

Analog of  $n \rightarrow \pi^*$  Transitions in Mono-Olefins

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The weak absorption of mono-olefins at wavelengths just greater than 2000 Å is ascribed to a transition analogous to the  $n \rightarrow \pi^*$  transition of formaldehyde. The assignment is based on several aspects of the ultraviolet spectra of ethylene and alkyl-substituted ethylenes, on ionization potentials, and on the electron impact excitation of ethylene recently observed by Kupperman and Raff. Several tests of the assignment are suggested and some consequences of such a process, particularly in photochemistry, are mentioned briefly.

**T**HIS article presents a series of inferences regarding the electronic spectra and states of ethylene and alkylated ethylenes. These inferences are drawn from available discussions of their ultraviolet spectra,<sup>1-9</sup> the spectrum,<sup>10,11</sup> ionization curves<sup>12-17</sup> and orbital energies and forms in formaldehyde,<sup>18,19</sup> the photochemical behavior of alkylated ethylenes<sup>20</sup> and from the recent experiments carried out on the excitation of ethylene by electron impact.<sup>21</sup> In particular, we shall consider the weak absorption in the 2300–2000 Å region. This absorption, assigned for many years to the lowest singlet-triplet process, must be reassigned in view of the  $T \leftarrow N$  transition found at 4.5 eV.<sup>8,9,22</sup>

We shall try to show that it can be assigned plausibly to a transition closely analogous to the  $n \rightarrow \pi^*$  transition of formaldehyde, which is responsible for the stronger component of the 3000-Å system of H<sub>2</sub>CO. Specifically, we shall consider the possibility that the upper state of the electron being excited is the  $\pi_z^*$  unfilled orbital and that the lower orbital is the highest filled CH bonding orbital. In ethylene, this orbital is bonding between carbons and adjacent hydrogens, antibonding between geminate hydrogens and antibonding between the olefinic carbons. Moreover, it goes over to the  $3d\pi_y$  of the united atom of sulfur, if the nuclei are all collapsed together.

The following paragraphs present: first, a brief summary of the pertinent ultraviolet absorption data; next, the relationship of the optical and electron impact excitation; third, the observations from photo-ionization; fourth, the pertinent information about formaldehyde; fifth, the implications of the proposed assignment and a comparison of the implications with the available data, and several possible tests of the assignment.

Ultraviolet spectra provide the following data:

(a) Most of the reported alkylated ethylene spectra show a weak and broad absorption from 2300 Å (sometimes 2500 Å) to the onset of stronger absorption around 2100 Å. The solution spectra show these absorptions as shoulders; in some of the vapor spectra, vibrational structure can be distinguished. Exceptions to this seem to be *trans*-2-butene,<sup>5</sup> conceivably *trans*-2-pentene,<sup>5</sup> also *trans*-3-hexene<sup>6</sup> and perhaps 1,1-dimethyl- and 1,1-diethyl-ethylene.<sup>6</sup> The *trans*-2-butene vapor absorption falls much more rapidly with increasing wavelength than does that of *cis*-2-butene, and has an altogether different vibrational structure. The *trans*-2-pentene absorption falls much faster than does the *cis*, but the vibrational structure is harder to distinguish. The *trans*-3-hexene solution spectrum clearly lacks the shoulder which the *cis* isomer shows. The molar extinction coefficients of the species which do

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<sup>1</sup> C. P. Snow and C. B. Alsopp, *Trans. Faraday Soc.* **30**, 93 (1934).

<sup>2</sup> E. P. Carr and M. K. Walker, *J. Chem. Phys.* **4**, 751 (1936).

<sup>3</sup> E. P. Carr and G. F. Walter, *J. Chem. Phys.* **4**, 756 (1936).

<sup>4</sup> E. P. Carr and H. Stücklen, *J. Chem. Phys.* **4**, 763 (1936).

