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Commentationes

Electronic Transitions in Mono-Olefinic Hydrocarbons

I. Computational Results*

F. H. WATSON, JR., A. T. ARMSTRONG**, and S. P. MCGLYNN

Coates Chemical Laboratories, Louisiana State University, Baton Rouge, Louisiana 70803

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Mulliken-Wolfsberg-Helmholz calculations have been performed on ethylene and methyl-substituted ethylenes. The Mulliken assignment (i.e., that the transition between 5–7 eV is $R(3s)\leftarrow N$ in nature) is validated. Spin-orbit coupling calculations indicate that the weakest olefin band at ~2700 Å is too intense to be triplet ← singlet, as is usually assumed. However, behaviour of a predicted low-energy $R^*(3s, 2s)\leftarrow N$ transition agrees well with the characteristics of these weak bands in the absorption spectra of liquid olefins. That these trends are believable is supported by the accuracy with which the computations predict the experimental changes of ionization potential and $V\leftarrow N$ transition energy caused by increased methylation. In particular, it is predicted that the excitation energy of the $V\leftarrow N$ transition should be strongly dependent on molecular geometry – in agreement with experiment. It is suggested, on the basis of intensity calculations, that the $R(3s)\leftarrow N$ transition gains part of its intensity, at least, *via* vibronic stealing from the $V\leftarrow N$ transition. Computations on cyclic olefins predict the possibility of several low-lying $\pi\rightarrow\pi^*$ transitions; the unusual broadening of the $V\leftarrow N$ transition in these molecules may possibly be associated with this complexity. Computations on methylene cycloalkanes and cycloalkylidene-cycloalkanes reveal that σ-strain can lead to low-lying $\pi\rightarrow\sigma^*$ (valence-shell) transitions. In general, it is found that the 3s atomic orbital can mix appreciably, in both bonding and antibonding combinations, with valence-shell orbitals.

Mulliken-Wolfsberg-Helmholz-Rechnungen werden für Äthylen und eine Reihe methylsubstituierter Äthylene durchgeführt. Die Mullikenzuordnung [d. h. der Übergang zwischen 5 – 7 eV entspricht $R(3s)\leftarrow N$] wird daraufhin für zutreffend erklärt. Spin-Bahn-Kopplungs-Berechnungen deuten darauf hin, daß das schwächste Olefinband bei 2700 Å zu intensiv ist, um – wie gewöhnlich angenommen – in Triplett-Singulett-Übergang zu sein. Andererseits stimmt das Verhalten eines energetisch tief liegenden $R^*(3s, 2s)\leftarrow N$-Übergangs gut mit den Charakteristika dieser schwachen Banden im Absorptionsspektrum der flüssigen Olefine überein. Daß diese Interpretation möglich ist, wird auch durch die Genauigkeit unterstützt, mit der eine Berechnung die experimentell gefundene Änderung von Ionisations- und $V\leftarrow N$-Übergangsenergie bei zunehmender Methylierung ergibt. Insbesondere wird auch vorhergesagt, daß die Anregungsenergie des $V\leftarrow N$-Übergangs stark von der molekularen Geometrie abhängt – in Übereinstimmung mit dem Experiment. Es wird deshalb auf Grund einer Intensitätsberechnung vorgeschlagen, daß der $R(3s)\leftarrow N$-Übergang zumindest einen Teil seiner Intensität durch eine „Schwingungs-Anleihe" vom $V\leftarrow N$-Übergang gewinnt. Berechnungen für cyclische Olefine weisen auf verschieden niedrig liegende $\pi\rightarrow\pi^*$-Übergänge hin; die ungewöhnliche Verbreitung der $V\leftarrow N$-Bande bei diesen Molekülen kann möglicherweise damit zusammenhängen. Berechnungen der Methyl-cycloalkane und der Cycloalkylidin-cycloalkane zeigen, daß eine Spannung im σ-Gerüst zu einem tief liegenden $\pi\rightarrow\sigma^*$-(Valenz-)Übergang führen kann. Im allgemeinen zeigt sich, daß 3s-Zustände merklich an Valenzzuständen beteiligt sein können, und zwar sowohl bei bindenden als auch bei lockernden Molekülzuständen.

Des calculs Mulliken-Wolfsberg-Helmholz ont été effectués sur l'éthylène et sur la série des éthylènes méthyl-substitués. Ces calculs confirment l'assignation de Mulliken: la transition entre 5–7 eV est de nature $N\rightarrow R(3s)$. Des calculs de couplage spin-orbite montrent que la bande oléfinique

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** Present address: Department of Chemistry, University of Texas, Arlington, Texas.

la plus faible à ~ 2700 Å est trop intense pour être une transition singulet-triplet comme on le suppose généralement. Cependant, le comportement d'une transition théorique de faible énergie $N \rightarrow R^*$ (3*s*, 2*s*) est en accord avec les caractéristiques de ces faibles bandes dans le spectre d'absorption des oléfines liquides. La vraisemblance de ce point de vue est renforcée par la précision avec laquelle les calculs prédisent l'évolution des potentiels d'ionisation, et des énergies des transitions $N \rightarrow V$ par méthylation croissante. En particulier, il est prévu que l'énergie d'excitation $N \rightarrow V$ dépend fortement de la géométrie moléculaire ce qui est en accord avec l'expérience. On suggère sur la base de calculs d'intensité que la transition $N \rightarrow R$ (3*s*) tire une partie de son intensité au moins par transfert vibronique à partir de la transition $N \rightarrow V$. Des calculs sur des oléfines cycliques prédisent la possibilité de plusieurs transitions $\pi \rightarrow \pi^*$ de faible énergie; l'élargissement inhabituel de la transition $N \rightarrow V$ dans ces molécules pourrait provenir de cette situation. Des calculs sur les méthylène-cycloalkanes et les cycloalkylidène cycloalkanes révèlent la possibilité pour une tension σ de provoquer l'existence de transitions $\pi \rightarrow \sigma^*$ (couche de valence) de faible énergie. On trouve qu'en général les orbitales atomiques 3*s* peuvent se mélanger d'une manière appréciable aux orbitales de la couche de valence donnant des combinaisons liantes et antiliantes.

Introduction

Much confusion has recently arisen in the interpretation of the ultraviolet absorption spectra of mono-olefinic hydrocarbons. Spectra of ethylene and simple mono-olefins have been reported by several workers; the reader is referred to excellent reviews on this subject by Kaldor and Shavitt [1] and Merer and Mulliken [2]. Here, we shall merely list the transitions which have been observed, and briefly review the assignments given them. We shall also note the trends observable as methyl groups are appended to the ethylene molecule.

