shows a continuation of the $N \rightarrow V$ followed by the second Rydberg system at $\sim 71600 \text{ cm}^{-1}$ which appears to be superposed on a second broad continuum. The resolution is not as good as in the first system of doublets because the slits were opened from 200 to 500 microns. Our observed frequencies agree well with those reported by Wilkinson and Mulliken^{I-21} and Wilkinson^{I-23}.

We shall now attempt to show how the vibronic stealing mechanism might account for the observed doublets in the Rydberg spectrum. Price and Tutte^{I-7} originally assigned the doublet spacing as being one quantum of the twisting vibration ν_4 . Wilkinson and Mulliken, assuming the R state to be planar, claimed the spacing must be two quanta of twisting since ν_4 is of a_u symmetry in D_{2h} . Being unable to account for anomalous isotopic ratios and intensities, they were forced to conclude that the R state is bent (D_2 symmetry).

Let us assume for the moment that our computed f-values are grossly in error, and that the first sharp Rydberg gets its

Figure IV-2

Ethylene Absorption Spectrum

Figure IV-3

Ethylene Absorption Spectrum (Continued)

intensity from dipole allowedness. Could not the second member of the doublet then be $N \rightarrow R + \nu_8$ and gain its intensity by vibronic stealing from the $N \rightarrow V$ transition? This vibration (ν_8) has a frequency of 943 cm^{-1} in the ground state. The ν_4 ground state frequency is 1027 cm^{-1} . Wilkinson and Mulliken have found the doublet spacings on the $N \rightarrow R$ transition in the 17448 region to vary between 400 and 550 cm^{-1} (average = 470 cm^{-1}) which they assigned as $2\nu_4$. Therefore the value of ν_4 in the excited state would be 200 to 275 cm^{-1} , in good agreement with the corresponding vibration in ethane²¹ ($\nu_4 = 275 \text{ cm}^{-1}$).

The isotopic ratio (C_2D_4/C_2H_4) for ν_8 in the ground state of ethylene is 0.827 , that of ν_4 is 0.707 . Both seriously disagree with the ratios observed for the $N \rightarrow R$ transition by Wilkinson and Mulliken of 0.559 to 0.585 . Comparison of ν_4 with the twisting vibration in ethane (also designated ν_4) reveals the latter to have an isotopic ratio of 0.727 . Multiplying this by $(m_{CH_2}/m_{CH_3})^{1/2}$ to account for the extra hydrogens in ethane yields 0.701 cm^{-1} , which agrees well with the ground state value of ν_4 in ethylene. The ν_8 vibration in ethylene may be compared with the ν_{11}^{21} vibration in ethane which has an isotopic ratio of 0.722 cm^{-1} . On multiplication by $(m_{CH_2}/m_{CH_3})^{1/2}$, this becomes 0.696 . This analogy with ground state ethane, which resembles the Rydberg state of ethylene in that it has a longer C-C distance and no π -bond, thus reveals that the isotopic

ratio for ν_8 might be less than that of ν_4 in the Rydberg state.

This makes the ν_8 assignment at least a little more feasible.

Zelikoff and Watanabe^{I-19} reported that in the 1744 $\text{\AA}$ Rydberg system, the first member of the doublet system is stronger than the second. In the system at 1392 $\text{\AA}$, the reverse is true. Higher systems again resemble the first system. If the second members of the doublets do gain intensity by this mechanism, we are unable to explain why it becomes more efficient in the 1392 $\text{\AA}$ system which lies at the beginning of the second broad transition [possibly $\pi \rightarrow \pi^*(3p_y, 2p_y)$] in a relatively transparent region.

