

ULTRAVIOLET SPECTRA AND EXCITED STATES OF ETHYLENE AND ITS ALKYL DERIVATIVES

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I. Introduction

The ultraviolet spectra of ethylene and its simple alkyl derivatives should in principle be a good source of information about the properties of the olefinic double bond. Unfortunately these spectra are not always very easy to interpret, because the bands are all diffuse, and some of the information content is thereby lost. The interpretation of these spectra is not made easier by the apparent contradictions in some of the experimental results, and many instances of confusion have arisen. In this review we summarize the available experimental results and give an account of the theory needed for an understanding of the spectra.

II. N, T, V, Z, and Rydberg States

The electronic states of ethylene bear a formal similarity to those of the hydrogen molecule, H_2 , since analogs of the well-known states of H_2 occur also in ethylene. We have drawn the potential curves¹⁻⁸ for some of the low-lying states of H_2 in Figure 1. These illustrate certain types of states, called N, T, V, Z, and Rydberg states. N is the normal state (the electronic ground state), T is the lowest triplet state, and V is the lowest excited singlet state. In terms of molecular orbitals (MO's) the N state may be represented as $(1\sigma_g)^2X^1\Sigma_g^+$, while

T (species $^3\Sigma_u^+$) and V ($^1\Sigma_u^+$) both have the same electron configuration $(1\sigma_g)(1\sigma_u)$; the Z state is another $^1\Sigma_g^+$ state, with configuration $(1\sigma_u)^2$. N, T, V, and Z are *valence-shell states*, in the sense that their MO's in LCAO approximation are constructed from valence-shell 1s atomic orbitals.^{8a}

$$1\sigma_g \approx \sigma_g 1s = 1s_a + 1s_b$$

$$1\sigma_u \approx \sigma_u 1s = 1s_a - 1s_b$$

Above these come the Rydberg states, with configuration $(1\sigma_g)(Ry)$, where (Ry) stands for any one of an infinite number of Rydberg MO's; each configuration gives one singlet and one triplet Rydberg state. Because the Rydberg MO's are much larger than the core (which here is just H_2^+), they can be described rather accurately in terms of united atom orbitals (UAO's) for the He atom. In order of increasing energy these are 2s, 3p σ , 3s, 3d σ , 3d π , 3d δ , etc. The T, V, and Z states *take on the character of Rydberg states* for small internuclear distance R , since $1\sigma_u$ becomes 2p σ ; they may therefore be called *semi-Rydberg* or *near-Rydberg* states, because at R values near the equilibrium distance R_e of state N the UAO description 2p σ is already rather good.

A hydrogen molecule in state N or T dissociates into two normal atoms. The wave function for the V state behaves at intermediate R values as if the molecule had to dissociate into two ions, $H^+ + H^-$, but in fact its nature changes at larger R values, and a molecule in the V state actually dissociates into a normal atom (1s) and an excited atom (2p). Yet at small R values both T and V states approach $(1s)(2p\sigma)$ in structure. The Z-state wave function again has an ion-pair structure, but because of an avoided crossing with the $(1\sigma_g)(2s)$ $^1\Sigma_g^+$ state near $R = 3$ au, it also dissociates into a normal atom and an excited atom.⁹ V states characteristically have a large equilibrium internuclear distance and a small vibration frequency, which are explicable in terms of their ionic nature. At the same time they have a relatively larger dissociation energy than do the Rydberg states which have the same dissociation asymptotes.

III. MO Description of Ethylene

The molecular orbitals of planar ethylene can be classified according to their behavior under the symmetry operations of the point group D_{2h} , for which the character table is given as Table I. There is an ambiguity for this point group in the assignment of the labels for the B irreducible representations, and much confusion exists in the literature as a result of dif-

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(1) W. Kolos and L. Wolniewicz, *J. Chem. Phys.*, **41**, 3663 (1964).

(2) W. Kolos and L. Wolniewicz, *ibid.*, **43**, 2429 (1965).

(3) W. Kolos and L. Wolniewicz, *ibid.*, **45**, 509 (1966).

(4) T. Namioka, *ibid.*, **43**, 1636 (1965).

(5) E. R. Davidson, *ibid.*, **35**, 1189 (1961).

(6) G. H. Dieke and S. P. Cunningham, *J. Mol. Spectry.*, **18**, 288 (1965).

(7) C. B. Wakefield and E. R. Davidson, *J. Chem. Phys.*, **43**, 834 (1965).

(8) G. Herzberg, *Sci. Light*, **16**, 14 (1967).

(8a) The figure 1 in $1\sigma_g$ is a number indicating that this is the first σ_g orbital in order of energy; in $\sigma_g 1s$ it means that the principal quantum number n is 1 in 1s.

(9) R. S. Mulliken, *J. Am. Chem. Soc.*, **88**, 1849 (1966).

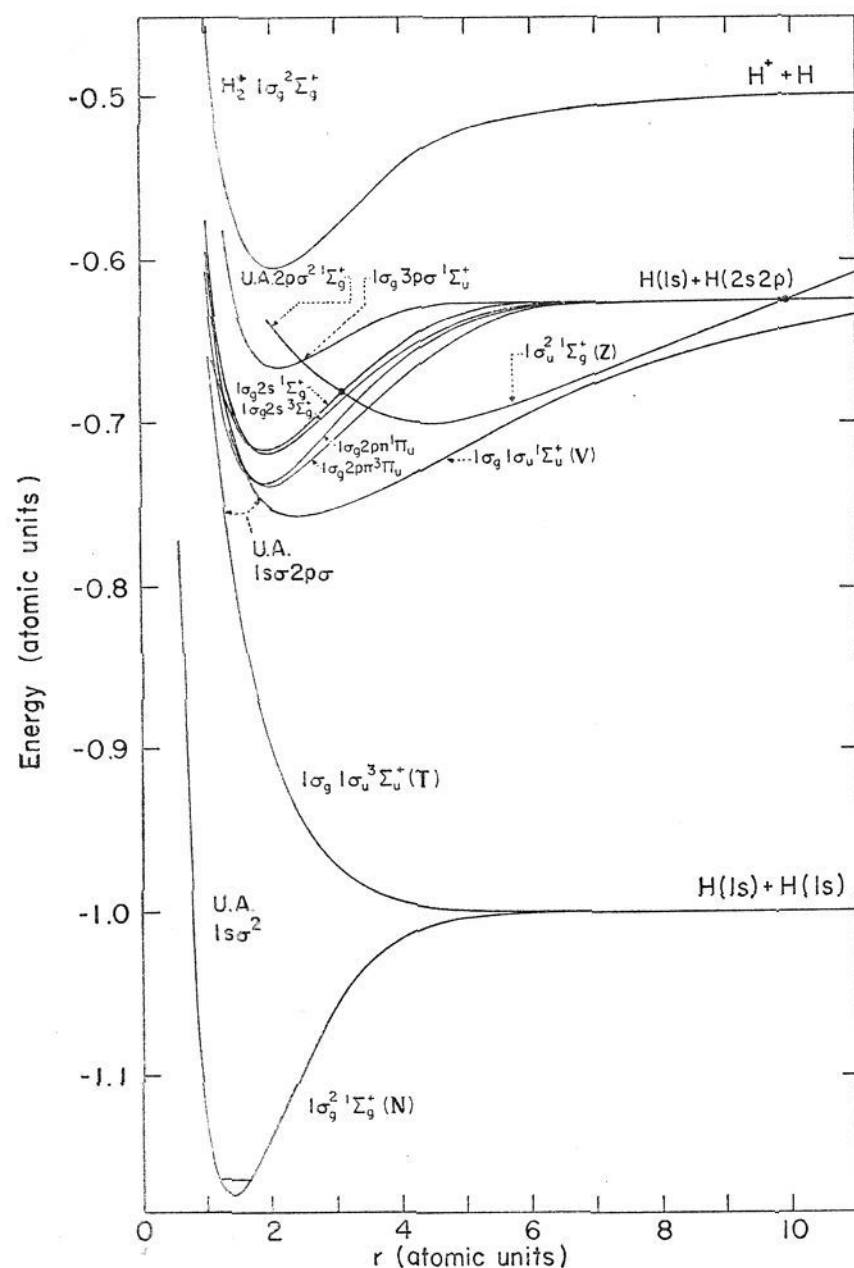


Figure 1. Potential curves for some low-lying electronic states of H_2 and H_2^+ . Following ref 6 we have not drawn avoided crossings between the $^1\Sigma_g^+$ states derived from the configurations $(1\sigma_u)^2$ and $(1\sigma_g)(2s)$ since the homogeneous perturbation viewpoint seems to be more appropriate. Note: The captions $1\sigma_g 2s^2 \Sigma_g^+$ and $1\sigma_g 2pn^3 \Pi_u$ have been interchanged in the drawing.

ferent choices of the appropriate labels made by different authors. The species B_1 , B_2 , and B_3 (both u and g) are characterized by their behavior for 180° rotations about the principal twofold axes of symmetry z , y , and x , but there are six possible ways of assigning the labels z , y , and x to the three axes. The choice recommended for ethylene by the Joint Commission on Spectroscopy of the IAU and the IUPAP¹⁰ is that the x axis be taken as that perpendicular to the plane of the molecule, and the z axis as that through the two carbon atoms. Another possible method of designation would be to label the species B_z , B_y , and B_x (each either g or u). In any event, it is obviously imperative to state how the labels x , y , and z are being assigned to the three axes!

Figure 2 shows the MO's of planar ethylene plotted according to the ionization potentials obtained¹¹ from photoelectron spectroscopy. The shapes of the MO's are roughly indicated by the small diagrams of the charge distributions, and the major bonding character is also indicated. The first two orbitals, $1a_g$ and $1b_{1u}$, which correspond to the K-shell electrons of the carbon atoms, have been omitted because they lie very

(10) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1997 (1955).

(11) A. D. Baker, C. Baker, C. R. Brundle, and D. W. Turner, *Int. J. Mass Spectry.*, **1**, 285 (1968). The IP for $2a_g$ of C_2H_4 is from work of W. C. Price, private communication.

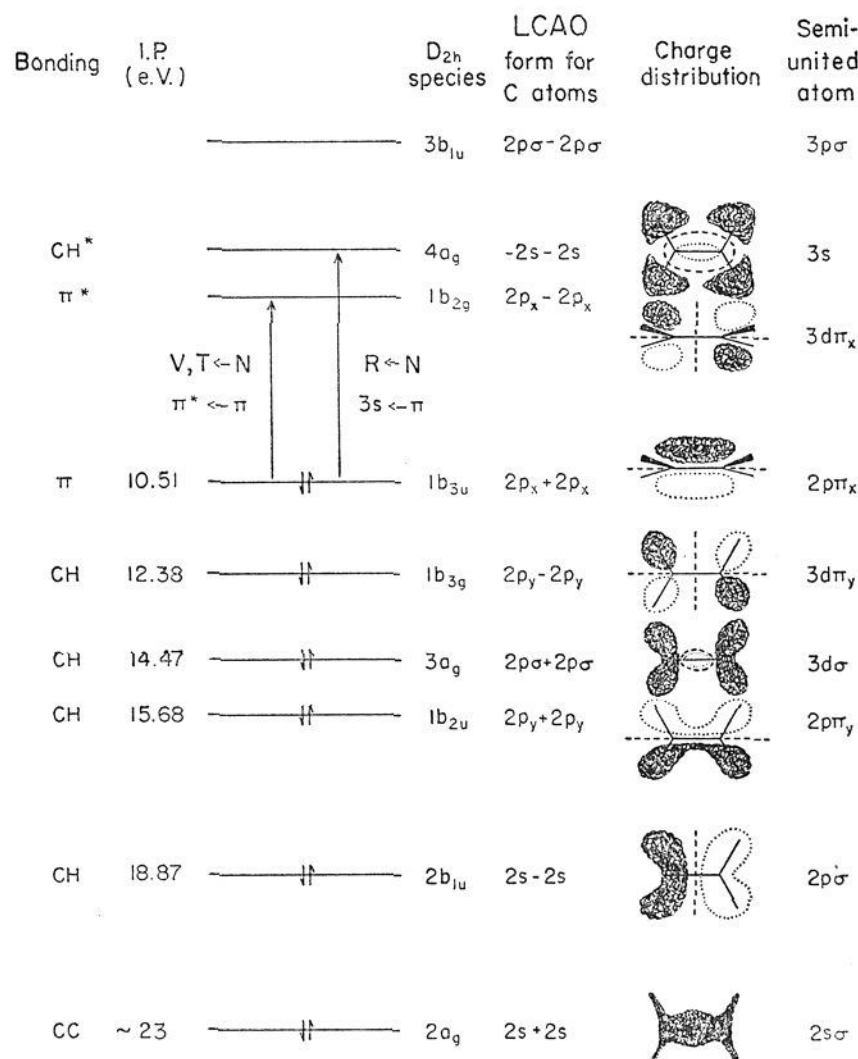


Figure 2. Molecular orbitals for the ethylene molecule. The MO's are drawn to an energy scale given by the IP's of ref 11 and are labeled according to their descriptions in LCAO and semi-united atom approximation. Small diagrams indicate the charge distributions and the positions of the nodes.

far down on the energy scale and we are not concerned with them. The photoelectron spectra are interesting since, by Koopmans' theorem, the orbital energies obtained from self-consistent-field MO calculations should be rather approximately equal to the ionization energies for removal of an electron from the respective MO's. The results from machine calculations of the orbital energies of ethylene agree quite well with those from photoelectron spectra (see, for example, ref 12-16).