The transitions which experimentally exist in the electronic absorption spectrum of ethylene are the following:

a) A weak transition ($\varepsilon = 10^{-3}$) at ~4.4 eV, first observed by Reid [3] in the absorption of liquid ethylene. He assigned it as $T \leftarrow N(\pi \rightarrow \pi^*)$ on the basis of its low intensity and because the observed vibrational spacing was similar to that of the $V \leftarrow N(\pi \rightarrow \pi^*)$ transition. This assignment was later confirmed by Evans [4] who observed the same transition in the vapor using the technique of singlet-triplet absorption enhancement by oxygen.

b) A broad continuum (maximum at 7.6 eV) having an oscillator strength [5–9] of about 0.3, generally assigned as $V \leftarrow N(\pi \rightarrow \pi^*)$. This transition has been reported by several investigators [10–13] to have diffuse vibrational structure at the onset of absorption (5.7 – 7.1 eV) with spacings of about 800 cm^{-1}. This spacing has been assigned by Merer and Mulliken [14] as combinations of C=C stretch (ν_2) and methyl twisting (ν_4). McDiarmid and Charney [13, 15] argue that the observed spacings are torsional (ν_4) frequencies only.

c) A sharp series of doublets starting abruptly at 7.12 eV and having an *f*-value [6, 8, 9, 11] of ~0.03. These were first assigned by Price and Tutte [16] as $R(3s) \leftarrow N$. The doublet spacing is about 470 cm^{-1}, the main spacing between doublets about 1370 cm^{-1}. Price and Tutte assigned the doublet spacing as one quantum of twisting (ν_4), and the spacing between doublets as a C=C stretch (ν_2). Wilkinson and Mulliken [12], assuming the Rydberg state to be planar, assigned the doublet spacing as $2\nu_4$. In order to account for anomalies in isotopic ratios and intensities, it was later concluded that the Rydberg state was bent [17–19].

d) Higher members of this Rydberg series [8, 16, 17] and three other Rydberg series [16, 17] extending out to an ionization continuum at about 10.5 eV. Each member of the $R(ns) \leftarrow N$ Rydberg series consists of doublets as does the $R(3s) \leftarrow N$ transition.

e) Optical rotatory dispersion [20] and electron-impact measurements [21] indicate an electric-dipole-forbidden, electric-quadrupole-allowed transition at about 7.45 eV; this transition was assigned by Yaris, Moscowitz and Berry [20] as $\pi \rightarrow b_{2u}(3p)$.

The ethylene spectrum should exhibit one further absorption band, the $T_R \leftarrow N$ transition [22] where T_R denotes a triplet Rydberg state. This band has not as yet been observed. A band at 6.5 eV was previously reported by Snow and Allsopp [10] as a shoulder in the ultraviolet absorption spectrum, and by Kuppermann and Raff [23] in the electron-impact spectrum. This band, according to overwhelming experimental evidence, does not exist [21, 24 – 30].

The spectra of the simple alkyl derivatives of ethylene are, in general, more diffuse, prohibiting any vibrational analyses. The electronic transitions which have been experimentally observed in alkyl-substituted ethylenes and cyclic olefins are the following:

a) A very weak, structureless band ($\log \varepsilon = -2.0 \rightarrow -1.0$) at 4–5 eV, observable only in liquid and solution phases [10, 31–33]. This is thought to be triplet←singlet in nature and was assigned by Snow and Allsopp [10], Carr and Stücklen [34], and Potts [33], as $T \leftarrow N$. Carr [35] later assigned it as $T_R \leftarrow N$. Mulliken [2] admits that this assignment could possibly be correct; however, these bands do appear to be stronger than one might expect for triplet Rydberg←singlet transitions.

b) A moderately intense, diffusely structured band [34, 36 – 44] in the range 5 – 7 eV with an f-value of $\sim 0.01 (\varepsilon = 10^3)$. This band was originally assigned by Carr and Stücklen [34, 45] as $R(3s) \leftarrow N$. This assignment was based on the fact that a plot of the position of this band versus the number of methyl groups yields a straight line which extrapolates to the first member of the Rydberg doublets in ethylene (zero alkyl groups). Some confusion developed when Berry [46], reasoning by analogy with the $n \rightarrow \pi^*$ transition of formaldehyde, assigned a transition in olefins as $\sigma \rightarrow \pi^*$. According to him, this transition corresponded to the weak absorption in alkylated ethylenes which begins at 2300 Å (sometimes 2500 Å) and extends to the onset of stronger absorption around 2100 Å. It appears that Berry was referring to the weak absorption observed in liquid and solution phases. However, this absorption in tetramethylethylene begins at 3300 Å. His reference to the fact that some structure accompanied these bands in the vapor phase indicated he was referring to the absorption assigned as $R(3s) \leftarrow N$ by Carr and Stücklen. Robin, Hart, and Kuebler [47], assuming Berry had reference to the absorption in the range 5 – 7 eV ($\varepsilon = 10^3$), compounded the confusion by assigning this transition as an "anti-Berry" $\pi \rightarrow \sigma^*$ (valence-shell) transition. This assignment was made on the basis of Gaussian-AO computations on ethylene. Because their basis set was Gaussian, these authors [47] were unable to distinguish properly between valence-shell and Rydberg character in their σ^* – MO. In a later paper by Robin, Basch, and Kuebler[48], using an indirect SCF calculation in a Gaussian basis, they reversed themselves and concluded that the low-lying $\pi \rightarrow \sigma^*$ exitations were Rydberg in nature. A later computation by Yaris, Moscowitz, and Berry [20] also agreed with the $R(3s) \leftarrow N$ assignment. Further evidence for this assignment was provided by Evans [49]. He showed that high pressures of an inert gas cause broadening and a "washing-out" of structure in the region 2400–2100 Å, indicating that the transition is to a large Rydberg orbit, probably 3*s*.

c) A broad, intense absorption in the range 6.5 – 7.5 eV with an *f*-value [6, 10, 40 – 43] of $\sim 0.30(\varepsilon = 10^4)$. This band is generally assigned to the $V \leftarrow N$ transition.

d) An electric-dipole-forbidden, electric-quadrupole-allowed transition in the region 6 – 6.5 eV in molecules possessing a twisted double bond. This band was assigned by Yaris, Moscowitz, and Berry [20] as $\pi \rightarrow \sigma^*(3p)$ Rydberg.

e) Sharp Rydberg series [16] at higher energies, as yet unassigned.

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

Cyclic olefins exhibit much the same transitions as do alkyl-substituted ethylenes [50 – 52]. The $V \leftarrow N$ absorptions are, however, much broader in the cyclic olefins. Cyclopentene seems to exhibit atypical behaviour in that its $R(3s) \leftarrow N$ transition exhibits a series of sharp, closely spaced ($\sim 130\ \mathrm{cm}^{-1}$) vibrational peaks. The main vibrational spacing on the $R(3s) \leftarrow N$ band in alkyl-substituted ethylenes is usually about 1000 to $1500\ \mathrm{cm}^{-1}$, and is generally taken to be C=C stretching. The $R(3s) \leftarrow N$ transition of cyclohexene shows structure very similar to that of cis-butene-2.

It has been shown by Robin, Basch, and Kuebler [48] that more complicated mono-olefins, especially those having much σ-strain, exhibit transitions to the red of the $V \leftarrow N$ band which include both Rydberg and valence-shell transition types.