Thus far we have considered the Rydberg state as being planar and of D_{2h} symmetry. We now consider what happens if it is bent as Wilkinson and Mulliken suggested. In this symmetry (D_2) the $N \rightarrow R$ transition becomes $A \rightarrow B_2$. The twisting vibration ν_4 becomes totally symmetric and can now couple as a single quantum. The possibilities for vibronic stealing are now increased since ν_8 , ν_9 and ν_{10} can all couple to the $N \rightarrow R(3s)$ and allow stealing from the $N \rightarrow V$ ($A \rightarrow B_3$) transition. ν_9 is an unlikely candidate since its ground state frequency is 3106 cm^{-1} . However, as Wilkinson has noted, ν_{10} with a ground frequency of 810 cm^{-1} and isotopic ratio of 0.723 is a candidate for assignment. It corresponds to the vibration denoted as ν_8^{21} in ethane with an isotopic ratio of

0.747. We thus have the same possibility of vibronic stealing in D_2 as in D_{2h} symmetry except now the mechanism is possible via ν_8 and ν_{10} .

We can postulate a further vibronic situation to account for the doublets in D_2 symmetry. Suppose our small calculated f-value for the $N \rightarrow R(3s)$ transition using $\xi_{3s} = 0.300$ is reliable. Then, both members of the doublets must gain intensity by stealing. The first member could be $N \rightarrow R + \nu_8$ (D_2 or D_{2h}), the second $N \rightarrow R + \nu_4 + \nu_{10}$ (D_2). The doublet spacing would correspond to a ground state frequency of $\nu_4 + \nu_{10} - \nu_8$, or 894 cm^{-1} . Since ν_4 is known to decrease greatly on going from ethylene to ethane, a frequency of 470 cm^{-1} in the Rydberg state seems very reasonable.

The reversal in relative intensities in the $1392\text{\AA}$ system may be due to the fact that the $N \rightarrow R + \nu_8$ lies farther from the maximum of the underlying continuous absorption, making the vibronic stealing less efficient. All the other doublet systems lie directly above strong underlying continuous absorption [$\pi \rightarrow \pi^*$ ($2p_y$) for the $1744\text{\AA}$ system and possibly $\pi \rightarrow \pi^*$ ($3p_y$, $2p_y$) for the higher systems]. Only the $1392\text{\AA}$ system lies in a region of relatively weak absorption.

By this mechanism the doublet spacing of C_2D_4 would correspond to a ground state frequency of 532 cm^{-1} . This predicts an isotopic ratio of 0.595, which is much better agreement with the observed ratio

of 0.559 - 0.585 than is obtained if ν_4 , $2\nu_4$ or ν_8 are assigned as the doublet spacing.

One further experimental fact needs explanation. It is observed that the relative intensities of the doublets in the 1744 $\text{\AA}$ system of C_2H_4 are reversed in C_2D_4 . We are unable to predict how deuteration will effect the two vibronic coupling modes ($R + \nu_8$ and $R + \nu_4 + \nu_{10}$). That they are effected, possibly in a manner which could account for the intensity reversal, is probable. It is less probable that such a reversal would be observed if the transition gains intensity only through electric dipole allowedness, and totally symmetric vibrations ($2\nu_4$ in D_{2h} or ν_4 in D_2) are coupled.

Figures IV-2 and IV-3 reveal shoulders at ~ 57050 , 58350 , and 71270 cm^{-1} . The first two we can now take to be the 0-0 and 0-1 bands of the allowed $N \rightarrow R(3s)$ transition. The latter would be the 0-0 band of the allowed $N \rightarrow R(4s)$ transition. The spacing between the first two bands, $\sim 1300 \text{ cm}^{-1}$, probably corresponds to the totally symmetric C=C stretching frequency.

Our postulated vibronic stealing mechanism thus offers a possible explanation for all the observed experimental data--something the previous assignments of ν_4 or $2\nu_4$ cannot do. It seems to us that the strongest evidence in favor of the ν_4 assignments is that the transitions appear as strong sharp bands, as would allowed transitions.

Might not an essentially Rydberg MO situated atop a strong transition, thus very efficiently stealing intensity, also appear as strong sharp bands? The situation is unique in this molecule and there is no precedence in any other molecular system by which we may, on comparison, answer this question. More will be said about the vibronic stealing mechanism in the case of cyclopentene which will lend further credence to its being a reasonable mechanism, and probably the correct one.