Table
Character Table for the Point Group D_{2h}

	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	i	$C_2(z)$	$C_2(y)$	$C_2(x)$
A_g	+1	+1	+1	+1	+1	+1	+1
A_u	+1	-1	-1	-1	+1	+1	+1
B_{1g}	+1	+1	-1	-1	+1	-1	-1
B_{1u}	+1	-1	+1	+1	+1	-1	-1
B_{2g}	+1	-1	+1	-1	+1	+1	-1
B_{2u}	+1	+1	-1	+1	-1	+1	-1
B_{3g}	+1	-1	-1	+1	-1	-1	+1
B_{3u}	+1	+1	+1	-1	-1	-1	+1

(12) H. Berthod, *Compt. Rend.*, **249**, 1354 (1959); *J. Chem. Phys.*, **45**, 1859 (1966).

(13) J. W. Moskowitz and M. C. Harrison, *ibid.*, **42**, 1726 (1965).

(14) M. B. Robin, R. R. Hart, and N. A. Kuebler, *ibid.*, **44**, 1803 (1966).

(14a) M. B. Robin, H. Basch, N. A. Kuebler, B. E. Kaplan, and J. Meinwald, *ibid.*, **48**, 5037 (1968).

(15) J. M. Schulman, J. W. Moskowitz, and C. Hollister, *ibid.*, **46**, 2759 (1967).

(16) U. Kaldor and I. Shavitt, *ibid.*, **48**, 191 (1968).

In the electronic ground state of ethylene all the MO's up to and including the $1b_{3u}$ orbital are occupied by two electrons. As can be seen from Figure 2, this orbital, which is constructed from the in-phase overlap of $2p_z$ orbitals on the carbon atoms, has a node in the plane of the molecule, and the electrons in it form the carbon-carbon π bond; it is ordinarily called the π orbital. The unoccupied $1b_{2g}$ orbital, made from the out-of-phase overlap of the carbon $2p_x$ AO's, is ordinarily called π^* .

If we write the electron configuration for the N state of ethylene as $\dots (\pi)^2$, excitation of an electron from the π MO gives T and V states of configuration $(\pi)(\pi^*)$, a Z state of configuration $(\pi^*)^2$, and Rydberg states $(\pi)(Ry)$. In the LCAO approximation the π and π^* orbitals are $2p\pi_a \pm 2p\pi_b$ (where a and b refer to the two carbon atoms), and in the UAO approximation they become $2p\pi$ and $3d\pi$, respectively. The core, $\dots (\pi)$, is of course much more complicated than in H_2 , and excitation of core electrons gives rise to a much greater variety of excited states than in H_2 . There will also be T, V, Z, and Rydberg states of ethylene derived from excitation of core electrons, but the most important states of these types are derived from excitation of an electron out of the π orbital.

The ethylene molecule in its ground state belongs to the point group D_{2h} ; partially twisted ethylene belongs to the point group D_2 , and 90° twisted ethylene to D_{2d} . The group theory symbols for the MO's change with the angle of twisting as given in the second, third, and fourth columns of Table II. This table shows how the electron configuration of the N state changes on twisting the molecule.¹⁷ The subscripts u and g for the planar molecule become meaningless for partly twisted ethylene since there is no longer a center of symmetry. Also, when the molecule is twisted by 90° , the energies of the $1b_2$ and $1b_3$ MO's become equal, and the two orbitals come together to form a degenerate MO, which transforms like the representation e of the point group D_{2d} ; similarly $2b_2$ and $2b_3$ become another degenerate MO. Next, starting from planar or 90° twisted ethylene, we can imagine the H atoms pushed into the C atoms to form O atoms, so that the C_2H_4 molecule is converted into the UM (united molecule) O_2 . The corresponding MO symbols, which are given in the first and fifth columns of the table, are now classified according to the point group $D_{\infty h}$; it will be noted that twisted (D_{2d}) ethylene is much more closely correlated with O_2 than is planar ethylene. Finally, regarding all but the carbon K-shell electrons like those of a single atom, we obtain the semi-united atom^{18,19} Si. The sixth column shows the corresponding AO's of the Si atom; although there is an "octet" of electrons $2s^2 2p\sigma^2 2p\pi^4$, like the L shell of Si, the four outer electrons (instead of being in 3s and 3p AO's as in the actual Si atom) are in orbitals with the forms of $3d\sigma$ and $3d\pi$ AO's, but greatly shrunken in size as compared to 3d AO's of a real Si atom.

Let us now consider what happens to the N, T, V, and Z states of ethylene when the molecule is twisted.²⁰ In the N state there are no electrons in the $1b_{2g}$ orbital, but on twisting the molecule by 90° we find that the $1b_{3u}$ and $1b_{2g}$ MO's have come together to form the 2e MO; although $1b_{3u}$ and $1b_{2g}$ are respectively strongly bonding and strongly antibonding in planar ethylene, they both become nonbonding for 90°

Table II
Orbital Correlations for the States of Ethylene^a

O_2 $D_{\infty h}$ (UM)	C_2H_4 D_2		D_{2d}	O_2 $D_{\infty h}$ (UM)	Si Semi-UA
$(1\pi_g)^2$	$(1b_{2g})^0$	$(2b_2)^0$	$(2e)^2$	$(1\pi_g)^2$	$(3d\pi)^2$
$(1\pi_u)^4$	$(1b_{3u})^2$	$(2b_3)^2$	$(1e)^4$	$(1\pi_u)^4$	$(2p\pi)^4$
$(3\sigma_g)^2$	$(3a_g)^2$	$(3a)^2$	$(3a_1)^2$	$(3\sigma_g)^2$	$(3d\sigma)^2$
$(2\sigma_u)^2$	$(1b_{2u})^2$	$(1b_1)^2$	$(2b_2)^2$	$(2\sigma_u)^2$	$(2p\sigma)^2$
$(2\sigma_g)^2$	$(2b_{1u})^2$	$(2b_1)^2$	$(2a_1)^2$	$(2\sigma_g)^2$	$(2s\sigma)^2$

^a The second, third, and fourth columns refer to planar, partly twisted, and 90° twisted ethylene, respectively. The first and fifth columns refer to the united molecule (O_2), and the sixth refers to the semi-united atom (Si).

twisted ethylene. Thus one part of the carbon-carbon double bond, the π bond, has apparently been abolished. However, in its place there is some marked hyperconjugation, so that twisted ethylene is not as unstable as one would otherwise have thought: what happens²⁰ is roughly that the orbital $2p_y + [1s(H_a) - 1s(H_b)]$ associated with one CH_2 group in the $1b_2$ member of the 1e MO mixes with the $2p_x$ orbital associated with the carbon atom of the other CH_2 group in the $1b_3$ member of 1e to give some C-C bonding; similarly $2p_x + [1s(H_a) - 1s(H_b)]$ of the other CH_2 group mixes with $2p_y$ of the first.

Now if, for planar ethylene, one electron is excited from the $1b_{3u}$ to the $1b_{2g}$ MO (π to π^*), the T state (species ${}^3B_{1u}$) or the V state (species ${}^1B_{1u}$) results. If two electrons are excited from π to π^* , the Z state (1A_g) results. Just as in H_2 there is considerable interaction between the MO configurations of the N and Z states, corresponding in valence bond terms to ionic-covalent resonance. On twisting the ethylene the N- and Z-state configurations mix more and more, until for 90° twisted ethylene they are fully mixed; the N^1A_g and Z^1A_g states have given rise to the 1A_1 and 1B_1 states of perpendicular ethylene, whose wave functions are each 50:50 mixtures of the wave functions for the N and Z states of planar ethylene. Thus, writing the part of the wave function associated with the π electrons as a Slater-type determinant,²⁰ the N and Z states of planar ethylene may be represented by

$$\Psi = N \begin{vmatrix} (x+x)\alpha(1) & (x+x)\alpha(2) \\ (x+x)\beta(1) & (x+x)\beta(2) \end{vmatrix} \quad N^1A_g$$

$$\Psi = N \begin{vmatrix} (x-x)\alpha(1) & (x-x)\alpha(2) \\ (x-x)\beta(1) & (x-x)\beta(2) \end{vmatrix} \quad Z^1A_g$$

where $(x \pm x)$ stands for $[2p\pi_x(a) \pm 2p\pi_x(b)]$. These functions both transform according to the representation A_g of the point group D_{2h} . For perpendicular ethylene the $(x+x)$ and $(x-x)$ orbitals become degenerate, and these functions do not transform according to any representation of the point group D_{2d} ; one has to take linear combinations (with equal absolute weights) to get the two pure states of perpendicular ethylene, N^1B_1 and Z^1A_1 .

$$\Psi = N \begin{vmatrix} (x+x)\alpha(1) & (x+x)\alpha(2) \\ (x+x)\beta(1) & (x+x)\beta(2) \end{vmatrix} \pm N \begin{vmatrix} (x-x)\alpha(1) & (x-x)\alpha(2) \\ (x-x)\beta(1) & (x-x)\beta(2) \end{vmatrix} \begin{cases} Z^1A_1 \\ N^1B_1 \end{cases}$$

(17) R. S. Mulliken and C. C. J. Roothaan, *Chem. Rev.*, **41**, 219 (1947).

(18) R. S. Mulliken, *Int. J. Quantum Chem.*, **1**, 103 (1967).

(19) S. Huzinaga, *Mem. Fac. Sci., Kyushu Univ.*, **3**, 57 (1963). (Reprinted in LMSS Technical Report, 1962-3, Part I.)

(20) R. S. Mulliken, *Phys. Rev.*, **43**, 279 (1933).

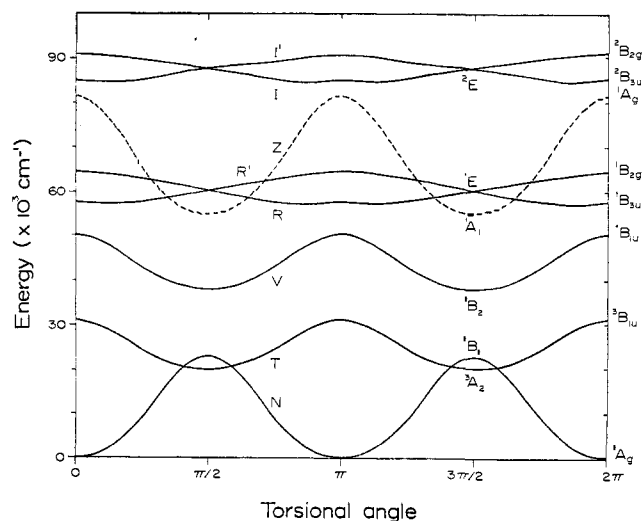


Figure 3. Potential energies of some important electronic states of ethylene as functions of the torsional angle (between the planes of the two CH_2 groups). The curves are drawn from the best available experimental data and are quantitatively correct (as far as can be achieved) for the states N, T, V, R, and I. The curves for states R' and I' are less accurate, and the curve for the unseen state Z represents only an estimate.

Table III

Correlation of the States of Planar and Perpendicular Ethylene with Those of the United Molecule, O_2

C_2H_4		O_2
D_{2h}	D_{2d}	$D_{\infty h}$ (UM)
$(1b_{2g})^2$ 1A_g (Z)	1A_1 (Z')	$(2e)^2$ $^1\Sigma_g^+$ $^1\Delta_g$ $^3\Sigma_g^-$
$(1b_{3u})(1b_{2g})$ $^1B_{1u}$ (V)	1B_2 (V)	
$(1b_{3u})(1b_{2g})$ $^3B_{1u}$ (T)	1B_1 (N')	
$(1b_{3u})^2$ 1A_g (N)	3A_2 (T)	
MIX		

At the same time the V state ($^1B_{1u}$) of planar ethylene goes smoothly over into the V state of perpendicular ethylene (1B_2), and the T state ($^3B_{1u}$) goes smoothly into the T state (3A_2), which for twisted ethylene should be the *lowest* state. These correlations are illustrated in Table III.

The correlation with the states of the lowest electron configuration of O_2 is also included in Table III. The configuration $(2e)^2$ of perpendicular ethylene becomes $(1\pi_g)^2$ of the O_2 molecule, and there is a simple correlation between the resulting electronic states: note how the degenerate $^1\Delta_g$ state of the O_2 molecule splits into the 1B_1 (N') and 1B_2 (V) states of perpendicular ethylene as the symmetry is lowered. Perpendicular ethylene is much more like oxygen than planar ethylene which, among other things, is diamagnetic and has a singlet ground state. Perpendicular ethylene, like oxygen, should have a triplet ground state.