Spectral Trends and Computational Methods

Regular shifts are observable on appending alkyl groups to ethylene. These trends are clearly demonstrated for the case of methyl substitution and are as follows:

a) The ionization potential shifts from 10.5 eV in ethylene to 8.3 eV in tetramethylene [16, 53]. This, says Mulliken [54], is due to negative charge transfer from the methyls to the double-bonded carbons.

b) The $R(3s) \leftarrow N$ transition is red-shifted from 7.1 eV to 5.4 eV with increased methylation. This shift seems to be dependent only on the number of alkyl substituents and not on their nature or arrangement about the double bond [33, 40 – 42]. This, also, is supposed to result from a charge-transfer mechanism [54].

c) The $V \leftarrow N$ transition is red-shifted less than the $R(3s) \leftarrow N$ on methylation from 7.6 eV in ethylene to 6.5 eV in tetramethylene. Mulliken [54] indicates that this behaviour is completely explicable on the basis of hyperconjugation. It was later found, in a study of isomeric butenes, pentenes and hexenes [40 – 42], that the transition energy does depend on the molecular geometry and on the dipole moment of the molecule.

d) The weak bands observed in the liquid spectra shift [32] from 4.8 eV in olefins of the form $\mathrm{RHC{=}CH_2}$ to 3.7 eV in olefins of the form $\mathrm{R_2C{=}CR_2}$.

We feel that much confusion has developed because semiempirical calculations have usually been done on ethylene and the results then extrapolated to larger olefins. The results of such computations on any one molecule serve only as a suggestion for assignments in that one molecule; furthermore, these assignments do require post facto experimental verification. It is our further contention that a semiempirical investigation of trends in a series of mono-olefinic compounds – involving at all points the same computational approximations has more meaning and should be helpful in fixing assignments to observed transitions. Since the shifts with increased methylation are clearly demonstrated by the series of methyl-substituted ethylenes, we chose, as did Clark [55], to investigate this series. In addition, we have performed computations on cyclic mono-olefins, methylene cycloalkanes, and cycloalkylidenecycloalkanes.

These one-electron calculations were done on the ground state configurations of the various molecules within the framework of the Mulliken-Wolfsberg-Helmholz method. Such computations have been described in detail elsewhere [56 – 63] and applied to a variety of systems, mainly inorganics. We employed as basis orbitals Clementi-type AO's [64] and included in our basis set the $2s$ and $3s$ orbitals of carbon (also the $3p$ in one case for ethylene) and the $1s$ orbitals of hydrogen. Coulomb integrals were approximated as atomic valence state ionization potentials and resonance integrals were evaluated by the method of Cusachs [65]. All computations involved an iteration to charge convergence utilizing a Mulliken population analysis.

Oscillator strengths were computed using Löwdin MO's, evaluating one-center terms using single Slater AO's, and neglecting all two-center ones. Such an approximation has been shown by Cusachs [66] to give rather reliable results. Static dipole moments were evaluated using the charges obtained from the MWH computations. In addition, we have performed VESCF-CI computations [67, 68] on the methylated ethylenes to determine $T \leftarrow N$ excitation energies, and spin-orbit coupling (SOC) computations [57, 69] to determine intensities of singlet-triplet transitions.

Computational Results: Ethylene

The z-axis was chosen along the double bond and the x-axis was chosen to be out of the molecular plane. Our group theoretical notation agrees with that of Mulliken [2]. We used 1.34 Å for the C=C distance, 1.07 Å for the C–H distance and 118° for the HCH angle.

Selection of a proper orbital exponent (ζ) for the virtual $3s$ orbital presented an initial difficulty. Slater's rules give $\zeta_{3s} = 0.20$ 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. Matching of the $3s$ function to best mimic the SCF overlaps indicated that an orbital exponent of 0.30 should be used. We decided to vary ζ_{3s} from 0.10 to see what effect this had on the computational results. The results of this variation in ζ_{3s} are shown in Fig. 1, in which we plot MO energies versus ζ_{3s}. For values of $\zeta_{3s} = 0.10$ to 0.45, the ordering of MO's is the same, having $b_{2g}(\pi^*)$ as the

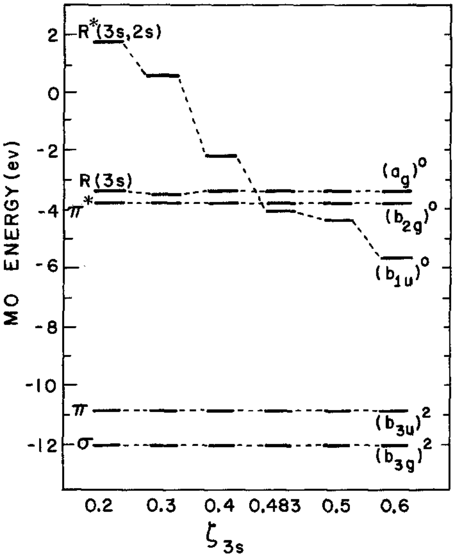

Fig. 1. Ethylene MO diagram, varying ζ_{3s}

Table 1. *Ethylene: Effect of varying* ζ_{3s}

ζ_{3s}	ΔE(eV), $\pi \to R(3s)$	% Rydberg	ΔE(eV), $\pi \to R^*(3s, 2s)$	% 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

lowest unfilled MO, the $a_g[R(3s)]$ next, and the $b_{1u}[R^*(3s, 2s)]^1$ third. At $\zeta_{3s} = 0.483$, 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 ζ_{3s} is increased to 0.65. The highest filled σ orbital, b_{3g}, is about 1.1 eV below the π level. Table 1 gives the energies predicted for the two low-lying $\pi \to \sigma$ type transitions, along with their percentage

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[1] In the text, we use the name"antibonding“ in describing this $R^*(3s, 2s)$ orbital. The name "antisymmetric" is equally apt. Mulliken [54] indicates 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 [47] situated his Gaussian representation of the virtual 3s. This does not allow for the possibility of "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) and since the $3s - 3s$ overlaps are also finite.

Table 2. *Computed intensities*[a, b] *for ethylene* ($\zeta_{2p_x} = \zeta_{2p_y} = \zeta_{2p_z} = 1.625$)

Transition	f_{total}	f_{ED}	f_{MD}	f_{EQ}	ΔE(eV)
$\sigma \to \pi^*$	8.24×10^{-6}	0.0	6.72×10^{-6}	1.52×10^{-6}	8.25 (8.26)
$\pi \to \pi^*$	0.280	0.280	0.0	0.0	7.12
$\pi \to R(3s)$	1.08×10^{-4} (3.02×10^{-3})	1.08×10^{-4} (3.02×10^{-3})	0.0	0.0	7.44
$\pi \to R^*(3s, 2s)$	2.27×10^{-8} (3.36×10^{-9})	0.0	1.85×10^{-8} (2.74×10^{-9})	4.17×10^{-9} (6.17×10^{-10})	11.50 (6.81)

[a] ED – electric dipole, MD – magnetic dipole, EQ – electric quadrupole.