(C) Experimental Results: Methyl Substituted Ethylenes, Cyclopentene, and Cyclohexene in the Vapor Phase: The vapor spectra in Figures IV-4 through IV-9 are all plotted in the same frequency range so that the shifts on decreased methylation may be easily seen. These data agree well with previously reported spectra and demonstrate the shifts predicted so well by the computations. The structure is very diffuse in most cases and no vibrational analysis could be made. The spacings between main peaks are 1000 to 1500 cm^{-1} which is usually assigned as C=C stretch.

Figure IV-10 shows the effect of varying self-pressure of tetramethylethylene. Tables IV-1 and IV-2 give the calculated extinction coefficients assuming ideal gas behavior for tetramethylethylene and trimethylethylene. If these data are believable, then

Figure IV-4

TEIME Vapor in 10.0 cm Cell at Room Temperature

Figure IV-5

TRIME Vapor in 10.0 cm Cell at Room Temperature

cis Butene-2 Vapor in 10.0 cm Cell at Room Temperature

Figure IV-7

Figure IV-8

trans Butene-2 Vapor in 10.0 cm Cell at Room Temperature

Figure IV-9

Ethylene and Propylene Vapors in 10.0 cm Cell at Room Temperature

Figure IV-10

Pressure Dependence of Molar Extinction in TETME

TABLE IV-1

PRESSURE DEPENDENCE OF ABSORPTION INTENSITY IN
TETRAMETHYLETHYLENE VAPOR

Transition	$\epsilon_{\max}$	Conditions
N $\rightarrow$ V	3.98×10^3	P=80 microns on thermocouple gauge, 10 cm cell
	4.44×10^3	P=160 microns on thermocouple gauge, 10 cm cell
	5.61×10^3	P=230 microns on thermocouple gauge, 10 cm cell
	8.21×10^3	P=335 microns on thermocouple gauge, 10 cm cell
	1.80×10^4	P=610 microns on thermocouple gauge, 1 cm cell
	1.23×10^4	P=15 mm on torr gauge, 0.1 cm cell
	$(1.00 \pm 0.47) \times 10^4$	Average Value
N $\rightarrow$ R(3s)	6.23×10^2	P=390 microns on thermocouple gauge, 10 cm cell
	6.23×10^2	P=390 microns on thermocouple gauge, 10 cm cell
	6.21×10^2	P=485 microns on thermocouple gauge, 10 cm cell
	1.04×10^3	P=500 microns on thermocouple gauge, 10 cm cell
	1.82×10^3	P=550 microns on thermocouple gauge, 10 cm cell
	6.36×10^2	P=24 mm on torr gauge, 1 cm cell
	6.54×10^2	P=100 mm on torr gauge, 0.1 cm cell
	$(8.60 \pm 0.33) \times 10^2$	Average Value

TABLE IV-2

PRESSURE DEPENDENCE OF ABSORPTION INTENSITY IN
TRIMETHYLETHYLENE VAPOR

Transition	$\epsilon_{\max}$	Conditions
N $\rightarrow$ V	2.85×10^3	P=160 microns on thermocouple gauge, 10 cm cell
	3.96×10^3	P=290 microns on thermocouple gauge, 10 cm cell
	4.49×10^3	P=390 microns on thermocouple gauge, 10 cm cell
	1.45×10^4	P=1 mm on torr gauge, 1 cm cell
	1.25×10^4	P=2 mm on torr gauge, 1 cm cell
	6.81×10^3	P=20 mm on torr gauge, 0.1 cm cell
	$(7.52 \pm 3.98) \times 10^3$	Average Value
N $\rightarrow$ R(3s)	5.68×10^2	P=390 microns on thermocouple gauge, 10 cm cell
	9.19×10^2	P=550 microns on thermocouple gauge, 10 cm cell
	1.68×10^3	P=610 microns on thermocouple gauge, 10 cm cell
	8.47×10^2	P=6 mm on torr gauge, 1 cm cell
	8.05×10^2	P=12 mm on torr gauge, 1 cm cell
	7.70×10^2	P=100 mm on torr gauge, 0.1 cm cell
	$(9.32 \pm 2.50) \times 10^2$	Average Value

both the transitions ($N \rightarrow V$ and $N \rightarrow R$) increase in intensity with increasing pressure, then fall off at higher pressures.