<sup>5</sup> E. P. Carr and H. Stücklen, *J. Am. Chem. Soc.* **59**, 2139 (1937).

<sup>6</sup> *Ultraviolet Spectra Data*, American Petroleum Institute Project 44, (Carnegie Institute of Technology, Pittsburgh, Pennsylvania 1953), especially Nos. 557–559, 564, 565, and 568.

<sup>7</sup> W. J. Potts, *J. Chem. Phys.* **23**, 65 (1955).

<sup>8</sup> C. Reid, *J. Chem. Phys.* **18**, 1299 (1950).

<sup>9</sup> D. F. Evans, *J. Chem. Soc.* **1960**, 1735.

<sup>10</sup> J. A. Pople and J. W. Sidman, *J. Chem. Phys.* **27**, 1270 (1957).

<sup>11</sup> S. F. Mason, *Mol. Phys.* **5**, 343 (1962).

<sup>12</sup> T. M. Sugden and W. C. Price, *Trans. Faraday Soc.* **44**, 116 (1948).

<sup>13</sup> K. Watanabe, *J. Chem. Phys.* **26**, 542 (1957); Preliminary Table of Ionization Potentials (Department of Physics, University of Hawaii, 1957).

<sup>14</sup> J. A. R. Samson, F. F. Marmo, and K. Watanabe, *J. Chem. Phys.* **36**, 783 (1962).

<sup>15</sup> B. Steiner, C. F. Giese, and M. G. Inghram, *J. Chem. Phys.* **34**, 189 (1961).

<sup>16</sup> R. I. Schoen, *J. Chem. Phys.* **37**, 2032 (1962).

<sup>17</sup> C. A. McDowell (private communication).

<sup>18</sup> J. M. Foster and S. F. Boys, *Rev. Mod. Phys.* **32**, 303 (1960).

<sup>19</sup> P. L. Goodfriend, F. W. Birss, and A. B. F. Duncan, *Rev. Mod. Phys.* **32**, 307 (1960).

<sup>20</sup> See, for example, J. R. Majer, B. Mile, and J. C. Robb, *Trans. Faraday Soc.* **57**, 1336 (1961).

<sup>21</sup> A. Kupperman and L. M. Raff, *J. Chem. Phys.* **37**, 2497 (1962).

<sup>22</sup> R. S. Mulliken, *J. Chem. Phys.* **33**, 1596 (1960).

absorb are about 1, throughout the absorption shoulder in the solution spectra.

(b) The wavelength at which absorption begins is proportional to the number of alkyl substituents on ethylene.

(c) The spectrum of gaseous ethylene was reported by Snow and Alsopp<sup>1</sup> to have a corresponding absorption "shelf" in the region 2100–2000 Å, but about a hundred fold weaker in intensity than the "shelf" of the substituted species. Evans,<sup>9</sup> using the conditions of Reid,<sup>8</sup> found the absorption to be about one twentieth of that given by Snow and Alsopp. Reid's method utilized liquid ethylene at 120°K. Evans felt that the absorption could be the tail of the next strong absorption. This transition has undergone a variety of assignments and reassignments, the most recent of which is that of Mulliken,<sup>22</sup> who ascribes it to a Rydberg triplet  $\pi \rightarrow 3s$  transition.

A second line of attack on the problem comes from the recent proof from Kupperman and Raff's electron impact excitation<sup>21</sup> that ethylene does indeed have an excited state at about 6.5 eV above the ground state. (The corresponding  $\lambda$  is  $\sim 2080$  Å.) Excitation by impact is, of course, subject to much less stringent selection rules than is light absorption. Furthermore, Kupperman and Raff find that the energy dependence of the excitation cross section indicates strongly that the transition is not to a triplet, but is spin allowed. We conclude from this and the foregoing that the transition is symmetry forbidden for ethylene and certain substituted species, especially the *trans*- and *gem*-symmetrically disubstituted species, but is allowed for all others. The transition would presumably be forbidden for any symmetrically substituted tetralkyl ethylene.