Both planar and perpendicular ethylene molecules in their N or T states should dissociate into two CH_2 radicals in their $^3\Sigma_g^-$ ground states.²¹ This behavior parallels that of H_2 . The V and Z states of ethylene on dissociation should give CH_2 radicals in excited electronic states; although the V state behaves as if it should dissociate into CH_2^+ ($^2\Pi_u$, or $^2A_1 + ^2B_1$) +

CH_2^- ($^2\Pi_u$, or $^2B_1 + ^2A_1$), in fact it probably dissociates to CH_2 (\tilde{a}^1A_1) + CH_2 (\tilde{c}^1A_1) because of avoided crossings.

Figure 3 shows how the potential energies of the states N, T, V, and Z change with the angle of twisting. We have also included the first Rydberg state (R), the ground state of the C_2H_4^+ ion (I), and the states R' and I' which are the doubly excited states where one electron is in the $1b_{2g}$ MO rather than the $1b_{3u}$ MO. The curves shown in Figure 3 are *quantitatively* correct (except for the states R', I', and Z, for which experimental data are lacking) and have been drawn from the best available data; this figure therefore supersedes Figure 1 of ref 17. Both experimentally and theoretically it is clear that the equilibrium configuration of the normal state is planar, so that the potential energy must go up on twisting, and must have a maximum which (theoretically at least) is at the perpendicular configuration. Experimentally,^{22, 22a} the barrier to internal rotation in the N state may be taken as the activation energy for thermal *cis-trans* isomerization of CHDCHD, and is about 65 kcal/mole. On the other hand, for the T and V states, it is clear from the theory that, on twisting, the potential energy must go down, giving curves like those shown, which have minima for the perpendicular configuration. The reason for this situation²¹ is roughly that the energy differences between planar and perpendicular ethylene depend only on that part of the energy of formation of C_2H_4 which is provided by the interaction of the two $2p_x$ electrons of the two CH_2 groups. In *perpendicular* C_2H_4 this energy is small (hyperconjugation energy only), and the V^1B_2 state lies probably 1 eV or so above the N^1B_1 state only because of Coulomb repulsion in the configuration $(2e)^2$. In *planar* C_2H_4 in its ground state, $\dots (x + x)^2$, this energy is that of the π bond, which gives a stabilization energy of 2.8 eV. In excited planar C_2H_4 , $\dots (x + x)(x - x)$, we expect the antibonding effect of $(x - x)$ to exceed considerably the bonding effect of $(x + x)$, thus raising the energy by 2 eV or so above that for perpendicular ethylene. Walsh²³ considers the problem for the ground state as one of two opposing effects: a $\text{CH}_2\text{-CH}_2$ antibonding effect of the two electrons in the filled $1b_{3g}$ ($2p_y - 2p_y$) MO, which tends to twist the molecule, and an effect of electrons in the π MO which tends to keep the molecule planar. In the T or V state the first effect is predominant since there is only one π electron, and it is already more than outweighed by the π^* electron. The possibility that the $-\text{CH}_2$ groups themselves are nonplanar in the T and V states has also been considered by Walsh; arguing that the $1b_{2g}$ MO of C_2H_4 should have maximum binding energy when the H-C-H angle is 90° , like the π^* MO of formaldehyde, he has suggested that the arrangement of the bonds in the two CH_2 groups of excited C_2H_4 could be pyramidal, giving a structure like that of hydrazine. Calculations by Burnelle and Litt^{24, 25} have taken this possibility into account, though the results suggest that this distortion does not occur.^{25a}

The nonplanarity of the first Rydberg state of C_2H_4 and of the ground state of C_2H_4^+ in Figure 3 is surprising at first sight. One might suppose that, since the presence of two π electrons in the state N is responsible for keeping ethylene stable in the planar form, the removal of just one of these in

(22) J. E. Douglas, B. S. Rabinovitch, and F. S. Looney, *J. Chem. Phys.*, **23**, 315 (1955).

(22a) B. S. Rabinovitch and F. S. Looney, *ibid.*, **23**, 2439 (1955).

(23) A. D. Walsh, *J. Chem. Soc.*, 2325 (1953).

(24) L. Burnelle, *J. Chem. Phys.*, **43**, S29 (1965).

(25) L. Burnelle and C. Litt, *Mol. Phys.*, **9**, 433 (1965).

(25a) L. Burnelle, private communication.

(21) R. S. Mulliken, *Phys. Rev.*, **41**, 751 (1932).

$C_2H_4^+$ would still leave this ion planar, but perhaps halve the barrier to internal rotation. However, as we shall see, the interpretation of the spectra leaves no doubt that in the Rydberg state and the ionic state the molecule is nonplanar. (These two states are shown here with similar curves, as is expected because the presence of an electron in the large MO of the Rydberg state should not affect the geometry very much.) This result was predicted for the $C_2H_4^+$ ion by Roothaan^{17,26} in 1947 on the basis of calculations made by an extension of the Hückel method, which gives useful results for ground states. The results of his calculations for the ground states of C_2H_4 and $C_2H_4^+$ using three different sets of empirical parameters²⁶ are shown in Figure 4. The full-line curves correspond to what are the most reasonable parameters as judged by calculations on other molecules. For the ion (state I) there is a maximum at 90° as expected,^{26a} but the stable form is not the planar form; the energy is a minimum for a twist of about $\pm 30^\circ$. Thus this early calculation gives good reason to think that the ethylene ion and the Rydberg state (which should have a similar configuration) would have equilibrium configurations which are slightly twisted. For state N the calculated energy maximum of about 3 eV at 90° twist agrees quite well with the experimental value.²² Robin, Hart, and Kuebler¹⁴ have also calculated that the R state should be twisted by about 30° , and Lorquet and Lorquet²⁷ have reached a similar conclusion for the positive ion in a recent theoretical computation.

The reason for the twisting of the R and I states at equilibrium is in terms of a mixing, on twisting, of the MO's $1b_{2u}$ and $1b_{2g}$, and of the MO's $1b_{3g}$ and $1b_{3u}$, of planar ethylene. These respective MO's become $1b_2$ and $2b_2$, and $1b_3$, $2b_3$ in twisted ethylene, and at 90° of twist, $1b_2$ and $1b_3$ become degenerate as $1e$, and $2b_2$ and $2b_3$ as $2e$ (see Figure 2). This mixing results in MO's of the forms $a[\alpha(2p_y)_A + \beta(1s_1 - 1s_2)] + b(2p_x)_B$ and $a[\alpha(2p_y)_B + \beta(1s_3 - 1s_4)] + b(2p_x)_A$ for $1e$, and $a(2p_x)_B - b[\alpha(2p_y)_A + \beta(1s_1 - 1s_2)]$ and $a(2p_x)_A - b[\alpha(2p_y)_B + \beta(1s_3 - 1s_4)]$ for $2e$, where $1s_1$ and $1s_2$, $1s_3$ and $1s_4$, are AO's of the H atoms attached respectively to the two carbon atoms (A and B), and where $a > b$; α and β have unequal values which are such that each of the expressions in brackets is normalized.²⁰ As a result, the four electrons in $1e$ contribute a very appreciable amount of C-C bonding which outweighs the corresponding antibonding of the *two* electrons in $2e$. (If a were equal to b , and the $1s_H$ terms were absent, the $1e$ and $2e$ MO's would be just like the π and π^* MO's of the oxygen molecule.) This net C-C bonding effect in the e -type MO's for 90° twisted ethylene may be described as isovalent hyperconjugation.²⁶ Roothaan's 1947 calculations²⁶ took this into account. It appears that the occurrence of minima away from the planar configuration can then be described as resulting from *incipient* isovalent hyperconjugation.

The simplest instance of hyperconjugation is the mild delocalization that occurs when a CH_2 or CH_3 group is conjugated to a multiple bond²⁸ as, for example, in ethylene or propylene. This type of weak hyperconjugation is called *sacrificial* hyperconjugation, and is illustrated in Figure 5 for ethylene and propylene. Two resonance structures for each molecule are shown, using a valence bond type of descrip-

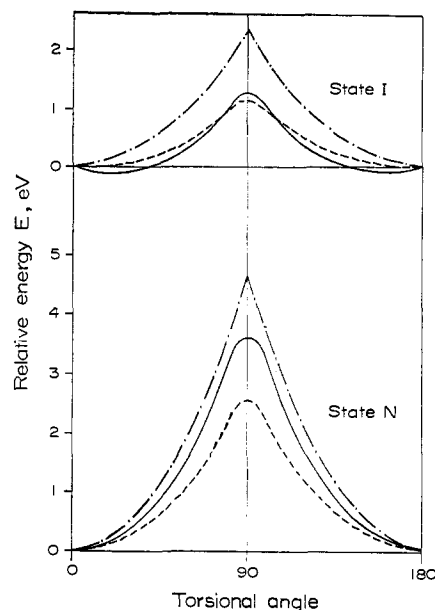


Figure 4. Hückel-method theoretically computed orbital energies (in eV) of the ground states of C_2H_4 (below) and $C_2H_4^+$ (above), as functions of the torsional angle. Full-line curves are for what are believed to be the best parameter values used ($\beta^* = 2\beta$, $\delta = 0$, $\beta = -3$ eV); dot-dash curves are for the case of *no* hyperconjugation; dashed curves are for $\beta^* = 1.5\beta$, $\delta = \beta$, $\beta = -3$ eV (from unpublished work of Mulliken and Roothaan (see ref 26)).

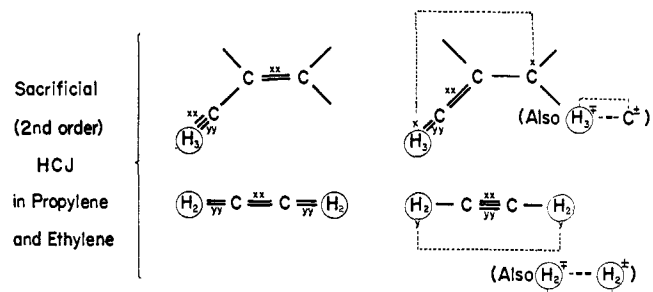


Figure 5. Resonance structures in hyperconjugation (z axes along σ or quasi- σ bonds; for π or quasi- π bonds x axes are perpendicular to plane, y axes in plane).

tion:^{28a} on the left the principal structure, on the right the modified structure whose presence in small amount accounts for sacrificial hyperconjugation. Each H_2 or H_3 group is treated as if it were an atom forming two or three bonds, respectively: H_2 forms the the equivalent of a double bond consisting of σ and π_x bonds, and H_3 forms the equivalent of a triple bond consisting of σ , π_x , and π_y bonds. In Figure 5 the letters x and y refer to π_x and π_y AO's, or to the equivalent hyperconjugation π_x and π_y MO's; a pair of symbols such as xx or yy refers to a π electron-pair bond or to the hyperconjugation equivalent of a π bond. Only a formal "long bond" is present in the sacrificial structures, between odd electrons some distance apart.

Figure 6 shows the different, stronger, kind of hyperconjugation present in perpendicular C_2H_4 and $C_2H_4^+$, called

(26) See R. S. Mulliken, *Tetrahedron*, 5, 253 (1959).

(26a) However, this maximum should *not* be flat as shown in the full-line curve in Figure 4 but should have a *cusp* as in the dot-dash curve, as shown in Figure 3. This requirement was first pointed out by Kaldor and Shavitt.¹⁶

(27) A. J. Lorquet and J. C. Lorquet, *J. Chem. Phys.*, 49, 4955 (1968).

(28) R. S. Mulliken, *J. Chem. Phys.*, 7, 339 (1939).

(28a) For descriptive purposes, the use of valence bond resonance structures is a helpful alternative to the otherwise preferable MO formulation, used above for the $1s$ and $2e$ MO's.

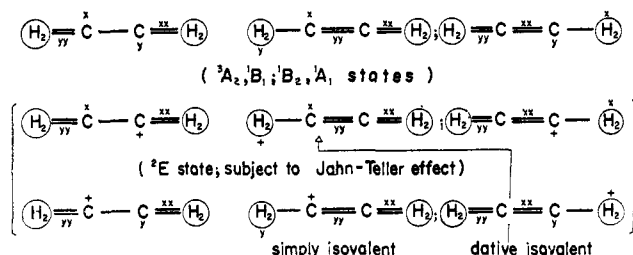


Figure 6. Isovalent (first order) hyperconjugation in *perpendicular* C_2H_4 and $C_2H_4^+$.

isovalent hyperconjugation. The principal structure for C_2H_4 (upper left) is supplemented and considerably stabilized by two isovalent resonance structures (that is, structures where there is *no* sacrifice in the total number of effective bonds). Mulliken has estimated the stabilization energy as almost 1 eV, but we may look forward to seeing before long what a machine calculation will give for this quantity. The structure for $C_2H_4^+$ (lower two lines) is similar, except that there is a twofold degeneracy since the $1b_{3u}$ and $1b_{2g}$ MO's have come together to form an e MO, and the single e electron now gives a 2E electronic state. The degeneracy must in principle be removed by a Jahn-Teller distortion, but this point will be discussed later.