[b] Values in parentheses are ones obtained using $\zeta_{3s} = 0.483$. We quote these only if they are different from the values obtained using $\zeta_{3s} = 0.300$ (no parentheses).

Rydberg character. These results suggest that both the $\pi \to R(3s)$ and the $\pi \to R^*(3s, 2s)$ lie in the range of, and possibly below, the $\pi \to \pi^*$. 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 $\sigma \to \pi^*$ transition of Berry appears to be valence-shell in nature and does not vary with changing ζ_{3s}, lying about 1 eV above the $\pi \to \pi^*$. The $\pi \to \pi^*$ transition 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 ζ_{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 ζ_{3s} on a carbon center if the $2p\pi$ population is omitted and an electron is considered as being in the virtual $3s$ orbital. It appears that a value of about 0.32 is consistently arrived at by this means. Since we had 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 $\zeta_{3s} = 0.483$.

The results of intensity calculations for ethylene are shown in Table 2. Although the computation predicts an f-value of 0.280 for the $\pi \to \pi^*$ transition, which agrees well with the experimental value of 0.30, it fails to predict the observed value of 0.03 for the sharp $\pi \to R(3s)$. The predicted value is an order of magnitude too small when $\zeta_{3s} = 0.483$ is used, and two orders of magnitude too small when $\zeta_{3s} = 0.300$ is used. We have been informed by Mulliken in a private communication that he feels this computed value is too low, and that the $\pi \to R(3s)$ transition dipole moment should be about the same as that for the $3p_x \to 4s$ 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 Å (using $\zeta_{4s} = 0.243$, $\zeta_{3p_x} = 1.817$ 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, however, with the oscillator strength predicted for the ethylene molecule using $\zeta_{3s} = 0.483$, and provides another reason for using this value in computations on the alkyl substituted ethylenes.

Table 2 also reveals that the computed f-value for the $\pi \to R^*(3s, 2s)$ 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.

Table 3. *Effect of including* $3p$ AO's *in ethylene* ($\zeta_{3p_x}=\zeta_{3p_y}=\zeta_{3p_z}=\zeta_{3s}=0.300$)

Transition	ΔE(eV)	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 % $2p_y$	38.66 % $3p_z^*$, 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

It is also seen that the electric-dipole-forbidden $\sigma\rightarrow\pi^*$ transition of Berry does gain some allowedness ($f\approx8\times10^{-6}$) through magnetic dipole ($f_{\mathrm{MD}}\approx6.7\times10^{-6}$) and electric quadrupole ($f_{\mathrm{EQ}}\approx1.5\times10^{-6}$) contributions.

One further MWH calculation was done on ethylene in which we included the $3p$ orbitals. Table 3 shows these results for the lowest transitions. 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, other than the $\pi\rightarrow R(3s)$, all Rydberg transitions from the π level are forbidden in D_{2h} symmetry until we reach the $\pi\rightarrow R^*(3p_x)$, which is the $\pi(2p_x)\rightarrow\pi^*(3p_x)$ transition. We presume this is the transition responsible for the second broad continuum [8] in the region 1300 to 1500 Å. Yet, Price and Tutte [16] observed 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 [17] 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 $\pi\rightarrow\pi^*(3p_x)$. Examination of the symmetries involved showed this could occur by various modes in D_{2h}. Stealing is allowed from the ${}^1A_g\rightarrow{}^1B_{1u}(\pi\rightarrow\pi^*)$ transition whenever a transition, plus coupling, becomes z-polarized. The possibilities for such an occurrence are shown in Table 4 which shows the vibrations, rotations, and combinations which can couple with various transitions making them z-vibronically allowed.

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. Albrecht [70] has treated this situation in benzene and arrived at an empirical vibronic coupling matrix element of 0.27 eV. His equation is

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

Table 4. *Vibrations, rotations, or combinations which can couple in* D_{2h} *and allow stealing from the* $^1A_g \rightarrow {}^1B_{1u}(\pi \rightarrow \pi^*)$ *transition*

Symmetry	Transition	z-polarized
$^1A_g \rightarrow {}^1B_{3u}$	$\pi \rightarrow R(3s)$	R_y ν_8 $R_z + \nu_5$ or ν_6
$^1A_g \rightarrow {}^1B_{2g}$	$\pi \rightarrow R^*(3s, 2s)$ $\pi \rightarrow R^*(3p_z, 2s, 3s)$	ν_7 $R_x + \nu_4$ $R_y + \nu_{11}$ or ν_{12} $R_z + \nu_9$ or ν_{10}
$^1A_g \rightarrow {}^1B_{1g}$	$\pi \rightarrow R(3p_y)$	ν_4 $R_z + \nu_{11}$ or ν_{12} $R_x + \nu_7$ $R_y + \nu_9$ or ν_{10}
$^1A_g \rightarrow {}^1A_g$	$\pi \rightarrow R(3p_x)$	ν_{11} or ν_{12} $R_z + \nu_4$ $R_y + \nu_7$ $R_x + \nu_9$ or ν_{10}

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 transition A and B in eV.
H_{vc} = vibronic coupling matrix element.
ΔE = $E_A - E_B$ 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 $\pi \rightarrow \pi^*$ transitions. This yielded $f(\pi \rightarrow R(3s)) = 0.075$. The mechanism thus provides plenty of intensity to account for the observed value. We will return, in the next section, to the application of vibronic ideas to this transition in the alkyl-substitued ethylenes.

The VESCF-CI calculation on ethylene yielded a manifold of singlets at -0.22, 7.32, and 11.66 eV. It predicts the $V(\pi \rightarrow \pi^*)$ transition to be at 7.54 eV and have an f-value of 0.433, in good agreement with experiment. It further predicts the $T(\pi \rightarrow \pi^*)$ state to lie 4.34 eV above the ground state, in excellent agreement with Reid's reported [4] 4.4 eV. Spin-orbit coupling calculations predict the oscillator strength of this latter transition (i. e., $T \leftarrow N$) 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 of about 10^{-3}. If we assume the $T \leftarrow N$ transition to be as broad as the $V \leftarrow N$ transition ($\varepsilon = 10{,}000, f = 10^{-1}$), then we expect the $T \leftarrow N$ band to have an oscillator strength of about 10^{-8}. This is in good agreement with our computed value.