A third pertinent set of data are the photo-ionization cross-section curves of simple olefins.<sup>13–17</sup> These curves, in contrast to those of aliphatic hydrocarbons, show distinct breaks, clearly indicating two ionization processes below 13 eV. The results of Schoen<sup>16</sup> and of Frost, McDowell, and Vroom<sup>17</sup> indicate thresholds for ethylene at about 10.5 and 12.1 eV. The propylene thresholds fall at about 9.5 and 12.1 eV.<sup>16</sup> The shape of the *cis*-butene curve makes it difficult to locate the upper threshold, but the lower seems to fall at about 9.5 eV and the upper in the vicinity of 12 eV. These data all indicate that in the ground states of the olefins, there are two filled orbitals which are rather close in energy.

Now we turn to a different system altogether for the final pieces of background information. Mason<sup>11</sup> has reviewed and reexamined the  $n \rightarrow \pi^*$  transition of formaldehyde. The band system of this transition consists of two components, the stronger of which involves transition from the highest filled orbital ( $n$ ) to the empty  $\pi_z^*$  antibonding orbital. Mason states in refer-

ence 10, p. 358: "The form of the highest occupied molecular orbital of formaldehyde,  $\psi_1$ , equation (14), indicates that a substantial portion of the one-electron charge density is situated in the region of the methylene group, so that the transition,  $\psi_1 \rightarrow \psi_2$ , involves the transfer of charge from the hydrogen atoms to the carbonyl  $\pi^*$  orbital." The formaldehyde orbital  $\psi_1$  is a mixture of oxygen  $p_y$ , carbon  $p_y$  and the hydrogen  $1s$  orbitals ( $h_1-h_2$ ). The atomic orbital coefficients in the molecular orbital are, respectively, about 0.9,  $-0.25$ , and  $-0.34$ .<sup>18,19</sup> That this is the lower orbital in the strong component of the 3000-Å band system seems well established. The out-of-plane methylene vibrations are credited with making the transition allowed.<sup>10,11</sup> The intensity ( $f=1.7 \times 10^{-4}$ ) could be greater than that of the ethylenic transition we are considering, but the latter is so severely blanketed at short wavelengths that its real intensity cannot be determined at present. Formaldehyde, like the olefins, shows more than one ionization threshold. The lowest three of these fall at 10.8, 11.8, and 13.1 eV,<sup>12</sup> and have been attributed to ionization from the  $n$ ,  $\pi_z$ , and lowest  $\sigma$  orbitals, respectively, in accord with the computed orbital energies (see below).

At this juncture we examine ethylene itself to construct the orbitals analogous to the  $n$  (nonbonding) orbital of formaldehyde. The methylene groups, iso-electronic with oxygen, each can be represented to have a  $\sigma$  orbital directed along the C-C bond axis and a  $\pi_y$ -like orbital whose density maximum is in the molecular plane, which has a node in the plane of the  $\pi_z$ -electron maximum, and which is made primarily of carbon  $p_y$  and hydrogen  $h_1-h_2$  orbitals. The  $\pi_y$ -like orbitals from the two methylenes will mix to give two orbitals which have symmetry appropriate to the molecule, and which we call  $\pi_y$  and  $\pi_y'$ . The first of these,  $\pi_y$ , corresponds to an orbital of formaldehyde which probably lies quite deep; its calculated energy in  $H_2CO$  is about  $-20$  eV.<sup>18,19</sup> It correlates with half of the bonding  $\pi_u$  orbital of  $O_2$  and therefore with the  $2p_y$  orbital of the united sulfur atom. The other half of the  $\pi_u$  orbital of oxygen becomes the  $\pi_z$  orbital of ethylene. The other orbital,  $\pi_y'$ , is directly analogous to the lower orbital involved in the  $n \rightarrow \pi^*$  transition of formaldehyde, with energy calculated as about 11 eV,<sup>18,19</sup> which is presumably responsible for the 10.8-eV ionization threshold.<sup>12</sup> The  $\pi_y'$  orbital of ethylene becomes half of the half-filled antibonding  $\pi_g$  pair of oxygen, if the protons are collapsed into the carbon nuclei. It is antibonding between carbons and between geminate hydrogens, and bonding only for carbons and adjacent hydrogens. It correlates with part of the  $3d$  orbital of sulfur. The other component of oxygen's  $\pi_g$  orbital corresponds to the  $\pi_z^*$  antibonding orbital of ethylene. The filled  $\pi_z$  orbital and highest filled  $\sigma$  orbital of formaldehyde have calculated energies of  $-12.8$ <sup>18</sup> (or  $-15.0$ )<sup>19</sup> and  $-15.5$ <sup>18</sup> (or  $-19.2$ )<sup>19</sup> eV,