IV. The N State (\dot{X}^1A_g) of Ethylene

We come now to a description of the various electronic states and transitions of ethylene, and will begin with a discussion of some relevant details of the ground state.

Ethylene of course has no microwave spectrum since it has a center of symmetry; however, its structure has been accurately determined by high-resolution infrared²⁹⁻³¹ and Raman³² spectroscopy, and by electron diffraction.³³ The infrared and Raman results give the structure

$$\begin{aligned} r_0(C-C) &= 1.338 \pm 0.003 \text{ \AA} \\ r_0(H-H) &= 1.086 \pm 0.002 \text{ \AA} \\ \angle CCH &= 121.3 \pm 0.5^\circ \end{aligned}$$

for the zero-point level, though Kuchitsu,³⁴ averaging the electron diffraction and spectroscopic data, obtains a slightly shorter C-C bond (1.335 Å) and longer C-H bonds (1.090 Å). The symmetrical structure of the molecule is nicely confirmed by the intensity alternations observed in the rotational structures of the infrared bands, which arise from the nuclear spins of the equivalent hydrogen atoms.^{30, 31}

The fundamental vibrations of C_2H_4 and C_2D_4 have been extensively studied by infrared^{29-31, 35-38} and Raman³⁹⁻⁴²

(29) W. S. Gallaway and E. F. Barker, *J. Chem. Phys.*, **10**, 88 (1942).

(30) H. C. Allen and E. K. Plyler, *J. Am. Chem. Soc.*, **80**, 2675 (1958).

(31) W. L. Smith and I. M. Mills, *J. Chem. Phys.*, **40**, 2095 (1964).

(32) J. M. Dowling and B. P. Stoicheff, *Can. J. Phys.*, **37**, 703 (1959).

(33) L. S. Bartell, E. A. Roth, C. D. Hollowell, K. Kuchitsu, and J. E. Young, *J. Chem. Phys.*, **42**, 2683 (1965).

(34) K. Kuchitsu, *ibid.*, **44**, 906 (1966).

(35) R. L. Arnett and B. L. Crawford, *ibid.*, **18**, 118 (1950).

(36) B. L. Crawford, J. E. Lancaster, and R. Inskeep, *ibid.*, **21**, 678 (1953).

(37) D. A. Dows, *ibid.*, **36**, 2833 (1962).

(38) M. E. Jacox, *ibid.*, **36**, 140 (1962).

(39) D. H. Rank, E. R. Schull, and D. W. E. Axford, *ibid.*, **18**, 116 (1950).

(40) B. P. Stoicheff, *ibid.*, **21**, 755 (1953).

(41) J. Romanko, T. Feldman, E. J. Stansbury, and A. McKellar, *Can. J. Phys.*, **32**, 735 (1954).

(42) T. Feldman, J. Romanko, and H. L. Welsh, *ibid.*, **34**, 737 (1956).

Table IV
Ground-State Vibration Frequencies
(cm^{-1}) of C_2H_4 and C_2D_4 ^a

			C_2H_4	C_2D_4
a_g	ν_1	C-H stretch	3026.4	2251
	ν_2	C-C stretch	1622.9	1515
	ν_3	\angle HCH bend	1342.2	981
a_u	ν_4	Torsion	1023	(726)
	b_{1u}	ν_5	C-H stretch	2988.7
ν_6		\angle HCH bend	1443.5	1077.9
b_{2g}	ν_7	CH_2 wagging	943	(780)
	b_{2u}	ν_8	C-H stretch	3105.5
ν_9		CH_2 rocking	826.0	(593)
b_{3g}	ν_{10}	C-H stretch	3102.5	2304
	ν_{11}	CH_2 rocking	(1222)	(1006)
b_{3u}	ν_{12}	CH_2 wagging	949.3	720.0

^a The g vibrations are Raman active, and the u vibrations infrared active, except ν_4 (a_u), which is inactive. Values in parentheses are calculated, or doubtful experimental, values.

spectroscopy. The currently accepted values of the vibration frequencies of these molecules are given in Table IV. The assignment of the vibrations has been complicated by the presence of strong Coriolis (vibration-rotation) interaction between the fundamentals ν_9 and ν_{12} of C_2H_4 , and the comparative weakness of some of the bands; further work on C_2D_4 is still needed. From the point of view of the electronic spectrum, the important frequencies are the C-C stretching frequency, ν_2 , and the twisting frequency, ν_4 . The twisting vibration is inactive according to the selection rules,⁴³ and therefore cannot be directly observed in gas-phase infrared or Raman spectra of C_2H_4 and C_2D_4 . In partially deuterated isotopic molecules with lower symmetry it is not forbidden by the selection rules, and Arnett and Crawford³⁵ were able to calculate the frequencies for C_2H_4 and C_2D_4 using the theoretical relations between the frequencies of isotopic molecules. These values have been confirmed by the absorption spectrum of matrix-isolated ethylene,^{37, 38} for which the matrix environment relaxes the strict selection rules. Another value of ν_4 was derived by Smith and Mills,³¹ from an analysis of the Coriolis interactions affecting the fundamental ν_9 in C_2H_4 .

An interesting conclusion³⁷ is that the potential function for the twisting motion cannot be exactly sinusoidal: according to the relation⁴³ $\omega = 4\sqrt{V_0A}$ between the twisting frequency, ω , the rotational constant, A , and the height of the internal rotation barrier, V_0 , for a sinusoidal function, the observed frequency of 1023 cm^{-1} in C_2H_4 would correspond to a barrier of 14,000 cm^{-1} (40 kcal), which is considerably lower than the experimental value^{22, 44} of 65 kcal. In part this is because the C-C bond in 90° twisted ethylene must be longer than in planar ethylene since the π bond has been largely abolished (as we saw in the last section). Therefore, in order to twist the molecule energy must also be supplied to stretch the C-C bond. This is equivalent to saying that there is a strong coupling between the twisting and the stretching motions: it has the effect of reducing the spacing of the twisting levels, so that, according to the relation above, the barrier to internal rotation is apparently lower. However, the results of this cou-

(43) G. Herzberg, "Infra-red and Raman Spectra," D. Van Nostrand Co., Inc., Princeton, N. J., 1945.

(44) A. Lifshitz, S. H. Bauer, and E. L. Resler, Jr., *J. Chem. Phys.*, **38**, 2056 (1963).

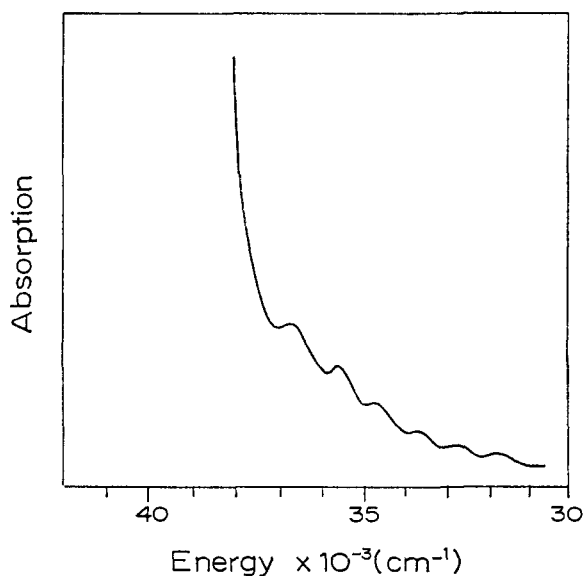


Figure 7. Densitometer trace from a photographic plate of part of the T-N system of C_2H_4 ; 1.4 m of liquid at 120°K (C. Reid, *J. Chem. Phys.*, **18**, 1299 (1950)).

pling cannot account for the entire difference, and one must assume that the barrier is not exactly sinusoidal.

The height of the ground-state barrier to internal rotation is of interest in studies of thermal *cis-trans* isomerization in the gas phase. Originally, Magee, Shand, and Eyring⁴⁵ considered two mechanisms for thermal isomerization in order to account for the experimental results. In their first mechanism, isomerization occurs as the molecule surmounts the *ground-state* potential barrier, without change of electronic state. In the second mechanism isomerization occurs *via* the T-state potential surface, with a lower activation energy; as can be seen in Figure 3 this mechanism is possible if there is interaction between the potential surfaces of the N and T states where they cross. However, recent studies^{22, 44, 46-51} have shown that the singlet mechanism is the only important thermal mechanism for pure simple olefins in the gas phase, though isomerizations with low activation energy can occur under certain circumstances in solution. On the other hand, the triplet mechanism is important for catalytic and photosensitized *cis-trans* isomerizations; these will be discussed in the next section.

V. The $V(\tilde{A}^1B_2)$ and $T(a^3A_2)$ States

The first ultraviolet absorption of ethylene is an exceedingly weak progression of diffuse bands in the region 2700–3500 Å, which was discovered in 1950 by Reid,⁵² using a 1.4-m path of liquid ethylene. Reid's spectrum is shown in Figure 7. The

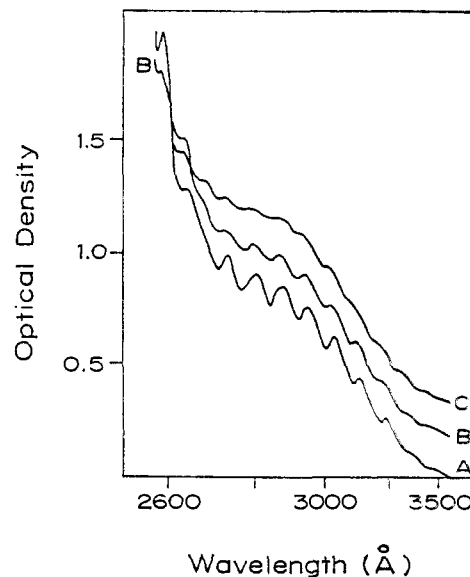


Figure 8. Absorption spectrum of 50 atm of ethylene + 25 atm of oxygen: (A) C_2H_4 , (B) *trans*-CHDCHD, (C) C_2D_4 . The optical density scale is shifted for (B) and (C) (D. F. Evans, *J. Chem. Soc.*, 1735 (1960)).

same bands were later observed in the gas phase by Evans,⁵³ using the technique of intensification by added oxygen. Evans boldly put 50 atm of ethylene (C_2H_4 , *trans*- $C_2H_2D_2$, or C_2D_4) in a cell with 25 atm of O_2 . The apparatus subsequently blew up, but luckily not before he had obtained the spectra shown in Figure 8.

This system of bands may be identified as T-N bands, that is, representing the transition from the ground state to the first triplet state $T(^3A_2)$ of ethylene. The intervals in the band progression are about 990 cm^{-1} and appear to change very little on deuteration; thus it would seem that the bands may represent a progression in the upper-state C-C stretching vibration ν_2 . According to the rule $r_0^{2-88}\omega_0 = \text{constant}$ (which fits the $B^3\Sigma_u^-$ and $X^3\Sigma_g^-$ states of O_2), the observed frequency implies⁵⁴ a C-C bond length of about 1.58 Å. However, as we shall see when we discuss the V-N system, the bands are probably composite, each consisting of overlapping stretching and twisting bands. Since the T state is expected to have a perpendicular equilibrium configuration, the observed bands are probably just the strongest bands of an extensive system. The remaining bands would then be too weak to be seen, being doubly forbidden on account of the spin selection rule and the unfavorable Franck-Condon factors.

This is unfortunate, because the position of the (0,0) band would have given the energy of the T-state potential minimum, which is an important quantity in consideration of catalytic and photosensitized *cis-trans* isomerizations. It appeared at first that the triplet mechanism (with electron spin as the essential factor) is the only important mechanism in catalytic isomerizations, where, for example, halogen atoms and the ground-state triplet molecules O_2 , S_2 , and Se_2 are very effective catalysts, and also nitric oxide has a very pronounced effect on the isomerizations of *trans*-dideuterioethylene^{22a} and butene-2.⁵⁰ Taking the case of oxygen, the reasoning is that O_2

(45) J. L. Magee, W. Shand, Jr., and H. Eyring, *J. Am. Chem. Soc.*, **63**, 677 (1941).

(46) B. S. Rabinovitch and M. J. Hulatt, *J. Chem. Phys.*, **27**, 592 (1957).

(47) W. F. Anderson, J. A. Bell, J. M. Diamond, and K. R. Wilson *J. Am. Chem. Soc.*, **80**, 2384 (1958).

(48) B. S. Rabinovitch and K. W. Michel, *ibid.*, **81**, 5065 (1959).

(49) C. Steel, *J. Phys. Chem.*, **64**, 1588 (1960).

(50) R. B. Cundall and T. F. Palmer, *Trans. Faraday Soc.*, **57**, 1936 (1961).

(51) R. B. Cundall, *Progr. Reaction Kinetics*, **2**, 167 (1964).

(52) C. Reid, *J. Chem. Phys.*, **18**, 1299 (1950).