Computational Results of Methyl Substituted Ethylenes

These molecules were all supposed to possess planar carbon skeletons. We chose their skeletal plane as the yz-plane with the z-axis along the double bond, making the out-of-plane x-axis the π-direction. All methyl hydrogens were placed

Table 5. MO's *predicted for methyl substituted ethylenes* ($\zeta_{3s} = 0.300$)

Molecule	MO	Symmetry	E(eV)	Percentage Rydberg character
Ethylene (D_{2h})	σ_B	b_{3g}	−12.03	0.0
	π, N	b_{3u}	−10.90	0.0
	π^*, V	b_{2g}	− 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_2	−11.63	0.0
	π	b_1	− 9.38	0.0
	$R(3s)$	a_1	− 3.32	88.1
	π^*	b_1	− 2.76	0.0
cis $B(C_{2v})$	σ_B	b_2	−11.41	0.0
	π, N	b_1	− 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_{3g}	−10.97	0.0
	π, N	b_{3u}	− 8.37	0.0
	$R(3s)$	a_g	− 3.08	94.4
	$\sigma^*(3s)$	b_{1u}	− 2.87	36.9
	π^*, V	b_{2u}	− 1.91	0.0

in a staggered configuration (one up and two down or vice-versa). This is probably the most stable arrangement although it does cause the molecules to deviate slightly from the 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 quite free to rotate. We have taken all C=C double bond distances to be 1.34 Å, C–C single bonds as 1.53 Å, CH as 1.07 Å when the carbon is double bonded, and CH as 1.09 Å when the carbon is a methyl carbon.

We first determined what effect rotation of the methyl groups had 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. There was little effect on the resulting MO energies.

We then performed MWH calculations on the series using a 3*s* orbital exponent of 0.300. The resulting MO energies along with their symmetries and percentage Rydberg characters are given in Table 5. We use the symbol σ_B for the highest

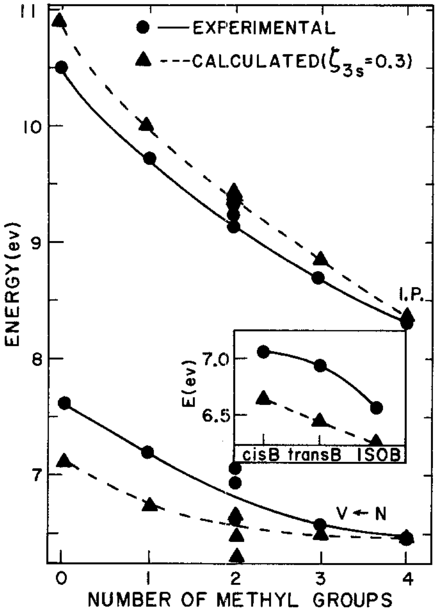

Fig. 2

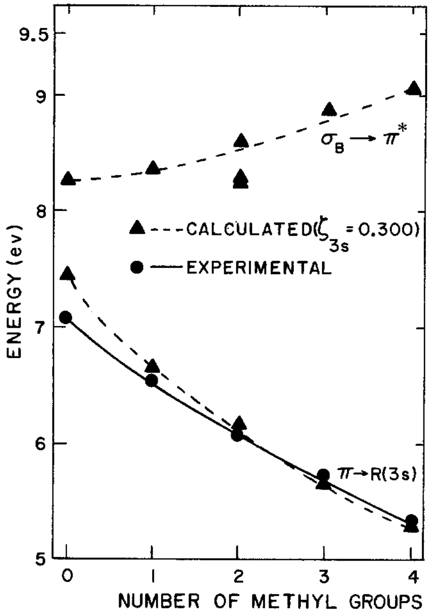

Fig. 3

Fig. 2. Ionization potentials and $V \leftarrow N$ energies in methyl substituted ethylenes. The experimental ionization potentials are taken from Refs. [16] and [53]. Experimental $V \leftarrow N$ energies are taken from Refs. [33], [40] and [54]

Fig. 3. $R(3s) \leftarrow N$ and $\sigma_B \rightarrow \pi^*$ energies in methyl substituted ethylenes. The experimental $R(3s) \leftarrow N$ energies are taken from Refs. [33], [40], and [54]

filled σ-orbital chosen by Berry in his $\sigma_B \rightarrow \pi^*$ assignment. It is antibonding in $2p_y$ and bonding between the carbons of the double bond and the methyl carbons.

The calculated excitation energies of the low-lying transitions and the ionization potentials are plotted versus number of methyl groups in Fig. 2 and 3. Fig. 2 shows a remarkable agreement between calculation and experiment for the ionization potentials and the $V \leftarrow N$ excitation. Both are seen to shift regularly with increased methylation. The $V \leftarrow N$ energy is seen to vary a great deal among the three isomeric butenes as was first observed by Gary and Pickett [40]. This variation is also predicted by the calculations as seen on the smaller graph inset in Fig. 2.

Inspection of the results failed to reveal the relative importance of various effects such as hyperconjugation, charge transfer, or molecular geometry, in determining the position of the $V \leftarrow N$ transition. Table 6 shows the negative charge accumulated by the two double-bonded carbons and the dipole moment calculated for the series of molecules. Also included are the percentage of $1s_H$ in the π and π^* MO's. These should, to some extent, reflect the degree of hyperconjugation. However, since the molecular ground state is planar and the $(\pi)(\pi^*)$ state is bent (90°), these numbers cannot correctly indicate the percentage of $1s_H$ character in the π^*-MO except for the single calculation done on 90° ethylene. The computed dipole moments do not agree well with what one expects from the molecular geometry. For example, tetramethylethylene should have a zero

Table 6. *Output charge, ground state dipole moments, and percentage* $1s_H$ *character in the* π *and* π^* MO's *for methyl substituted ethylenes* ($\zeta_{3s}=0.300$)

Molecule	Output charge[a]		D	D_y	D_x	D_z	Percentage $1s_H$	
	C_1	C_2	(Debyes)	(Debyes)	(Debyes)	(Debyes)	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	-2.42	1.92	1.29	6.46	0.55
ISOB	4.121	3.992	0.44	0.0	-0.28	0.34	9.90	5.57
cis B	4.054	4.054	3.84	0.0	-3.84	-0.14	11.54	7.18
trans B	4.044	4.044	0.52	0.0	-0.28	-0.44	13.85	6.79
TRIME	4.078	4.015	2.22	-1.42×10^{-3}	-1.65	1.48	14.50	10.74
TETME	4.044	4.044	0.52	-0.21	0.48	0.0	21.68	13.74

[a] C_1 and C_2 represent the two double-bonded carbons. The output charges are those obtaining at charge convergence. 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.

dipole moment but the calculations produce small moments in the x and y directions. This is partially 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 $V \leftarrow N$ transition will lie at lower energies if the largest moment vector lies along the axis of polarization (z-axis for the $V \leftarrow N$). 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 $V \leftarrow N$ excitation energy (z-polarized). The precicted ordering for the $V \leftarrow N$ energy is thus *cis*-butene-2 > *trans*-butene-2 > isobutene. This is the order found experimentally.

In Fig. 3 we have plotted the calculated energies for both the $\sigma_B \rightarrow \pi^*$ transition of Berry and the $R(3s) \leftarrow N$ transition 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 $R(3s) \leftarrow N$ assignment. We note that the calculated values agree with the experimental observation that the $R(3s) \leftarrow N$ energy varies little within the isomeric butenes, being seemingly dependent only on the number of methyl groups.