respectively, which may be compared with the second and third ionization thresholds at 11.8 and 13.1 eV.<sup>12</sup>

We see that the transition in question is probably singlet-singlet and that there are apparently two high-energy filled levels in the simple olefins. Hence, it may not be necessary to postulate two closely spaced empty orbitals to assign the transition. The analogy with formaldehyde and even oxygen almost compels us to investigate the possibility of a transition in ethylene of the form  $\pi_y' \rightarrow \pi_z^*$ , like the  $n \rightarrow \pi_z^*$  transition of formaldehyde.

The first consideration is an examination of the selection rules for the  $\pi_y' \rightarrow \pi_z^*$  transition, as well as those for other possible processes. The symmetries of  $\pi_z^*$ ,  $\pi_z$ ,  $\pi_y$  and  $\pi_y'$  are, respectively,  $b_{2g}$ ,  $b_{1u}$ ,  $b_{2u}$ , and  $b_{1g}$  in the  $D_{2h}$  symmetry group of ethylene. The operators  $x$ ,  $y$  and  $z$  have the transformation properties  $b_{3u}$ ,  $b_{2u}$  and  $b_{1u}$ , respectively. From these we conclude that both  $\pi_y \rightarrow \pi_z^*$  and  $\pi_y' \rightarrow \pi_z^*$  are forbidden. The mono- and trisubstituted ethylenes have at most one plane of symmetry so that all transitions are allowed. In the  $C_{2v}$  symmetry appropriate to 1,1-symmetrically substituted species, both  $\pi_y \rightarrow \pi_z^*$  and  $\pi_y' \rightarrow \pi_z^*$  transitions are forbidden. In the  $C_{2v}$  symmetry of symmetrical 1,2-*cis*-disubstituted species, the  $\pi_y \rightarrow \pi_z^*$  transition is forbidden but the  $\pi_y' \rightarrow \pi_z^*$  process is *allowed*, with polarization perpendicular to the molecular plane ( $z$ -polarized, in our notation). If the symmetry is  $C_{2h}$  appropriate to the symmetrical *trans*-1,2-disubstituted molecules, then  $\pi_y \rightarrow \pi_z^*$  is allowed with  $z$  polarization and  $\pi_y' \rightarrow \pi_z^*$  is forbidden. These are all very much in accord with experimental data.

Two apparent anomalies appear now. First, tetramethylethylene is one of the better examples of molecules absorbing in the region in question, yet it would seem to have the symmetry of ethylene. Second, ethylene itself does absorb in the 2100-2000 region, according to Snow and Alsopp. Turning to the former problem, we note that if the tetramethylethylene molecule were slightly twisted, then its symmetry would be reduced to  $D_2$ , in which case the  $\pi_y' \rightarrow \pi_z^*$  transition would become allowed, with polarization along the  $x$  axis, the C-C bond axis. (The reported structure of tetramethylethylene<sup>23</sup> is based on the assumption that it is planar.)