(53) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

(54) P. G. Wilkinson and R. S. Mulliken, *J. Chem. Phys.*, **23**, 1895 (1955).

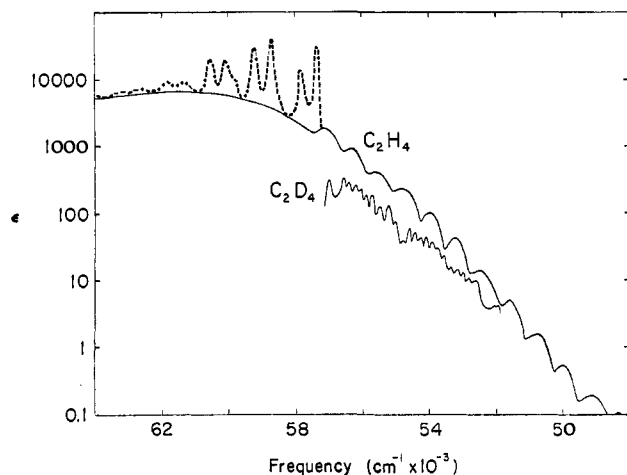


Figure 9. Absorption coefficients for C_2H_4 and C_2D_4 from 1550 to 2050 Å. The dashed and solid curves correspond to the R–N and V–N transitions, respectively (P. G. Wilkinson and R. S. Mulliken, *J. Chem. Phys.*, **23**, 1895 (1955)).

plus singlet ethylene represents a triplet state, which should be able to go over easily to the triplet state derived from O_2 plus triplet ethylene. In photosensitized isomerizations a sensitizing molecule which has been excited to its lowest triplet state (by light absorption to a singlet state and subsequent internal conversion) causes the isomerization; this is presumably just another instance of the same effect. However, in the case of catalysis by NO the activation energy drops to 27.5 kcal/mole, and it appears that the isomerization must occur *via* a chemical intermediate. Hence the triplet mechanism is suspect in the catalytic cases, but there seems no reason to doubt it in the case of photosensitized isomerizations.

Much of the early experimental work on *cis-trans* isomerization seems to be suspect.⁵¹ Thus, Kistiakowsky and Smith's value⁵⁵ of 0.8–0.9 eV for the activation energy for the *cis-trans* isomerization of butene-2, which is frequently quoted for the difference between the minima of the T and N states, has not been substantiated by later work. Similarly, Eyring's^{45,56,57} value of 1.0–1.2 eV (from the activation energy of the triplet mechanism of thermal *cis-trans* isomerization) was obtained from large conjugated molecules where the reaction may be quite different from that in simple olefins. Recent evidence suggests⁵¹ that the triplet states of simple olefins may actually lie as much as 60 kcal/mole above the (planar) ground states, that is, close to the tops of the potential barriers of the ground states. For example, photosensitized isomerization of butene-2 occurs only if the photosensitizing species has a triplet energy in excess of 65 kcal/mole:^{58,59} styrene and biacetyl (with triplet energies of 62 and 56 kcal/mole, respectively) do not cause isomerization. With 3-methylpentene-2, the $\pi^* \leftarrow n$ triplet states of benzaldehyde and benzophenone (71.5 and 68.0 kcal/mole, respectively) are very efficient in causing isomerization, while the $\pi^* \leftarrow \pi$ triplet state of triphenylene (66.5 kcal/mole) is completely ineffective.^{59a} However, the authors of ref 59a

suggest that the effectiveness of the former in overcoming the severe Franck–Condon inhibition toward converting planar into twisted ethylene is due to a strong polarizing action of the $\pi^* \leftarrow n$ state with its partially vacant n orbital, an action which cannot occur with the $\pi^* \leftarrow n$ triplet state of triphenylene. Thus an energy less than 66 kcal/mole for the 90° twisted olefin may still be possible. Applying these considerations to butene-2, the ineffectiveness of the $\pi^* \leftarrow \pi$ triplet state of styrene as a photosensitizer with butene-2 may not exclude an olefin triplet energy lower than 62 kcal/mole, while the ineffectiveness of the $\pi^* \leftarrow n$ triplet state of biacetyl probably does indicate that the triplet state of butene-2 is higher than 56 kcal/mole. Further evidence is the fact⁵⁰ that the $\pi^* \leftarrow \pi$ benzene triplet state at 84 kcal/mole photosensitizes *cis-trans* isomerization. As suggested by N. C. Yang in conversation, the energy is so high here that the olefin could still be nearly planar during the energy transfer, thus not encountering a severe Franck–Condon inhibition.

In the spectrum of ethylene the separation of the (0,0) band and the strongest band of the T–N system should be a little less than the corresponding separation in the V–N system, since the C–C bond length is not as great in the T state of planar ethylene as it must be in the V state. With the assumption that the barriers to internal rotation in the T and V states are similar, the spectroscopic evidence suggests that the (0,0) band of the T–N system may lie somewhere near 20,000 cm^{-1} (~ 57 kcal/mole). If the $-CH_2$ groups themselves are nonplanar, the (0,0) band may lie even lower than this.

Comparison of Figures 7 and 8 shows the considerable intensification of the T–N bands by O_2 . Reid⁵² used 250 times as great an absorbing path of ethylene as Evans,⁵³ yet the spectra look much alike. In connection with Reid's Figure 7, one may wonder⁵³ if the presence of small amounts of oxygen from exposure to air could have caused the appearance of the T–N bands there.

The steeply rising absorption near 2650 Å in these T–N spectra is apparently^{59b} the beginning of the V–N system.^{54,60–62} Figure 9 shows a tracing of this system as observed at lower pressures in the gas phase;⁵⁴ it consists of a long progression of broad diffuse bands, starting⁶⁶ at 2150 Å, and rising rapidly in intensity with decreasing wavelength. In C_2H_4 the banded region at the long wavelength end of the transition appears to consist of a single rather irregular progression of bands spaced about 800 cm^{-1} apart, but in C_2D_4 the spectrum is much more complicated. At 1744 Å the V–N bands disappear under the intense bands of the first Rydberg transition, but the V–N system obviously continues, and finally reaches a broad flat maximum⁶⁴ at about 1620 Å. At yet shorter wavelengths the absorption decreases fairly steadily, down to the next strong Rydberg transition^{63,67} which begins at 1393 Å.

(59a) N. C. Yang, J. I. Cohen, and A. Shani, *J. Am. Chem. Soc.*, **90**, 3264 (1968).

(59b) It is not clear why this steeply rising absorption should occur at almost the same wavelength in the two spectra. It seems probable that in Evans' spectrum this absorption is after all not the beginning of the V–N system, but rather represents a contact charge-transfer system involving C_2H_4 and O_2 , since it is far stronger than expected for the V–N system at this wavelength.

(60) J. Stark and P. Lipp, *Z. Physik. Chem.*, **86**, 36 (1913).

(61) G. Scheibe and H. Grieneisen, *ibid.*, **25B**, 52 (1934).

(62) C. P. Snow and C. B. Allsopp, *Trans. Faraday Soc.*, **30**, 93 (1934).

(63) W. C. Price, *Phys. Rev.*, **47**, 444 (1935); W. C. Price and W. T. Tuttle, *Proc. Roy. Soc. (London)*, **A174**, 207 (1940).

(64) M. Zelikoff and K. Watanabe, *J. Opt. Soc. Am.*, **43**, 756 (1953).

(65) L. C. Jones, Jr., and L. W. Taylor, *Anal. Chem.*, **27**, 228 (1955).

(66) R. McDiarmid and E. Charney, *J. Chem. Phys.*, **47**, 1517 (1967); R. McDiarmid, *ibid.*, **50**, 2328 (1969).

(55) G. B. Kistiakowsky and W. R. Smith, *J. Am. Chem. Soc.*, **58**, 766 (1936).

(56) R. A. Harman and H. Eyring, *J. Chem. Phys.*, **10**, 557 (1942).

(57) H. M. Hulbert, R. A. Harman, A. V. Tobolsky, and H. Eyring, *Ann. N. Y. Acad. Sci.*, **44**, 371 (1943).

(58) R. B. Cundall, F. J. Fletcher, and D. G. Milne, *J. Chem. Phys.*, **39**, 3536 (1963).

(59) R. B. Cundall, F. J. Fletcher, and D. G. Milne, *Trans. Faraday Soc.*, **60**, 1146 (1964).

In general, V-N transitions are expected theoretically and known experimentally to be of high intensity.^{67a} In agreement with this rule, the oscillator strength f for the V-N transition of ethylene⁶⁴ is about 0.34. The superimposed Rydberg bands are also rather intense (total f perhaps about 0.04).

Although Snow and Allsopp assert⁶² that there is a distinct shoulder in the V-N absorption curve near 2100 Å, which might be a triplet-singlet transition, this shoulder has not been confirmed by later work, either in the gas phase^{63,64,66} or in single crystals of ethylene,⁶⁸ so that it must be ascribed to impurities in the ethylene sample they used. Unfortunately, early electron-impact spectra of ethylene showed a peak in this region⁶⁹⁻⁷¹ at 6.5 eV (1940 Å), which has led to some speculation: again, this peak has not been confirmed by later work⁷²⁻⁷⁸ and seems to have been caused by "some unusual experimental circumstances."¹⁶ We must conclude that there is definitely no evidence for any other transition of ethylene in the region near 2000 Å except the V-N transition, even though other predicted (very weak) transitions remain to be found, as we shall see.

The vibrational analysis of the V-N system is a problem which has not been solved yet. However, the qualitative approach that should be taken is clear from the theory. As we have already said, there should be strong isovalent hyperconjugation²⁶ in the T and V states of 90° twisted ethylene, which should tend to reduce the C-C bond length considerably below that expected for a trigonal-trigonal σ bond. This last quantity must be about 1.50 Å, so that we may expect perhaps 1.44 Å for the resulting C-C bond length in the V state of perpendicular ethylene. On the other hand, this hyperconjugation cannot occur in the V state of planar ethylene: we now have an antibonding and a bonding π electron, and it is known that in such cases the antibonding effect predominates, so that the equilibrium C-C bond length should be much greater than in the ground state. The left-hand side of Table II tells us that there must be a close analogy between the V-N system of planar ethylene and the Schumann-Runge ($B^3\Sigma_u^- - X^3\Sigma_g^-$) system⁷⁹ of O₂, since the electron configuration of planar ethylene, $\dots(1b_{3u})(1b_{2g})$, becomes the configuration $\dots(1\pi_u)^3(1\pi_g)^8$ of the united molecule, O₂, and this gives rise to the $B^3\Sigma_u^-$ state. In the Schumann-Runge bands of O₂ the bond length increases⁷⁹ from 1.207 Å in the ground state to 1.604 Å, so that we can expect the C-C bond length in the V state of planar ethylene to have increased^{79a} to perhaps 1.80 Å. But of course we cannot get away from the twisting,

since it is clear from the theory that the V state has a potential minimum for the perpendicular configuration. It now appears that the strongest vibrational bands according to the Franck-Condon principle should go to upper state levels lying at the top of the barrier to internal rotation (where the wave function of the twisting motion has largest amplitude at the planar configuration), but within addition so many quanta of the C-C stretching vibration excited that the C-C bond length at the turning point of this vibration is the same as in the ground state. The (0,0) band, in contrast, would correspond to a 90° twisted upper state with the C-C bond only a little longer than in the ground state. We thus expect a relation between the stretching vibration, ν_2' , and the twisting vibration, ν_4' , such that the strongest band in the spectrum associated with a given torsional level ν_4' , has relatively few quanta of ν_2 excited if ν_4 is small, but many quanta of ν_2 if ν_4 is large.

As in the ground state, we do not expect the vibrational energy levels to behave as if the barrier to internal rotation were sinusoidal, since when we twist the molecule from perpendicular to planar, we have to stretch the C-C bond from about 1.44 to about 1.80 Å. This must again result in a coupling of the twisting and stretching motions, changing the apparent shape of the barrier to internal rotation.

With the aid of a computer it is possible to calculate the Franck-Condon overlap integrals of all the bands, and hence predict the detailed appearance of the V-N transition. It now appears that the analysis of the V-N system given by Wilkinson and Mulliken⁵⁴ cannot be right: they have assigned the long progression of bands in terms of the C-C stretching vibration only, but calculations show that the twisting vibration must figure prominently in the spectrum as well.⁸⁰ Quite recently McDiarmid and Charney⁶⁶ have studied the spectra of C₂H₄ and C₂D₄ at -78° and have shown that an interval between bands of about 550 cm⁻¹ is prominent in the C₂D₄ spectrum. The spacing of the bands in the C₂H₄ spectrum is about 800 cm⁻¹, so that the isotope ratio of these frequencies, 1.45:1, is very close to the ratio, $\sqrt{2}$:1, expected for the twisting frequency. However, their vibrational analysis places all the prominent bands in a single regular twisting progression for each isotope. We cannot accept this, for one thing because the observed progressions are not really very regular (the intervals for C₂H₄ varying from 696 to 958 cm⁻¹ according to their results), also because the potential function they derive from the seeming regularity of the progressions has cusps at the planar configuration, which is a highly unlikely situation, and finally, because they have neglected the expected pronounced stretching of the C-C bond.