The MWH computations were repeated on these molecules using $\zeta_{3s}=0.483$. The resulting MO's and their energies are given in Table 7. As noted in the previous section a new 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 ($\zeta_{3s}=0.483$) becomes $\sigma^*(3s, 2s)$ because it has 45.2% Rydberg character.

Table 7. MO's *predicted for methyl substituted ethylenes* ($\zeta_{3s} = 0.483$)

Molecule	MO	Symmetry	E(eV)	Percentage Rydberg
Ethylene	σ_B	b_{3g}	−12.04	0.0
	π, N	b_{3u}	−10.89	0.0
	$\sigma^*(3s, 2s)$	b_{1u}	− 4.08	45.2
	π^*, V	b_{2g}	− 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_2	−11.69	0.0
	π, N	b_1	− 9.41	0.0
	$R(2s^*, 3s)$	b_2	− 3.84	71.6
	$R(3s)$	a_1	− 3.00	54.6
	π^*, V	b_1	− 2.78	0.0
cis B	σ_B	b_2	−11.40	0.0
	π, N	b_1	− 9.47	0.0
	$R^*(2s, 3s)$	b_2	− 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
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_{3g}	−11.03	0.0
	π, N	b_{3u}	− 8.49	0.0
	$\sigma^*(2s)$	b_{1u}	− 5.14	48.7
	$R(2px)$	b_{2u}	− 3.64	66.5
	$R(3s, 2s)$	a_g	− 3.10	74.7
	π^*, V	b_{2g}	− 1.94	0.0

The ionization potentials, and excitation energies for $\sigma_B \rightarrow \pi^*$, $R(3s) \leftarrow N$, and $V \leftarrow N$ are all relatively unaffected by using $\zeta_{3s} = 0.483$ instead of $\zeta_{3s} = 0.300$. However, a new trend now appears in this series of molecules. The $\pi \rightarrow \sigma^*(3s, 2s)$ transition is now the lowest transition in ethylene. It is seen to shift greatly with increased methylation as shown in Fig. 4. 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 $R^* \leftarrow N$.

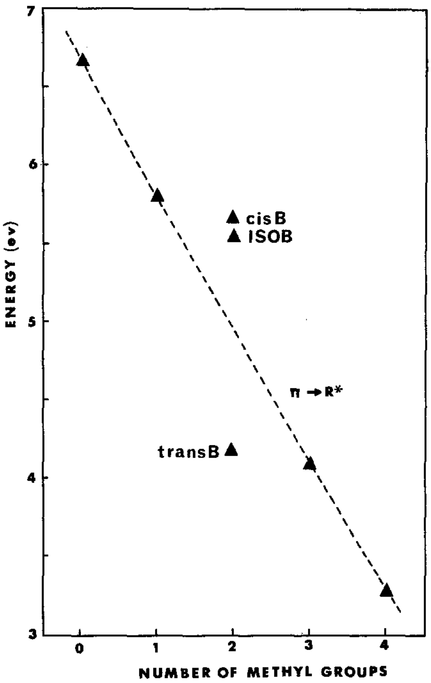

Fig. 4. $R^* \leftarrow N$ excitation energies in methyl-substituted ethylenes. ($\zeta_{3s}=0.483$)

Table 8. *Calculated f-numbers for the $V \leftarrow N$ transition*

Molecule	f ($\zeta_{3s}=0.300$)	f ($\zeta_{3s}=0.483$)	$f_{(\text{experimental})}$
Ethylene	0.280	0.280	0.34 ± 0.15[a], 0.29[b]
Propylene	0.280	0.281	
ISOB	0.302	0.301	–
cis B	0.319	0.322	–
trans B	0.310	0.299	–
TRIME	0.327	0.331	0.34 ± 0.09[c], 0.33[d]
TETME	0.332	0.336	0.45 ± 0.10[c], 0.33[e]

[a] See Ref. [6]. – [b] See Ref. [9]. – [c] See Ref. [33]. – [d] See Ref. [41]. – [e] See Ref. [47].

Computed oscillator strengths for the $V \leftarrow N$ transition are given in Table 8, along with experimental values where reported. The agreement between experiment and computation is excellent.

Column 1 of Table 9 gives the experimental values reported for the $R(3s) \leftarrow N$ transition. We initially computed f-values for this transition using $\zeta_{3s}=0.300$. The results are shown in column 2 of Table 9. Computed f-numbers are about two orders of magnitude too small for ethylene and one order of magnitude too low for trimethylethylene and tetramethylethylene. Calculations predict 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.

Table 9. *Calculated f-numbers for the $R(3s) \leftarrow N$ transition*

Molecule	$f_{(\text{experimental})}$	f $(\zeta_{3s} = 0.300)$	f (vib. stealing)	f $\langle 2p_x \vert x \vert 3s \rangle$	f $(\zeta_{3s} = 0.483)$
Ethylene	0.03 ± 0.01^a, 0.04^b	1.08×10^{-4}	0.081	1.85×10^{-3}	3.02×10^{-3}
Propylene	0.02^c	2.16×10^{-4}	0.047	5.40×10^{-4}	1.27×10^{-3}
ISOB	0.02^c	4.8×10^{-5}	0.086	2.03×10^{-4}	4.38×10^{-3}
cis B	0.02^c	3.52×10^{-3}	0.045	2.13×10^{-4}	3.64×10^{-3}
trans B	0.03^c	2.50×10^{-3}	0.069	2.24×10^{-4}	1.65×10^{-2}
TRIME	0.02^c, $\sim 0.01^d$	9.90×10^{-4}	0.012	1.14×10^{-4}	3.09×10^{-3}
TETME	0.02^c, $\sim 0.01^d$	1.20×10^{-3}	0.014	7.21×10^{-5}	5.55×10^{-3}

[a] See Ref. [6]. – [b] See Ref. [9].

[c] Estimated from our absorption spectra (to be published in Part II).

[d] Approximated from the molar extinction coefficients of 10^3 reported by several workers.

This computed 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 the previous section. Since the $R(3s) \leftarrow N$ is red-shifting with respect to the $V \leftarrow N$ 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, we computed the f-values given in column 3 of Table 9. The mechanism of vibronic stealing from the $V \leftarrow N$ accounts nicely for both the observed intensities and the decrease in f-value as one goes from zero to four methyl groups.

As mentioned in the previous section, 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 $R(3s) \leftarrow N$ of ethylene to be about the same as that calculated from the element $\langle 3p_x|x|4s \rangle$ 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 $\langle 2p_x|x|3s \rangle$ element. If we assume the $R(3s) \leftarrow N$ transition to be pure $2p_x \rightarrow 3s$ on carbon and multiply by the appropriate MO coefficients, we obtain the f-values given in column 4 of Table 9. They do, indeed, show the proper trend, decreasing with increasing methylation; but, again, they are two to three orders of magnitude too low.

We next computed the intensities of the $R(3s) \leftarrow N$ transition using $\zeta_{3s} = 0.483$. The results are shown in column 5 of Table 9. 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 invoked 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 to be a necessary assumption in the case of ethylene.