Ethylene itself, and in fact any of the other species for which the transition is electronically forbidden, can exhibit absorption because the  $\pi_y' \rightarrow \pi_z^*$  process becomes *vibronically allowed* under a wide variety of vibrational perturbations, including the  $A_u$  twisting mode (1027  $\text{cm}^{-1}$  in ethylene)<sup>24</sup> and the  $b_{2g}$  and  $b_{1u}$  hydrogen out-of-plane bending modes (943 and 949.2

$\text{cm}^{-1}$  in ethylene).<sup>24</sup> If the Snow-Alsopp transition were vibronically allowed, its intensity would depend on the population of the first excited vibrational state. At room temperature, the first excited state of  $\nu_8$  has a population 0.009 as large as the ground state, a ratio comparable to the intensity ratio found by Snow and Alsopp for the ethylene and substituted ethylene bands. At 120°K, the temperature used by Reid, the excited-state population drops to  $1.4 \times 10^{-5}$  of the ground state and absorption would be indetectably small. We recall that Evans, working under Reid's conditions, found no unusual step like that of Snow and Alsopp.

The progressive red shift of the absorption is very much in accord with the  $\pi_y' \rightarrow \pi_z^*$  assignment. The ionization potential and therefore the orbital energy of a C-H single bond is certainly higher than that of a C-C single bond by about 1 eV<sup>13,25</sup> or a bit more. The red shifts of the "centers" of the transitions reported by Potts are somewhat irregular but are not inconsistent with this magnitude. A closer correlation occurs with the wavelengths at which the absorption starts ( $\epsilon = 10^{-2}$ ), which were reported by Carr and Walter.<sup>3</sup> They found several very distinct classifications, depending on the number of alkyl groups, which gave a shift of about 3000  $\text{cm}^{-1}$  per alkyl group. Moreover, there appears to be a difference between the 1,2-disubstituted and 1,1-disubstituted species. This is to be expected, since the  $\pi_y'$  orbitals of these two would be somewhat different.

The vibrational structure found in the bands is consistent with the  $\pi_y' \rightarrow \pi_z^*$  assignment since there seem to be totally symmetric modes available at frequencies within the experimental error of the observed progressions. This is weak evidence, however, since many of the uncertainties in the ultraviolet progressions are large. Progressions of the in-plane bending and stretching modes would be expected if an electron were removed from a bonding orbital of a methylene group, because, stated crudely, one methylene would retain its structure while the other should change its equilibrium shape, so that the transition should carry the molecule to any of a set of excited vibrational levels of the upper state.

Returning now to the ionization data and the problem of the electronic structure of the olefins, we must consider the order of the  $\pi_z$  and  $\pi_y'$  orbitals. Their separation, about 1.5 eV in ethylene, is small enough to be consistent with the order  $E(\pi_z) > E(\pi_y')$ , but fits so closely with the separation of the weak and strong transitions of ethylene that we should consider the possibility that the  $\pi_y'$  orbital is above the  $\pi_z$ . If

<sup>23</sup> *Tables of Interatomic Distances and Configuration in Molecules and Ions*, edited by L. E. Sutton (The Chemical Society, London, (1958).

<sup>24</sup> G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand, Inc., Princeton, 1945); R. L. Arnett and B. L. Crawford, Jr., *J. Chem. Phys.* **18**, 118 (1950).

<sup>25</sup> R. S. Mulliken, *J. Chem. Phys.* **3**, 517 (1935).