The answer probably lies somewhere between these two interpretations,^{80a} since Merer, Mulliken, and Watson⁸⁰ have been able to reproduce many features of the spectra using a simple model of coupled twisting and stretching. In particular, this model suggests the reason for the observed difference between the simple C₂H₄ spectrum and the complex C₂D₄ spectrum: the C₂H₄ "bands" each consist of a number of overlapping bands with the same value of $\nu_2' + \nu_4'$, because the twisting and stretching frequencies are similar, but this overlapping effect does not occur for C₂D₄ since the twisting frequency drops sharply on deuteration. The calculations also

(67) P. G. Wilkinson, *Can. J. Phys.*, **34**, 643 (1956).

(67a) R. S. Mulliken, *J. Chem. Phys.*, **7**, 20 (1939).

(68) A. Lubezky and R. Kopelman, *ibid.*, **45**, 2526 (1966).

(69) A. Kuppermann and L. M. Raff, *ibid.*, **37**, 2497 (1962).

(70) A. Kuppermann and L. M. Raff, *Discussions Faraday Soc.*, **35**, 30 (1963).

(71) A. Kuppermann and L. M. Raff, *J. Chem. Phys.*, **39**, 1607 (1963).

(72) J. A. Simpson and S. R. Mielczarek, *ibid.*, **39**, 1606 (1963).

(73) E. N. Lassetre and S. A. Francis, *ibid.*, **40**, 1208 (1964).

(74) C. P. Bowman and W. D. Miller, *ibid.*, **42**, 681 (1965).

(75) J. Geiger and K. Wittmaack, *Z. Naturforsch.*, **20A**, 628 (1965).

(76) K. J. Ross and E. N. Lassetre, *J. Chem. Phys.*, **44**, 4633 (1966).

(77) J. P. Doering, *ibid.*, **46**, 1194 (1967).

(78) J. P. Doering and A. J. Williams, *ibid.*, **47**, 4180 (1967).

(79) G. Herzberg, "Spectra of Diatomic Molecules," 2nd ed, D. Van Nostrand Co., Inc., Princeton, N. J., 1950.

(79a) G. H. Kirby and K. Miller, *Chem. Phys. Letters*, in press, have made calculations of the orbital energies by the CNDO method, and do not confirm the large change of C-C bond length with twisting angle in the V state. We find this rather surprising, since a bonding π electron has been excited to an antibonding π^* MO in the V state of planar ethylene, and in other molecules it is known that considerable changes of bond length occur in the corresponding transitions.

(80) A. J. Merer, R. S. Mulliken, and J. K. G. Watson, 1969, to be published.

(80a) A recent suggestion by J. F. Ogilvie, *J. Chem. Phys.*, **49**, 474 (1968), that the structure is due to excitation of the CH₂ wagging vibration ν_{12}' (i.e., disregarding both the stretching of the C-C bond, and the twisting) cannot be taken seriously.

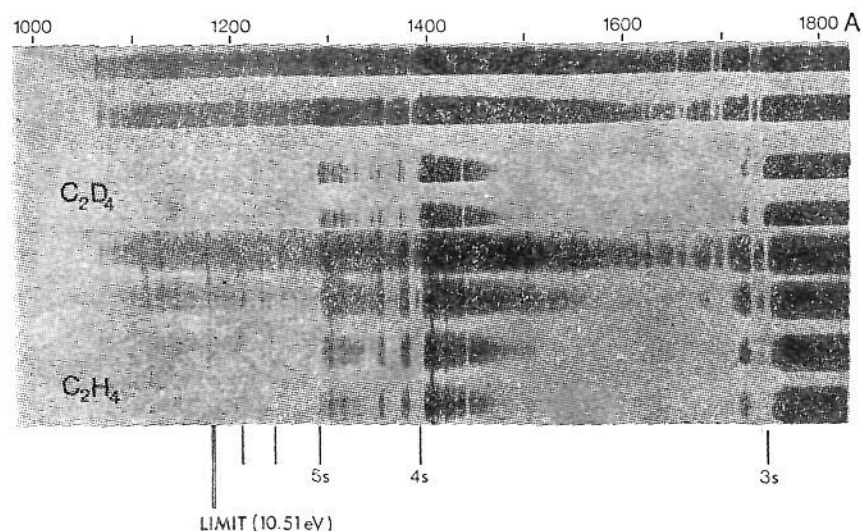


Figure 10. Absorption spectra of C_2H_4 and C_2D_4 in the region from 1000 to 1800 Å at various gas pressure (W. C. Price and W. T. Tutte *Proc. Roy. Soc. (London)*, A174, 207 (1940)).

show that the strongest bands of the transition must be more than 10^{12} times as intense as the (0,0) band.

Although a definitive vibrational analysis of the V–N system has not been achieved yet, it seems likely that the (0,0) band lies near 2650 Å ($38,500\text{ cm}^{-1}$), and that the barrier to internal rotation in the V^1B_2 upper state is $16,000 \pm 3000\text{ cm}^{-1}$ ($46 \pm 9\text{ kcal}$).⁸⁰ The Franck–Condon maximum of the transition lies at 1620 Å ($61,730\text{ cm}^{-1}$). There is no direct evidence in the spectrum for the direction of polarization of the transition because the bands are very diffuse and exhibit no rotational structure; however, on theoretical grounds the bands must be type A (parallel) bands.

Beyond the Franck–Condon maximum the V–N transition does not have banded structure, and one is led to ask what happens when radiation is absorbed in the transition to the V state of ethylene at frequencies high enough to permit dissociation into two CH_2 radicals. Here spontaneous twisting competes with dissociation, but also Franck–Condon factors are involved because the H–C–H angle in the CH_2 groups of ethylene must change in going to the product states of the CH_2 radical. Just what happens is a very interesting question about which no one knows much, although we do know that the somewhat analogous photodissociation of O_2 gives one oxygen atom in the 3P state and one in the 1D state. Experimentally it is known^{81–83} that photolysis of ethylene with radiation in the vacuum ultraviolet causes elimination of H_2 and the formation of acetylene. The reactions occurring⁸³ are probably quite complex, since more acetylene than H_2 is formed, and considerable amounts of *n*-butane also occur. Evidence from the photolysis of partially deuterated ethylenes indicates that terminal elimination of hydrogen (producing CCH_2 radicals, which then rearrange to give C_2H_2) is an important process predominating over 1,2 elimination. It seems that any H atoms formed are scavenged by C_2H_4 to form C_2H_5 radicals, which disappear by association to give *n*-butane. Another reaction path involving very short-lived excited C_2H_3 radicals must also be invoked⁸¹ in order to account for the excess of acetylene formed.

The formation of some H_2 and D_2 in the photolysis of *trans*-CHDCHD is evidence⁸² that the excited state of the ethylene

molecule is capable of free internal rotation, since both terminal and 1,2 elimination would otherwise give HD as the only product. This finding agrees with the spectroscopic evidence, since at these wavelengths strong absorption occurs to levels near the top of the barrier to internal rotation of the V state, and also to levels of the Rydberg states, where the barrier to internal rotation is only about 8 kcal. One might expect that *cis*–*trans* isomerizations could be brought about by absorption of light near the maxima of the V–N systems, but this effect does not seem to have been demonstrated yet; instead it is found that dissociation of the molecule predominates.^{83a}

VI. Rydberg States of C_2H_4 and the Ground State of $C_2H_4^+$

Figure 10 shows the vacuum ultraviolet absorption spectra of C_2H_4 and C_2D_4 in the region 1800–1000 Å as obtained by Price and Tutte.⁶³ The spectra are from a series of photographs with successively increasing gas pressures. In the higher pressure pictures, the broad white area corresponds to the strong absorption of the V–N system. Standing out on top of this continuous or pseudo-continuous absorption is a series of pairs of bands, starting at 1744 Å, which Price identified as belonging to the lowest energy Rydberg electronic transition (see also Figure 9). Successive pairs are separated by intervals of about 1350 cm^{-1} , which can be identified with the C–C stretching frequency of the upper state, ν_2' . Since ethylene is unlikely to have a totally symmetric vibration with a very small frequency, Price and Tutte⁶³ suggested that the second member of each pair corresponds to excitation of the upper-state twisting vibration. However, according to the Franck–Condon principle, the twisting vibration would not be expected to appear in the spectrum unless there is a large change in its frequency in the transition. Even then it should only appear weakly and, according to rigorous selection rules, must be excited by *even numbers* of quanta. Hence we must interpret the first and second members of each pair as (0,0) and (2,0) torsional transitions.^{54,84}

At 1393 Å the pattern is repeated in another succession of pairs, corresponding to the second member of a Rydberg series of electronic transitions, while higher members of the series follow at still shorter wavelengths.^{63,67} The patterns of bands overlap confusingly for the higher members, but Price and Tutte⁶³ have found them to converge to a limit at $84,750\text{ cm}^{-1}$, which gives the first (π) ionization potential of C_2H_4 as 10.51 eV. The Rydberg MO's involved in the upper electronic states of this series have been identified⁸⁵ as *ns* in UAO description, starting with 3s for the first member of the series at 1744 Å; for planar ethylene the electronic states should then be of species $^1B_{3u}$, derived from the electron configuration ... $(1b_{3u})(ns)$.

In Figure 11, we give *microphotometer tracings* of the 1744-Å transition at higher dispersion.⁵⁴ Considerable differences may be seen in comparing the twisting doublets for C_2H_4 and C_2D_4 . For example, the relative intensities of the doublet bands are different for the two isotopes: for C_2H_4 the first band is

(83a) Dissociation of the molecule is extensive during *cis*–*trans* isomerization of partly deuterated ethylenes photosensitized by the 2537-Å Hg line, but is not significant when the corresponding Cd line (3261 Å) is used (H. E. Hunziker, *J. Chem. Phys.*, 50, 1288 (1969)). These observations may allow an estimate of the dissociation energy of $C_2H_4 \rightarrow C_2H_3 + H$.

(84) R. S. Mulliken, *Rev. Mod. Phys.*, 14, 65 (1942).

(85) G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1966.

(81) M. C. Sauer, Jr., and L. M. Dorfman, *J. Chem. Phys.*, 35, 497 (1961).

(82) H. Okabe and J. R. McNesby, *ibid.*, 36, 601 (1962).

(83) J. R. McNesby and H. Okabe *Advan. Photochem.*, 3, 157 (1964).

Table V
Twisting Potential and Torsional Energy Levels in the
First Rydberg State of Ethylene

	C_2H_4		C_2D_4	
	Exptl	Calcd ^a	Exptl	Calcd ^a
Band intervals (cm^{-1})	$4\nu_4'-0$	(1084)	1139	715
	$3\nu_4'-\nu_4'$...	670	427
	$2\nu_4'-0$	468	464	286
	$\nu_4'-0$	96 ^b	114	41 ^b
Relative intensities	$I_{2,0}/I_{0,0}$	0.73	0.67	1.25
	$I_{3,1}/I_{1,1}$...	0.80	~ 1.5
	$I_{4,0}/I_{0,0}$	0.09	0.12	0.23

^a V (cm^{-1}) = $3149(1 - \cos \alpha) - 188(1 - \cos 4\alpha) - 194(1 - \cos 6\alpha)$; $V_{min} = -290$ cm^{-1} at $\alpha = \pm 25^\circ$; $V = 0$ at $\alpha = 0$; $V = 3050$ cm^{-1} (0.38 eV) at $\alpha = \pm \pi/2$. ^b Based on $\nu_4'' = 1023$ cm^{-1} for C_2H_4 , 726 cm^{-1} for C_2D_4 (ref 31, 35), and positions of (1,1) bands.

much stronger than the second, but the situation is completely reversed in C_2D_4 . Also the band positions are irregular: theoretically the twisting frequencies of these two isotopes should be in the ratio $\sqrt{2}:1$, but the observed ratio is actually 1.67:1. At higher frequencies there is a shoulder in C_2H_4 that can be identified as a (4,0) band, but the spacings from (0,0) to (2,0) and from (2,0) to (4,0) are quite different, so that the vibrational motion must be very anharmonic. The (4,0) band of C_2D_4 is much more clearly defined.

The interpretation of these peculiar vibrational features is that the twisting vibration has a double minimum potential function in the upper state. Following Mulliken and Roothaan's conclusion^{17,26} that the ground state of the $C_2H_4^+$ ion should be twisted by about 30° at equilibrium, Merer and Schoonveld^{86,87} set up a machine program to calculate the energy levels and band intensities resulting from a potential function of this type, and with it tried out various expressions for the potential energy as a function of the angle of twisting.