That the effect is not due to an error in our pressure measurements is evidenced by the fact that the $N \rightarrow V$ transition is more effected by increasing pressure than is the $N \rightarrow R$ transition. Also, the maximum extinction coefficient occurs at different pressures for the two transitions. It is surprising that, even at such low pressure (0.1 to 100 mm), the $N \rightarrow R$ is not more effected. It should, being a transition to a large diffuse atomic-like orbital, decrease in intensity with increasing pressure. We might take this to mean that the $n = 3$ quantum level of carbon compounds is not so atomic-like as everyone assumes. Maybe it does behave a little like valence-shell AO's since only extremely high pressures or condensed phases actually wash out the Rydberg transitions.

Figures IV-4 through IV-9 and Figures IV-11 and IV-12 present formulae for converting optical density to molar extinction coefficient. These formulae are in every case normalized to the average conversion factor observed in tetramethylethylene and trimethylethylene.

Figures IV-11 and IV-12 show the vapor absorptions of cyclohexene and cyclopentene. The structure and position of the $N \rightarrow R$ transition in cyclohexene is remarkably similar to that of cis-butene-2. The main spacing is usually assumed to be C-C stretch.

Figure IV-11

Cyclohexene Vapor in 10.0 cm Cell at Room Temperature

Cyclopentene Vapor in 10.0 cm Cell at Room Temperature

Figure IV-12

Cyclohexene thus appears to exhibit the typical spectral characteristics of olefins. However, cyclopentene's $N \rightarrow R$ transition appears to differ from that of all other olefins, having a spacing of $\sim 130 \text{ cm}^{-1}$. This spacing is shown more clearly in Figure IV-13 where the data is plotted on an expanded frequency scale. The peaks agree well with those of Carr and Stücklen^{II-13} with the additional feature that the peak they reported at 48490 cm^{-1} appears as a doublet in our spectrum at 48450 and 48497 cm^{-1} . The usual interpretation of this spectrum is that the average spacing ($\sim 130 \text{ cm}^{-1}$) is due to either ring puckering (ν_p) or a torsional ring vibration (ν_T). No explanation has been offered as to why totally symmetric vibrations do not appear on this supposedly allowed transition.

The ν_T is essentially a torsion about the double bond and has been observed at 386 cm^{-1} in the Raman effect.²² Such a vibration would be expected to be greatly decreased in energy on going to the excited R state and the observed spacing of 130 cm^{-1} is very reasonable.

The ν_p is a puckering vibration of the cyclopentene ring and has been shown by Laane and Lord²³ to have strongly anharmonic energy levels. Such a vibration, in which the double-bonded carbons move together, should be less effected by electronic excitation. Table IV-3 gives the spacings measured from the 47596 cm^{-1} peak in the U.V. spectrum. This is compared with I.R. frequencies reported by Laane and Lord. Since they report no levels above ν_{10} , we assume a

N → R Transition in Cyclopentene Vapor

Figure IV-13

TABLE IV-3

ANALYSIS OF VIBRATIONAL STRUCTURE ON THE $N \rightarrow R(3s)$ TRANSITION
IN CYCLOPENTENE BY COMPARISON WITH ν_p FROM IR DATA*

U.V. Spacing (cm^{-1}) [†]	IR Spacing (cm^{-1})	Assignment
91	127	$0 \rightarrow 2\nu_p$
205	215	$0 \rightarrow 4\nu_p$
343	384	$0 \rightarrow 6\nu_p$
458	484	$0 \rightarrow 7\nu_p$
597	592	$0 \rightarrow 8\nu_p$
737	705	$0 \rightarrow 9\nu_p$
854	824	$0 \rightarrow 10\nu_p$
901	944	$0 \rightarrow 11\nu_p$
1042	1064	$0 \rightarrow 12\nu_p$
1184	1184	$0 \rightarrow 13\nu_p$
1328	1304	$0 \rightarrow 14\nu_p$
1472	1424	$0 \rightarrow 15\nu_p$
1592	1544	$0 \rightarrow 16\nu_p$
1714	1664	$0 \rightarrow 17\nu_p$
1836	1784	$0 \rightarrow 18\nu_p$