the reverse were true, then the total change in electron repulsions, exchange, and correlations would have to be about 2.5 eV smaller in the  $\pi_y' \rightarrow \pi_z^*$  transition than in the  $\pi_x \rightarrow \pi_z^*$ . This is by no means unreasonable, but there is a bit of evidence that  $\pi_y'$  may be higher in energy than  $\pi_x$ . First, we must note the similarity of the energy differences of the strong and weak transitions and of the two lowest ionization potentials. Second, the lower-energy thresholds, the ionization potentials of the alkenes, are much more sensitive to alkyl group substitution than are the second thresholds. The shift in ionization energy of the substituted olefins correlates roughly with the positions at which the long-wavelength absorption sets in. On the other hand, the presence of a long-wavelength tail in the photo-ionization curve has been attributed to the ionization of  $\pi_x$ -electrons by Steiner *et al.*<sup>15</sup> and by Schoen.<sup>16</sup> Also a rather limited and approximate SCF calculation by Berthod<sup>26</sup> places the  $\pi_x$  level 6.4 eV above the  $\pi_y'$ . However, the approximations used in a similar calculation of acetylene are known to introduce errors of several electron volts, in the direction of raising  $\pi_x$  and lowering the C-H bonding orbitals.<sup>27-30</sup>

Mulliken has pointed out that one would expect on chemical grounds that the  $\pi$  electrons of acetylene should be more easily ionized than the  $\pi_x$  electrons of ethylene; the acetylenic carbons are more negative than those of ethylene.<sup>31</sup> The observed first ionization potential of acetylene is 11.41 eV,<sup>13</sup> above the first threshold of ethylene but below the second. This would be consistent with the assignment of the highest orbital of ethylene as  $\pi_y'$ , and the next as  $\pi_x$ .

Finally, the  $\pi_y' \rightarrow \pi_z^*$  assignment is in accord with the observation that C-C bonds  $\alpha$  to the double bonds in alkylated mono-olefins can be broken when these molecules are subjected to the 2537-A radiation of mercury.<sup>20</sup> The removal of a bonding electron of methylene could well be expected to lead, not just to a change in shape as mentioned above, but to dissociation and free radical production. The process must be inefficient because the extinction coefficients are small, even when the transition is allowed. (Note also that in the photolysis of ethylene itself by 2537-A light, the decomposition to  $H_2 + C_2H_2$  occurs directly, without production of H atoms.<sup>32</sup> This wavelength is too great to excite the 6.4 eV process in ethylene.)

In summary, the arguments on which the  $\pi_y' \rightarrow \pi_z^*$  assignment is made are these:

(1) The transition exists in ethylene as well as in

substituted ethylenes (from electron impact and spectra);

(2) Mono-olefins show two closely spaced filled orbitals (from ionization thresholds);

(3) The formaldehyde molecule, isoelectronic with ethylene, also has two closely spaced filled levels known to be responsible for  $n \rightarrow \pi_z^*$  and  $\pi_x \rightarrow \pi_z^*$  transitions;

(4) The observed olefin spectra are in accord with the selection rules for a  $\pi_y' \rightarrow \pi_z^*$  transition;

(5) The temperature dependence of the ethylene spectrum is in accord with the assignment;

(6) The red shift with alkylation and the vibrational fine structure are consistent with the assignment, and

(7) The photochemical behavior of the olefins is in accord with the assignment.

We have discussed the orbital energies and ionization processes in terms of delocalized symmetry orbitals rather than localized CH bonding orbitals. This is the proper description because, first, the uncertainties in the ionization potentials are considerably smaller than the exchange integrals between the methylene  $\pi_y$ -like orbitals. (The latter estimated from the percentage of carbon  $\pi_y$  character of the formaldehyde  $CH_2$  group exchange interaction between ethylenic  $\pi_x$ -orbitals, must be about 1 eV, while the ionization potentials are known to accuracies better than 0.1 eV.) Therefore, the electrons must have time to delocalize into proper symmetry orbitals. Second, we are trying here to formulate a picture, qualitative as it is at present, which corresponds to a Hartree-Fock analysis of the olefins; that is to say, to the best description possible in terms of one-electron states. And it is the Hartree-Fock orbital energies which are the best approximations to orbital energies and ionization potentials, within the one-electron limitation.