Table 10, column 1 shows the $R^* \leftarrow N$ transitions to have the proper intensity in trimethylethylene and tetramethylene 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.

Table 10. *Computed f-numbers for the $R^* \leftarrow N$, $T \leftarrow N$, and $T_R \leftarrow N$ transitions*

Molecule	$f(R^* \leftarrow N)$, $\zeta_{3s} = 0.483$	$f(T \leftarrow N)$	$f(T_R \leftarrow N)$	$f_{(\text{experimental})}$
Ethylene	3.36×10^{-9}	1.57×10^{-9}	3.88×10^{-7}	
Propylene	3.07×10^{-3}	1.31×10^{-9}	2.22×10^{-6}	
ISOB	1.36×10^{-3}	1.35×10^{-8}	6.55×10^{-9}	2.4×10^{-5} [a]
cis B	4.06×10^{-3}	9.93×10^{-10}	2.53×10^{-9}	1.7×10^{-5} [a]
trans B	1.06×10^{-7}	1.04×10^{-9}	1.71×10^{-7}	
TRIME	5.14×10^{-4}	8.45×10^{-10}	1.75×10^{-8}	$1.0 \pm 0.5 \times 10^{-5}$ [b]
TETME	6.09×10^{-4}	1.63×10^{-10}	1.40×10^{-9}	1.8×10^{-5} [a] $4.2 \pm 1.0 \times 10^{-5}$ [b]

[a] Estimated from our absorption spectra (to be published in Part II).

[b] These numbers refer to the oscillator strengths for the weak absorption in the quartz region reported by Potts, Ref. [33].

Table 11. VESCF-CI *results for the $T \leftarrow N$ 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

That this weakest transition observed in absorption is $T \leftarrow N$ or $T_R \leftarrow N$ is also a possibility. We have performed spin-orbit coupling computations on the series and obtained the results shown in Table 10, columns 2 and 3. The calculated oscillator strengths are much lower 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 $T \leftarrow N$ nor $T_R \leftarrow N$. However, it is possible that the experimental values may be high owing to absorbed-oxygen enhancement of the $T_1 \leftarrow S_0$ process. This would bring calculation and experiment more into line so that the $T \leftarrow N$ and $T_R \leftarrow N$ assignment are still vaguely possible.

Although the VESCF-CI programs can handle only planar π-systems, we used the charges generated by the MWH calculations and treated the methyl groups as in-plane hydrogens. In such a simple molecular system, the π-approximation allows interaction only between the ground (A_1) configuration and the doubly-excited (A_1) configuration; the singly-excited π, π^* configuration being of B_{1u} symmetry. We hoped this would give us some idea of how the $T \leftarrow N$ shifts with increased negative charge transfer from the methyls. The results are shown in Table 11. The agreement with the small observed shift in the weakest olefin transition is quite good, again pointing to the $T \leftarrow N$ assignment. The choice between $R^* \leftarrow N$ or $T \leftarrow N$ (or $T_R \leftarrow N$) 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 $R^* \leftarrow N$. If the shift is small, it would likely be $T \leftarrow N$ (or $T_R \leftarrow N$). Rigorous degassing and/or flushing with N_2 should decrease its intensity if it is singlet→triplet, but have no effect on the $R^* \leftarrow N$.

Computational Results on Cyclic Mono-Olefins

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. For these computations we maintain the same coordinate frame as used previously, i. e., the z-axis along the double bond, the x-axis out of the molecular plane. The symmetry operations for C_{2v} are thus $E, C_2(y), \sigma_v(xy), \sigma'_v(yz)$. The results using $\zeta = 0.300$ and $\zeta = 0.483$ are shown in Tables 12 and 13. Here we encounter the unusual opportunity of having extensive π-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 $\pi^{*\prime}(a_2)$ at -11.89 eV. The highest filled π-MO is $\pi(b_1)$ at -10.33 eV. All transitions between π-MO's are allowed, being y-polarized if $A_1 \to A_1$ and z-polarized if $A_1 \to B_2$. This molecule could thus display three low-lying π, π transitions: $\pi^{*\prime} \to \pi^*(A_1 \to A_1)$ at 7.66 eV, $\pi \to \pi'(A_1 \to A_1)$ at 7.05 eV, and $\pi \to \pi^*(A_1 \to B_2)$ at 6.10 eV. 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 by Loeffler, Eberlin, and Pickett [52] which shows continuous strong absorption in cyclobutene from 50,000 to 65,000 cm^{-1}.

Table 12. *Low-lying* MO's *in cyclic mono-olefins* ($\zeta_{3s} = 0.300$)

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

Table 13. *Low-lying* MO's *in cyclic mono-olefins* ($\zeta_{3s} = 0.483$)

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

The same is true of the spectrum of cyclopentene as reported by Pickett, Muntz, and McPherson [51]. 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 remains very strong from 50,000 to 65,000 cm^{-1}.

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

In addition, we have performed MWH computations on methylenecycloalkanes (ring compounds with a methylene double-bonded to a carbon of the ring) and cycloalkylidenecycloalkanes (two rings joined by a double bond). We found the trends to be not so regular as in the methyl substituted ethylenes, but again obtain low-lying σ and σ^* orbitals of both valence-shell and Rydberg types.

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 $V \leftarrow N$ ($\pi \rightarrow \pi^*$) in nature. Its position and intensity ($f = 0.30$) in the spectra of methyl substituted ethylenes agree very well with computational results. The position of this transition is 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 $R(3s) \leftarrow N$ in nature. The position seems mainly dependent on the number of methyl groups attached to the double bond and not on the nature or arrangement of these methyl groups. Agreement between calculation and experiment is extremely good.

3. The calculated shift in ionization potential with increased methylation agrees very well with experiment.

4. A weaker transition at the onset of absorption has been predicted by the computations to be $R^* \leftarrow N(\pi \rightarrow \sigma^*)$ in nature. This may well correspond to the weak, initial absorption observed in olefins in the region 4 – 5 eV with an oscillator strength of $\sim 10^{-5}$.

5. It is suggested that the $R(3s) \leftarrow N$ transition in olefins gains at least a part of its intensity *via* vibronic stealing (from the $V \leftarrow N$) mechanism. More will be said about this mechanism in a later paper (Part II) in which we will discuss the vibrational structure in the $R(3s) \leftarrow N$ bands of ethylene and cyclopentene.

6. In cyclic mono-olefins, a new spectral feature appears. The strong $V \leftarrow N$ absorption is broadened considerably due to overlapping of low-lying π, π^* transitions resulting from $p\pi$ orbitals on the ring.

7. 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 $\pi \rightarrow \sigma^*$.