* I.R. data is taken from Laane and Lord, J. Chem. Phys., 47, 4941 (1967). They report frequencies up to $10\nu_p$. Above this level we assume $\nu_p \approx 120 \text{ cm}^{-1}$.

[†] Spacings are measured from the initial peak at 47596 cm^{-1} .

spacing of 120 cm^{-1} beyond this level. The agreement is remarkable. They were able to explain the I.R. spectrum on the basis of a double-minimum potential function. Low energy transitions were observed to occur only as two-quanta transitions ($1 \rightarrow 3$ and $0 \rightarrow 2$). Such a situation existing in the R state would explain why two quanta are observed for the first three vibrational peaks in the U.V. spectrum.

One of the two assignments (ν_P or ν_T) or a combination of them must be used to explain the structure on the $N \rightarrow R$ transition. In our coordinate frame, the symmetry operators in C_{2v} become E , $C_2(x)$, $\sigma_v(xz)$, and $\sigma'_v(xy)$. Under these operations the $N \rightarrow R$ transition is $A_1 \rightarrow B_2$ and is y-allowed, the $N \rightarrow V$ transition is $A_1 \rightarrow B_1$ and is z-allowed, ν_P is of b_2 symmetry, and ν_T is of a_2 symmetry. We now call on our vibronic stealing mechanism to explain why a non-totally symmetric vibration should dominate the observed structure in an allowed transition. The reason again appears to be because most of the intensity is obtained via the stealing mechanism. The ν_T can couple to the $N \rightarrow R$ transition, making it vibronically z-allowed and enabling it to steal intensity from the $N \rightarrow V$ ($\pi \rightarrow \pi^*$) at 5.34 eV from the computations. The ν_P can couple to the $N \rightarrow R$ transition, making it vibronically x-allowed and enabling it to steal intensity from the $\pi \rightarrow \pi''$ transition computed to be at 7.36 eV. No matter which vibrational analysis of the spectrum is accepted (ν_P or ν_T , or both), this mechanism explains the presence of non-totally symmetric vibrations

and the absence of totally symmetric ones. Cyclopentene thus becomes not an atypical case, but behaves as do the other olefins. It appears different from the others only because it is the only case where the totally symmetric vibrations differ greatly in energy from the non-totally symmetric ones which allow vibronic stealing to occur. We have not as yet analyzed the vibrational structure on the Rydberg bands in the methyl substituted olefins. It is known²⁴ that the isomeric butenes possess vibrational modes of the correct symmetry [b_2 in isobutene (C_{2v}), a_2 in cis-butene-2 (C_{2v}), and b_g in trans-butene-2 (C_{2h})] to allow stealing from the $N \rightarrow V$ transition. Further, these modes are energetically of the same order of magnitude as the totally symmetric C=C stretching mode. Since our intensity calculations (using $\xi_{3s} = 0.483$) agree well with experiment for the isomeric butenes, we expect vibronic stealing and dipole allowedness to be of comparable efficiency. The $N \rightarrow R$ transition in these compounds should exhibit both totally symmetric and non-totally symmetric vibrational modes. It appears from the intensity calculations that in ethylene, tetramethylethylene, trimethylethylene, and cyclopentene, the vibrational stealing mechanism predominates.