The triplets corresponding to the  $\pi_x \rightarrow 3s$  and  $\pi_y' \rightarrow \pi_z^*$  excitations are, according to our scheme, yet to be observed. The  $\pi_x \rightarrow 3s$  may well contribute to the absorption in the Snow-Alsopp transition, but since the Rydberg singlet process is somewhat weaker than the  $V \leftarrow N$  transition and the  $T \leftarrow N$  process is known to be extremely weak, the spin-forbidden Rydberg process is probably contributing no more than a few percent to the intensity of the Snow-Alsopp transition. The same reasoning applies to the  $\pi_y' \rightarrow \pi_z^*$  singlet-triplet process, to a much greater degree, because of the very low intensity of the corresponding spin-allowed process. Both triplets may very well be buried in the 6.5 eV maximum for impact excitation found by Kupperman. Since the  $\pi_y - \pi_z^*$  and  $\pi_x - 3s$  exchange integrals are presumably much smaller than the  $\pi_x - \pi_z^*$  exchange, the singlets and triplets of these two transitions must be much closer together than the  $T$  and  $V$  states, and could easily fall within the broad peak of the impact spectrum. The weakness of the transition

<sup>26</sup> H. Berthod, *Compt. Rend.* **249**, 1354 (1959).

<sup>27</sup> A. D. McLean, *J. Chem. Phys.* **32**, 1595 (1960).

<sup>28</sup> L. Burnelle, *J. Chem. Phys.* **32**, 1872 (1960).

<sup>29</sup> A. D. McLean, B. J. Ransil, and R. S. Mulliken, *J. Chem. Phys.* **32**, 1873 (1960).

<sup>30</sup> L. Burnelle, *J. Chem. Phys.* **35**, 311 (1961).

<sup>31</sup> R. S. Mulliken (private communication).

<sup>32</sup> R. J. Cvetanović and A. B. Callear, *J. Chem. Phys.* **23**, 1182 (1955).

and the proximity of excited singlet and triplet in  $n \rightarrow \pi^*$  absorption has been known in formaldehyde for some time.<sup>33</sup>

The  $\pi_y \rightarrow \pi_z^*$  assignment probably does not force any reinterpretation of the spectra or first ionization potentials of the conjugated hydrocarbons since these display spectra far more intense than the  $\pi_y' \rightarrow \pi_z^*$  in regions where they would generally hide the weaker process, and because their first ionization potentials are generally lower than those of the mono-olefins.<sup>13</sup> There is the possibility, of course, that in a molecule like butadiene the highest CH bonding orbital (like the ethylenic  $\pi_y'$  in each  $C_2H_3$  group and bonding between the middle carbons) has an energy comparable to the highest filled  $\pi_z$  orbital.

A few simple predictions can be made to test this assignment. Obviously the polarizations must be consistent with the assignment. This requires care because the  $z$ -allowed transitions might also have weak  $x$ -polarized vibronically allowed contributions, especially in the heavier species. The planarity of tetramethylethylene can be checked. The temperature dependence of

the spectra of ethylene, the *trans*-symmetrically alkylated and 1,1-symmetrically alkylated ethylenes can be checked. Another feature to be studied in more detail is the difference of wavelength of absorption in the 1,1- and 1,2-disubstituted species. The spectrum of ethylene can be examined for a magnetic dipole-allowed transition in the 2100-Å region, since  $\pi_y' \rightarrow \pi_z^*$  is allowed, with an  $x$ -polarized magnetic field, as in formaldehyde where it has been observed.<sup>11</sup> Moreover the transition in appropriately substituted olefins should give rise to an optically active band. This possibly provides the easiest means of testing the consistency of the assignment. Finally, the photochemical behavior, especially photodissociation of  $\alpha$  bonds, can be examined as a function of excitation wavelength and, particularly in cases of species for which the transition is forbidden, the simultaneous temperature and wavelength dependence of photodissociation can be studied.

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<sup>33</sup> A. D. Cohen and C. Reid, J. Chem Phys. **24**, 85 (1956).