In Table V the experimental energy levels for the twisting vibration are compared with their "best" calculated set. The experimental data for levels $\nu_4' = 2$ and 4 are taken from ref 54, while those for $\nu_4' = 1$ and 3 are based on high-temperature ethylene spectra in which Merer and Schoonveld observed^{86,87} the (1,1) and (3,1) "hot" bands of C_2D_4 and the (1,1) band of C_2H_4 . It is seen that the experimental data, including intensities, agree as well as could reasonably be expected with the calculated. The potential function has minima for an out-of-plane angle of 25° , which is quite close to Roothaan's original calculated value for state I; the depth of the minima is 290 cm^{-1} (0.036 eV).

The bands of the 1744-Å transition are not sharp enough for rotational analysis, but under high resolution^{4,85,87} the strongest bands show two distinct heads, one in the center of the band and one at the short-wavelength edge. They are therefore type C (perpendicular) bands, which is in agreement with the predicted $^1B_{3u}$ upper state. The degradation of the bands to the red shows that the hydrogen atoms in the upper state lie a little further from the z axis (through the C-C bond) than they do in the ground state.⁸⁷ The difference is probably enough for us to expect to see the bands ν_1' or ν_3' , according to the Franck-Condon principle, if the change of shape involved only stretching of the C-H bonds or only a change of HCH

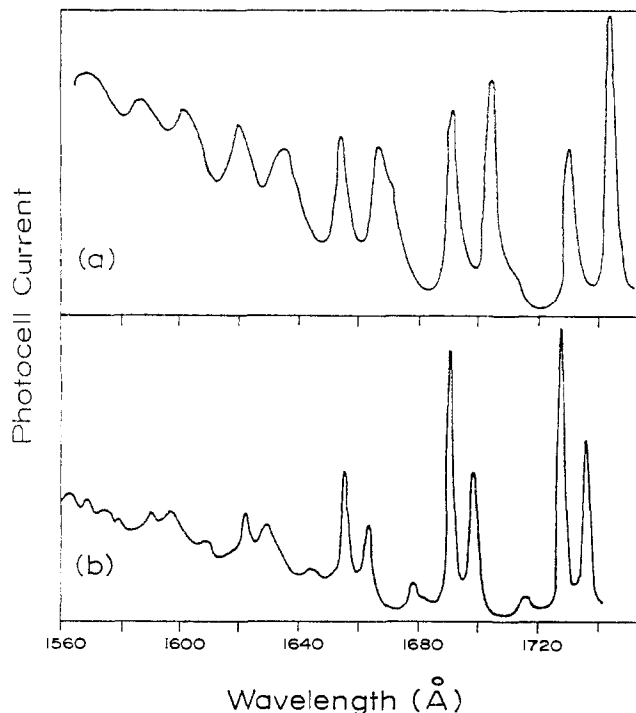


Figure 11. Microphotometer tracings of (a) C_2H_4 and (b) C_2D_4 spectra taken on a 21-ft vacuum spectrograph, using xenon continuum as background (P. G. Wilkinson and R. S. Mulliken, *J. Chem. Phys.*, **23**, 1895 (1955)).

angle; since neither band has been found, the change of shape probably involves both parameters. From the intensity distribution in the C-C stretching progression, we can deduce that the C-C bond length is 1.41 ± 0.01 Å in the upper state; estimated values for the other structural parameters are $r(C-H) = 1.11 \pm 0.03$ Å, and $\angle HCH = 120 \pm 2^\circ$. As given above, $\alpha_{min} = 25 \pm 1^\circ$.

The Rydberg MO in state R is almost certainly the CH antibonding orbital $4a_g$, and, as we have said, almost certainly corresponds to the UAO 3s. The reasoning is as follows. From what we know from SCF MO calculations made with large digital computers, $2a_g$ in Table II corresponds to 2s of the "semi-united atom" (semi-UA), $3a_g$ to $3d\sigma$ of the semi-UA.¹⁹ From our knowledge of the MO's of N_2 where $2\sigma_g$ corresponds to 2s, and $3\sigma_g$ to $3d\sigma$ of the semi-UA, it is safe to conclude that $4\sigma_g$ in N_2 and $4a_g$ in C_2H_4 correspond to the UAO 3s, and must be the most tightly bound Rydberg MO, since in first-row atoms 3s is the most tightly bound excited AO.

Before discussing Rydberg states further it is instructive to consider a simple formula⁸⁸ giving the position of the maximum radial density of the outermost loop of a Rydberg AO, $r_{max} = a_0 n^{*2}/Z$; in this formula a_0 is 0.529 Å, the radius of the $n = 1$ orbit of the hydrogen atom according to the Bohr theory, Z is the charge on the atomic core in units of the electron charge, and n^* is the effective principal quantum number. Because of their large size, all true Rydberg MO's are approximately UAO's except for their innermost loops, so that, within certain limitations, we can apply this formula to Rydberg MO's as well. The MO occupied in the first Rydberg state of ethylene is 3s in UAO approximation. To allow for

(86) A. J. Merer and L. Schoonveld, *J. Chem. Phys.*, **48**, 522 (1968).

(87) A. J. Merer and L. Schoonveld, *Can. J. Phys.*, in press.

(88) R. S. Mulliken, *J. Am. Chem. Soc.*, **86**, 3183 (1964).

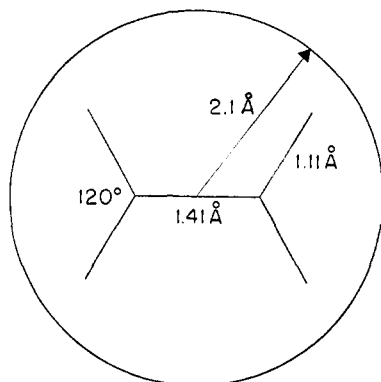


Figure 12. Scale drawing of the ethylene molecule in the R state, showing the radius of maximum radial electron density r_{\max} for the $3s$ Rydberg MO.

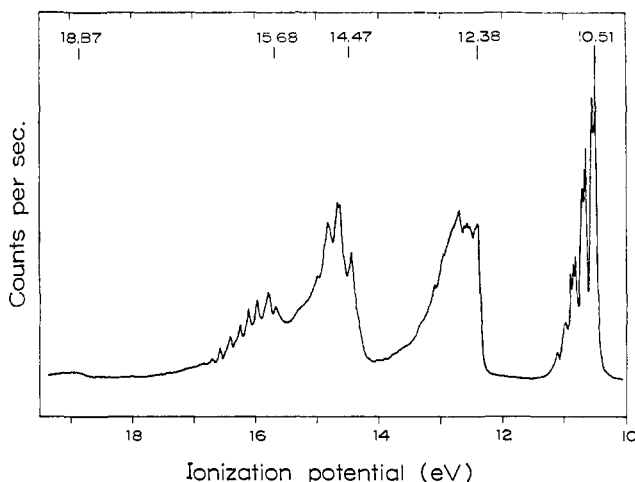


Figure 13. High-resolution photoelectron spectrum of C_2H_4 (D. W. Turner, private communication).

the quantum defect of the s electron we define the effective principal quantum number, $n^* = Z(R/T)^{1/2}$, where R is the Rydberg constant ($109,678 \text{ cm}^{-1}$) and T is the difference between the ionization limit and the energy of the Rydberg state (in this case $27,400 \text{ cm}^{-1}$). With $Z = 1$ for a neutral molecule, this last formula gives $n^* = 2.00$ for the first Rydberg state of ethylene. Substituting into the previous formula with $n^* = 2.0$, we obtain $r_{\max} \approx 2.1 \text{ \AA}$.

When this radius is laid out from the center of a diagram showing the nuclear skeleton of ethylene, as in Figure 12, it is seen to lie outside the H nuclei of the skeleton, as it should for a Rydberg MO. Still, r_{\max} is small enough so that the electron even in the outer loop should be distinctly affected by the core; for higher energy Rydberg MO's ($n^* > 2$), r_{\max} is always very much larger than the core.

Figure 13 shows a photoelectron spectrum of C_2H_4 compiled from spectra taken by Turner, *et al.*^{11,89} Photoelectron spectra show the distribution of the residual energies of photoelectrons after absorption by ethylene of quanta of monochromatic radiation. The ionization energy corresponding to any peak in the spectrum is obtained by subtracting the observed

photoelectron energy from the energy of the incident radiation (in this case the He line at 584 \AA , or 21.21 eV). Each major peak shows vibrational substructure, from which it is possible to tell whether the electron involved is bonding, nonbonding, or antibonding. The position of the first peak, at 10.51 eV , agrees well with the spectroscopic value for the first ionization potential (IP). Especially interesting is the fact that it shows a doublet pattern similar to that in the 1744-\AA Rydberg transition (Figure 10). As we have seen, the electron in a Rydberg transition goes to an MO so large that one may expect the nuclear configuration and the pattern of vibration frequencies to be similar to those for the positive ion. The fact that the spectra are so similar for the Rydberg transitions and for photoionization confirms that these transitions are definitely Rydberg transitions, and also shows that the ground state of $C_2H_4^+$ must be twisted by about 25° at equilibrium (in agreement with Roothaan's early computations,²⁶ and the recent computations by Lorquet and Lorquet²⁷). The H-C-H angle in the ground state of $C_2H_4^+$ is probably not the same as in the R state of C_2H_4 , since the photoelectron spectrum shows additional peaks which may be attributed¹¹ to ν_3' ; the photoelectron spectrum in fact corresponds more closely to the 1393-\AA system of ethylene^{11,68} than to the 1744-\AA system, as one would expect from the arguments of the previous paragraph.

So far we have discussed the Rydberg states derived from ns UAO's almost exclusively. The next Rydberg MO's in order of energy are expected to be $3b_{1u}$ ($3p\sigma$ in UAO) and $2b_{2u}$ ($3p\pi_y$), but these should not give strong Rydberg series leading to the first IP because the resulting electronic states are g , and therefore transitions to them are forbidden by the electric dipole selection rules. Four of the five possible Rydberg series involving nd UAO's are allowed by the electric dipole selection rules, though for $n = 3$ only the two transitions to $3d\delta$ orbitals can occur, because the UAO's $3d\sigma$, $3d\pi_y$, and $3d\pi_x$ correspond to the occupied valence shell MO's $3a_g$, $1b_{3g}$, and $1b_{2g}$. Further Rydberg transitions arising by excitation of an electron from the $1b_{2g}$ MO, and leading to the second IP at 12.50 eV , should also occur near 1000 \AA , but these have not yet been identified.

Indications that one of the excited g electronic states lies at 7.45 eV have been found by Ross and Lassetre⁶⁶ in the electron impact spectrum of ethylene. In electron-scattering experiments the spectra are obtained by counting the number of electrons that reach a detector after exciting a gas molecule and losing the corresponding excitation energy. When the electrons counted are those that continue to travel in the direction of the incident beam, by far the more prominent transitions are those that are optically allowed by the electric dipole selection rules. However, their scattering cross sections are proportional to the excess kinetic energy, after impact, of the impinging electrons, whereas the cross sections for electric dipole-forbidden optical transitions (*e.g.*, quadrupole-allowed transitions) are independent of this kinetic energy. Hence for low excess kinetic energy the *relative* cross sections of optically forbidden transitions may become large enough so that they can be detected. Ross and Lassetre have discovered⁶⁶ one of these forbidden transitions in ethylene at 7.45 eV and have interpreted it as a quadrupole transition, although they have not assigned the MO's involved. The transition is probably from the $1b_{3u}$ (π) MO to the $2b_{2u}$ Rydberg MO ($3p\pi_y$) or the $3b_{1u}$ MO ($3p\sigma$); absorption to the resulting $^1B_{1g}$ or $^1B_{2g}$ electronic state is forbidden for electric dipole radiation but allowed for electric quadrupole radiation.

(89) D. W. Turner, private communication; see also M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.*, 4434 (1964).

A few of the lowest energy observed and predicted electronic levels of ethylene are illustrated in Figure 14. On the left are the V and T states, shown at their respective vertical excitation energies of 7.6 and 4.6 eV above the N state. The R state is at 7.15 eV, and the estimated position of the corresponding triplet Rydberg state (T_R) whose existence is theoretically necessary, even though it has not been found experimentally, is given as 6.15 eV. Because the Rydberg MO extends further out from the core than the π^* MO, the estimated singlet-triplet separation $R-T_R$ has been shown as smaller than the $V-T$ separation. This separation corresponds approximately to $2K$, where K is an exchange integral which should be smaller when the overlap with the core is smaller. The approximate positions of other Rydberg levels can be predicted; some of the predicted B_{1g} and B_{2g} states are included at the right-hand side of Figure 14.

One final point needs discussion before we leave the electronic states of ethylene itself. The ns Rydberg states of C_2H_4 (and the ground state of $C_2H_4^+$) are particularly clear cases of Jahn-Teller distortion⁹⁰ of a degenerate electronic state of a symmetric top molecule. The Rydberg states of perpendicular ethylene arise from the electron configuration $\dots (2e)(Ry)$, so that a degenerate 1E electronic state is expected for excitation to an ns Rydberg orbital: the ground state of perpendicular $C_2H_4^+$ is a 2E state. The degeneracy is removed by distortion of the molecule, since, by the Jahn-Teller theorem,⁹⁰ there is always at least one nontotally symmetric normal coordinate that causes a splitting of the potential function for a degenerate electronic state of a nonlinear molecule, such that the potential minima are not at the symmetrical position.