References

1. Kaldor, U., Shavitt, I.: J. chem. Physics **48**, 191 (1968).
2. Merer, A. J., Mulliken, R. S.: Chem. Rev. **69**, (1969).
3. Reid, C.: J. chem. Physics **18**, 1299 (1950).
4. Evans, D. F.: J. chem. Soc. (London) 1735 (1960).
5. Mulliken, R. S., Rieke, C. A.: "Reports on progress in physics", Physic. Soc. (London) **8**, 231 (1941).
6. Platt, J. R., Klevens, H. B., Price, W. C.: I chem. Physics **18**, 190 (1948).
7. Wilkinson, P. G., Johnston, H. L.: J. chem. Physics **18**, 190 (1950).
8. Zelikoff, M., Watanabe, K.: J. opt. Soc. America **43**, 756 (1954).
9. Hammond, V. J., Price, W. C.: Trans. Faraday Soc. **51**, 605 (1955).
10. Snow, C. P., Allsop, C. B.: Trans. Faraday Soc. **30**, 93 (1934).
11. Scheibe, G., Grieneisen, H.: Z. physik. Chem. **25**, 52 (1934).
12. Wilkinson, P. G., Mulliken, R. S.: J. chem. Physics **23**, 1895 (1955).
13. McDiarmid, R., Charney, E.: J. chem. Physics **47**, 1517 (1967).
14. Merer, A. J., Mulliken, R. S.: J. chem. Physics **50**, 1026 (1969).
15. McDiarmid, R.: J. chem. Physics **50**, 1794 (1969).
16. Price, W. C., Tutte, W. T.: Proc. Roy. Soc. (London) **174**, 207 (1940).
17. Wilkinson, P. G.: Canad J. Physics **34**, 643 (1956).
18. Mulliken, R. S.: Tetrahedron **5**, 253 (1959).
19. Merer, A. J., Schoonveld, L.: J. chem. Physics **48**, 522 (1968).
20. Yaris, M., Moscowitz, A., Berry, R. S.: J. chem. Physics **49**, 3150 (1968).
21. Ross, K. J., Lassettre, E. N.: J. chem. Physics **44**, 4633 (1969).
22. Mulliken, R. S.: J. chem. Physics **33**, 1596 (1960).
23. Kuppermann, A., Raff, L. M.: J. chem. Physics **37**, 2497 (1962); Discuss. Faraday Soc. **35**, 30 (1963); J. chem. Physics **39**, 1607 (1963).
24. Lubezky, A., Kopelman, R.: J. chem. Physics **45**, 2526 (1966).

25. Simpson, J. A., Mielczarek, S. R.: J. chem. Physics **39**, 1606 (1963).
26. Al-Joboury, M. I., Turner, D. W.: J. chem. Soc. (London) 4434 (1964).
27. Lassettre, E. N., Francis, S. A.: J. chem. Physics **40**, 1208 (1964).
28. Bowman, C. R., Miller, W. D.: J. chem. Physics **42**, 681 (1965).
29. Geiger, J., Wittmaack, K.: Z. Naturforsch. **20** A, 628 (1965).
30. Doering, J. P.: J. chem. Physics **46**, 1194 (1966).
31. Carr, E. P., Walker, M. K.: J. chem. Physics **4** , 751 (1936).
32. —, Walter, G. F.: J. chem. Physics **4**, 756 (1936).
33. Potts, W. J., Jr.: J. chem. Physics **4**, 760 (1936).
34. Carr, E. P., Stücklen, H.: J. chem. Physics **4**, 760 (1936).
35. — Chem. Rev. **41**, 293 (1947).
36. Stark, J., Steubing, W., Enklaar, C. J., Lipp, P.: Jahrbuch der Radioaktivität und Elektronik **10**, 139 (1913).
37. —, Lipp, P.: Z. physik. Chem. A **86**, 36 (1914).
38. Carr, E. P., Stücklen, H.: Z. physik. Chem. B **25**, 57 (1934).
39. — — J. Amer. chem. Soc. **59**, 2138 (1937).
40. Gary, J. T., Pickett, L. W.: J. chem. Physics **22**, 599 (1954).
41. Semenow, D., Harrison, A. J., Carr, E. P.: J. chem. Physics **22**, 638 (1954).
42. Gary, J. T., Pickett, L. W.: J. chem. Physics **22**, 1266 (1954).
43. Jones, L. C., Jr., Taylor, L. W.: Analytic. Chem. **27**, 228 (1955).
44. Samson, J. A. R., Marmo, F. F., Watanabe, K.: J. chem. Physics **26**, 783 (1962).
45. Carr, E. P., Stücklen, H.: J. chem. Physics **7**, 631 (1939).
46. Berry, R. S.: J. chem. Physics **38**, 1934 (1963).
47. Robin, M. B., Hart, R. R., Kuebler, N. A.: J. chem. Physics **44**, 1803 (1966).
48. —, Basch, H., Kuebler, N. A., Kaplan, B. E., Meinwald, J.: J. chem. Physics **48**, 5037 (1968).
49. Evans, D. F.: Proc. Roy. Soc. (London) 378 (1963).
50. Carr, E. P., Stücklen, H.: J. chem. Physics **6**, 55 (1938).
51. Pickett, L. W., Muntz, M., McPherson, E. M.: J. Amer. chem. Soc. **73**, 4862 (1951).
52. Loeffler, B. B., Eberlin, E., Pickett, L. W.: J. chem. Physics **28**, 345 (1958).
53. Turner, D. W.: Advances physic. org. Chem. **4**, 64 (1966).
54. Mulliken, R. S.: Rev. mod. Physics **14**, 265 (1942).
55. Clark, P. A.: J. chem. Physics **48**, 4795 (1968).
56. Carroll, D. G., Armstrong, A. T., McGlynn, S. P.: J. chem. Physics **44**, 1865 (1966).
57. —, Vanquickenborne, L. G., McGlynn, S. P.: J. chem. Physics **45**, 2777 (1966).
58. —, McGlynn, S. P.: J. chem. Physics **45**, 3827 (1966).
59. Armstrong, A. T., Carroll, D. G., McGlynn, S. P.: J. chem. Physics **47**, 1104 (1967).
60. Carroll, D. G., McGlynn, S. P.: Inorg. Chem. **7**, 1285 (1968).
61. Srinivasan, B. N., Russell, J. V., McGlynn, S. P.: J. chem. Physics **48**, 1931 (1968).
62. Vanquickenborne, L. G., McGlynn, S. P.: Theoret. chim. Acta (Berl.) **9**, 390 (1968).
63. Armstrong, A. T., Bertus, B., McGlynn, S. P.: Spectroscopy Letters **1**, 43 (1968).
64. Clementi, E.: IBM Research Paper RJ-256 (1963).
65. Cusachs, L. C.: J. chem. Physics **43**, 5157 (1965).
66. — J. chem. Physics **46**, 1532 (1967).
67. Brown, R. D., Hefferman, M. L.: Trans. Faraday Soc. **54**, 757 (1950).
68. — — Austral. J. Chem. **12**, 319 (1959).
69. Vanquickenborne, L., McGlynn, S. P.: J. chem. Physics **45**, 4755 (1966).
70. Albrecht, A. C.: J. chem. Physics **38**, 354 (1963).

Prof. S. P. McGlynn
Department of Chemistry
Louisiana State University
Baton Rouge, Louisiana 70803, U.S.A.