(D) Absorption Spectra of Liquid Olefins: Figures IV-14 through IV-17 show the initial absorption in various liquid olefins in the range 29000 to 50000 cm^{-1} . The spectra of tetramethylethylene,

Figure IV-14

Absorption Spectrum of Liquid Tetramethylethylene

Figure IV-15

Absorption Spectrum of Liquid Trimethylethylene

Figure IV-16

Absorption Spectrum of Liquid Isomeric Butenes

Figure IV-17

Absorption Spectrum of Liquid Cyclopentene and Cyclohexene

trimethylethylene, cyclopentene, and cyclohexene were run at room temperature. The isomeric butenes were collected as liquids at dry-ice temperatures and maintained as liquids in the cells at temperatures below room temperature. Extinction coefficients were calculated using densities and molecular weights as given in Table IV-4 to compute molarities of the pure liquids. The spectra are all plotted on the same wavenumber scale. Tetramethylethylene shows a band with three structured peaks at about 34000 cm^{-1} with an extinction coefficient of 0.8. No such peak is apparent in trimethylethylene. However, isobutene and cis-butene-2 show definite shoulders at ~ 44000 and 45000 cm^{-1} . Both have extinctions of ~ 1 and are located in a region where the intensity is rising on higher excitations. Cyclopentene shows a shoulder at $\sim 39000\text{ cm}^{-1}$ with a molar extinction of about 1. Cyclohexene shows a definite peak at 39000 cm^{-1} with a molar extinction of ~ 2 .

These peaks may well be the $N \rightarrow R^*$ (or $N \rightarrow \sigma^*$) as the computations predict. Because of the diffuse underlying absorption ($\epsilon = 10^{-2} - 10^{-1}$), we are unable to estimate f-values. However, the spectra show the transition to be weaker in tetramethylethylene than in isobutene and cis-butene-2 as computations predict. The transition is not observed in trans-butene-2 as predicted by the calculations ($f = 10^{-7}$). Table IV-5 shows a comparison between experiment and calculations. The agreement, although not as impressive

TABLE IV-4

MOLARITIES OF LIQUID OLEFINS

Compound	Density (g/ml)	Molecular Weight (g/mole)	Molarity (moles/e)
ISOB	0.59 at 20°C*	56	10.5
cis B	0.6213 at 20°C	56	11.1
trans B	0.6041 at 20°C	56	10.8
TRIME	0.6620 at 20°C	70	9.46
TETME	0.7081 at 20°C	84	8.43
Cyclopentene	0.7743 at 18°C	68	11.4
Cyclohexene	0.8110 at 20°C	82	9.89

* This value for isobutene is taken from Lang's Handbook of Chemistry (9th edition), Handbook Publishers Inc. (1956). All other densities are from The Handbook of Chemistry and Physics (46th edition), The Chemical Rubber Co. (1964, 1965).

TABLE IV-5

COMPARISON OF EXPERIMENTAL AND CALCULATED EXCITATION ENERGIES
FOR THE $N \rightarrow R^*$ ($\pi \rightarrow \sigma^*$) TRANSITION

Molecule	$E(\text{cm}^{-1} \times 10^{-4})$, calcd.	$E(\text{cm}^{-1} \times 10^{-4})$, exp.
ISOB	4.49	4.4
cis B	4.50	4.5
trans B	3.49 ($f=10^{-7}$)	not observed
TRIME	3.37	not observed
TETME	2.74	3.4
Cyclopentene	3.90	3.9
Cyclohexene	----	3.9

as for the $N \rightarrow V$ and $N \rightarrow R$ transitions, is good. We offer no explanation for the failure to observe the peak in trimethylethylene. It should occur at 33700 cm^{-1} according to the computations.

In each molecule, the underlying absorption ($\epsilon = 10^{-2} - 10^{-1}$) might be due to $N \rightarrow T$ and $N \rightarrow T_R$ transitions. Assuming the peaks to be as wide as their corresponding singlet-singlet transitions, they would have f-values of $\sim 10^{-7}$. This agrees well with our spin-orbit coupling computations. In Figure IV-16 the spectra of the isomeric butenes show what appear to be two weak transitions at about 34000 and 40000 cm^{-1} . These are tentatively assigned as $N \rightarrow T$ and $N \rightarrow T_R$, respectively.

We feel rather confident that these peaks are real and not the result of impurity absorptions. The manufacturers' specifications quote probable impurities as being other mono-olefins, which have no strong peaks in this region. Even aromatics or conjugated hydrocarbons could not cause an extinction of 1 if present in such low concentrations. We thus feel pleased to have experimentally found the $N \rightarrow R^*$ transition (actually $\pi \rightarrow \sigma^*$ in most cases) which was predicted by MO calculations prior to the experiment.

CHAPTER V

SUMMARY OF RESULTS

Our results may be summarized as follows:

- (1) The strongest transition in olefins lies in the range $5 \rightarrow 7$ eV and is $N \rightarrow V$ ($\pi \rightarrow \pi^*$) in nature. Its position and intensity ($f = 0.30$) in the spectra of methyl substituted ethylenes agree very well with computational results. The shift in this transition on increased methylation appears to be due to both charge transfer and hyperconjugation. It is also strongly dependent on molecular geometry and ground state static dipole moment. The order observed for the excitation energies in the isomeric butenes (where charge transfer and hyperconjugation effects are equal) is nicely reproduced by the calculations.
- (2) The next-strongest transition ($E = 5 \rightarrow 6.5$ eV, $f \sim 10^{-2}$) observed in the vapor spectra is undoubtedly $N \rightarrow R(3s)$ in nature. The position seems mainly dependent on the number of methyl groups attached to the double bond, not on the nature or arrangement of the methyl groups. Agreement between calculation and experiment is extremely good.
- (3) The ionization potential shifts with increased methylation as predicted by the calculations. It seems mostly dependent on the charge transfer mechanism.
- (4) A weaker transition at the onset of absorption has been predicted by the computations to be $N \rightarrow R^*$ ($\pi \rightarrow \sigma^*$) in nature. Such

a transition does appear to exist in the spectra of the pure liquid olefins.

(5) The diffuse initial absorption in olefins ($\epsilon = 10^{-2} - 10^{-1}$) appears to be due to $N \rightarrow T$ and $N \rightarrow T_R$ transitions. This tentative assignment is made on comparison of experimental intensities with those calculated by spin-orbit coupling.

(6) It is proposed that the $N \rightarrow R(3s)$ transition in olefins gains at least a part of its intensity via a vibronic stealing (from the $N \rightarrow V$) mechanism. Such a mechanism provides an explanation for the doublet systems in the Rydberg series of ethylene. It also offers an explanation for the observed anomalies in isotopic ratios and intensities, here-to-fore inexplicable in terms of the transition being dipole allowed and the doublet spacing being due to the twisting vibration. This mechanism also explains the predominance of non-totally symmetric vibrations in the $N \rightarrow R(3s)$ transition in cyclopentene. We feel this is strong evidence in support of the mechanism's validity. In tetramethylethylene, trimethylethylene, cyclopentene and ethylene, the $N \rightarrow R(3s)$ gains most of its intensity via this mechanism. In propylene, cyclohexene, and the isomeric butenes, dipole allowedness and vibronic stealing seem to be of comparable importance--allowing both totally symmetric and non-totally symmetric vibrations to appear in the Rydberg spectra.

- (7) In general we conclude that the $n=3$ quantum level of carbon compounds is not so Rydberg (atomic-like) in nature as is generally assumed. The possibility of mixing with low-lying valence-shell MO's in both bonding and antibonding combinations is clearly demonstrated.
- (8) In cyclic mono-olefins, a new spectral feature appears. The strong $N \rightarrow V$ absorption is broadened considerably due to overlapping low-lying π, π transitions resulting from $p\pi$ orbitals on the ring.
- (9) Computations on cyclic mono-olefins, methylene cycloalkanes, and cycloalkylidene cycloalkanes indicate that σ -strain increases the contribution of valence-shell AO's to low-lying transition of the type $\pi \rightarrow \sigma^*$.

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VITA

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EXAMINATION AND THESIS REPORT

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Major Professor and Chairman

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EXAMINING COMMITTEE:

Date of Examination:

July 22, 1969