The Jahn-Teller effect in molecules with a fourfold axis of symmetry is an interesting case which has been considered by Hougen.⁹¹ Unlike the situation in molecules with a threefold symmetry axis, the Jahn-Teller active vibrations in the point group D_{2d} are the *nondegenerate* b_1 and b_2 vibrations. The twisting vibration belongs to the representation b_1 and is thus active. This means that there are *linear* terms in its coordinate Q_4 in the potential energy expression for a degenerate electronic state. Figure 15 illustrates⁹² increasing distortions of the potential function of a 1E state of perpendicular ethylene by the twisting coordinate Q_4 . For small distortion it does not matter that the twisting coordinate is actually periodic, and the potential function is merely split into two parabolic potentials side by side. With larger distortion, or larger amplitude of vibrational motion, the periodic nature of the twisting coordinate becomes important, and the potential function becomes a periodic double minimum function. It is then obvious that the double minimum in the R state of ethylene is an instance of a large *static* Jahn-Teller distortion of an E state of a D_{2d} molecule, treated in periodic coordinates.^{92a} In the limit, the 1E state is split into two electronic states with maxima and minima, respectively, at the planar configuration. More detailed examination shows that if the twisting vibration is associated (as in the R state) with large Jahn-Teller

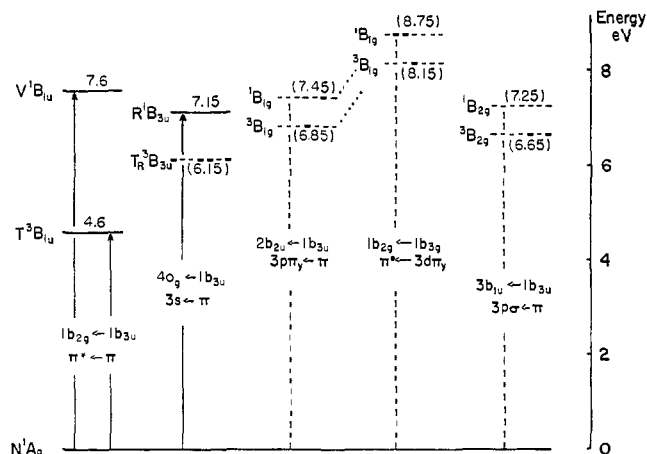


Figure 14. Observed and predicted low-lying electronic levels of ethylene (vertical excitation energies).

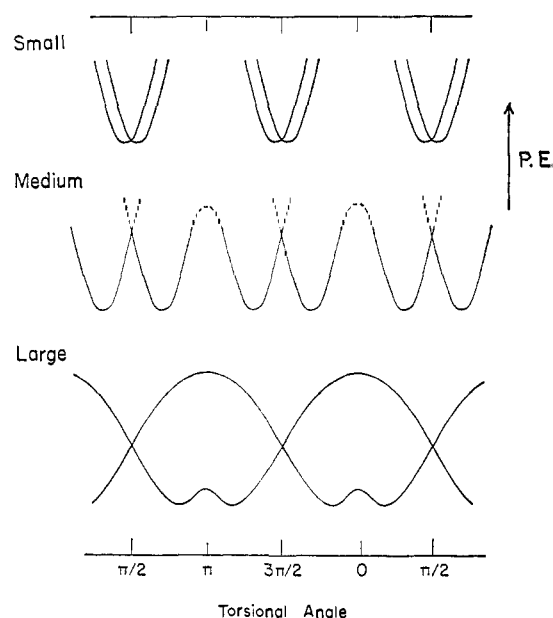


Figure 15. Potential energy curves for a 1E electronic state of ethylene for small, medium, and large Jahn-Teller distortions induced by the torsional vibration.

distortions of the potential curves of an E electronic state, and the b_2 vibrations are not, the problem of the coupling between the electronic and vibrational motions becomes approximately separable, and the energy levels are those of a potential function with period 2π . In other words, we have a large *static* Jahn-Teller effect but no *dynamic* effect. In agreement with this, the observed vibrational levels of the $R' B_{3u}$ electronic state can be fitted adequately^{86,87} by a simple periodic double minimum potential (see Table V), showing that they lie in a part of the potential curve which is quite far from the perpendicular configuration.

The Jahn-Teller effect is still important in considerations of *cis-trans* isomerization of ethylene in the R state, even though there can be no degenerate electronic states for the partly deuterated molecules, which have lower symmetry. There are still two separate electronic functions (belonging to the representations A and B of the point group C_2) which have essen-

(90) H. A. Jahn and E. Teller, *Proc. Roy. Soc. (London)*, **A161**, 220 (1937).

(91) J. T. Hougen, *J. Mol. Spectry.*, **13**, 149 (1964).

(92) J. K. G. Watson and A. J. Merer, to be published.

(92a) The Jahn-Teller effect is not the *reason* for the double minima in the R and I states; that has already been discussed in terms of hyperconjugation. The Jahn-Teller theorem states that perpendicular ethylene is unstable in an E state and lists the ways in which it can distort itself to remove the degeneracy; it makes no prediction about the form and magnitude of the actual distortion that occurs.

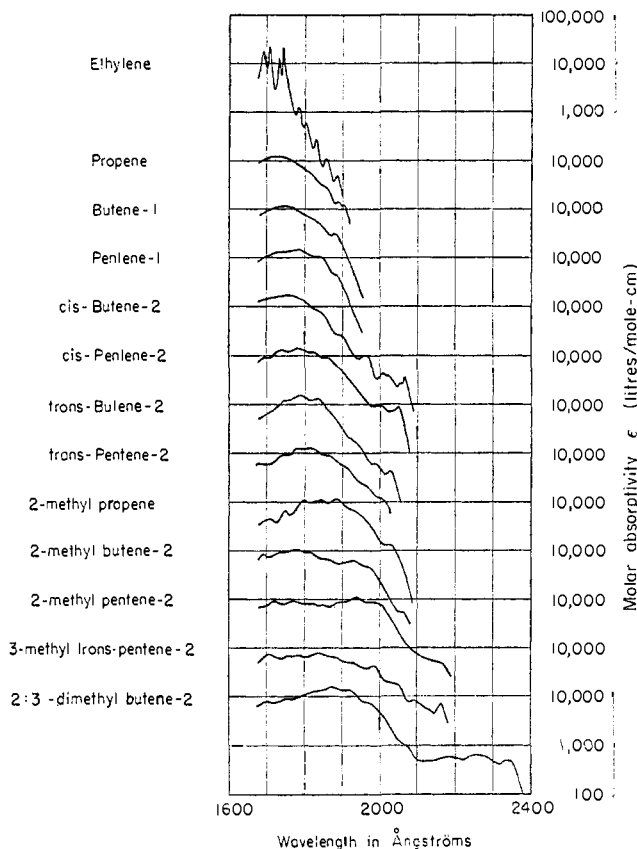


Figure 16. Far-ultraviolet spectra of some selected olefins (after Jones and Taylor⁶⁵).

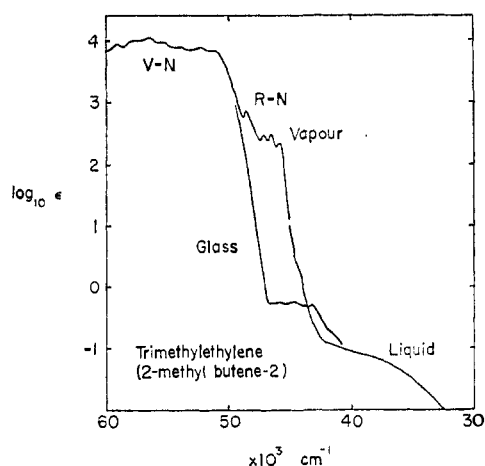


Figure 17. Composite absorption spectrum of 2-methylbutene-2 (trimethylethylene).

tially the same form as those for C_2H_4 and C_2D_4 . However, there will be strong interaction between the potential curves near the point where they cross at the perpendicular configuration, which allows isomerization to occur. The potential barrier to isomerization in the R state is probably about 8 ± 2 kcal.

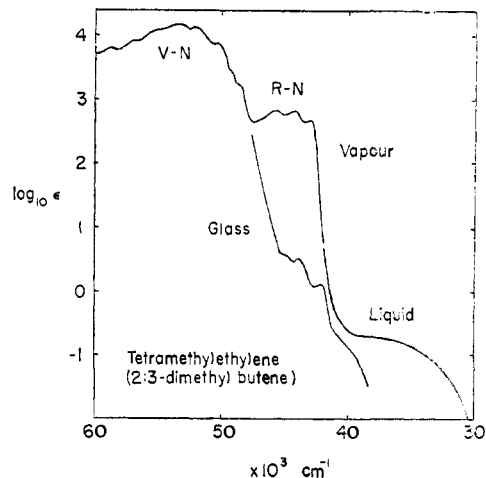


Figure 18. Composite absorption spectrum of 2,3-dimethylbutene-2 (tetramethylethylene).

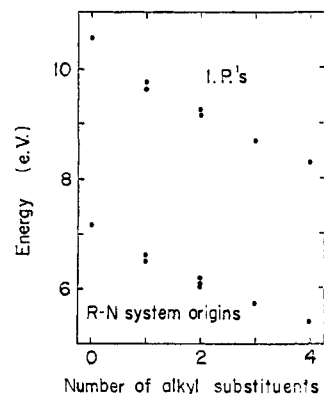


Figure 19. IP's and R-N system origins for ethylene, butene-1, and the methyl-substituted ethylenes.

VII. Spectra of the Alkyl-Substituted Ethylenes

A. SIMPLE ALKYL DERIVATIVES

We have so far considered only the spectrum of ethylene itself but can now apply some of the conclusions to the spectra of the alkyl-substituted derivatives of ethylene. The spectra of these molecules have been studied fairly fully in the last 35 years; for example, at least seven published spectra of tetramethylethylene (2,3-dimethylbutene-2) may be found in the literature. All the same, confusions have arisen over the interpretation of the electronic transitions observed, and we feel that a detailed discussion of the evidence is needed.

The vapor spectra of some selected alkylethylenes are shown in Figure 16; these spectra, taken from the extensive compilation of Jones and Taylor,⁶⁵ show the strongest bands of these molecules in the region 1600–2400 Å. These spectra are not at such high resolution as the previous ethylene spectra of Figures 9 and 11, but still show the essential characteristics of the transitions. For ethylene itself (top line), the twisting doublets of the R-N transition and some of the small peaks belonging to the V-N transition are visible. In the substituted ethylenes, the complications introduced by the alkyl groups can be held accountable for the much smoother profiles. How-

ever, if we follow how the positions of the bands change with the number of substituents, we can see that what is observed is in all cases roughly the same:⁹³⁻¹⁰⁰ there is a strong V-N transition, with a broad maximum of absorption (where the molar absorptivity ϵ_{\max} is about 10,000), falling rapidly in intensity toward longer wavelengths, plus a superposed R-N transition, which is fairly intense, with a maximum ϵ of about 500-1000, but which stops abruptly at its long wavelength end, just as in ethylene itself.

To the red of the R-N systems the absorption coefficient drops rapidly, but, in the liquid or solution, the heavier alkylethylenes show very weak absorption in the region 2400-2800 Å. This is probably genuine, since various authors have reported it, although in view of its weakness one cannot entirely rule out the possibility that it is due to impurities. Figures 17 and 18 show composite spectra of two typical compounds, trimethylethylene^{62,65,94,95,96,101} and tetramethylethylene,^{14,65,93-95,101} drawn from the various available sources; the room-temperature vapor and solution spectra are shown, together with spectra taken in a rigid hydrocarbon glass¹⁰¹ at 77°K which we shall discuss later.

The position of the V-N maximum moves slightly to the red with increasing numbers of substituents on the ethylenic carbons; thus in the 1-alkenes the V-N maxima lie near 1750 Å, but in tetramethylethylene the maximum is at 1875 Å. The 0,0 band of the R-N bands moves much more rapidly to the red with increasing numbers of substituents. As a result, the R-N bands, which in C_2H_4 occur fairly close to the V-N peak, move relatively further out until in tetramethylethylene they stand out clearly beyond the red end of the V-N system (Figure 18). In ethylene itself the R-N bands are only seen at all because of their relatively simple vibrational structure, a simplicity which is lost in the alkylated ethylenes.

There is general agreement about the identity of the V-N ($\pi^* \leftarrow \pi$) transitions in the alkylated ethylenes, but the evidence that the upper states of the R-N transitions are really Rydberg in nature needs to be reiterated.

(i) The first line of evidence is that the first ionization potentials^{102,103} of the alkylethylenes drop, with increasing numbers of substituents, at almost exactly the same rate as the R-N systems are shifted to the red.⁸⁴ Figure 19, which illustrates this for the methylethylenes, makes this clear.

The almost linear dependence of the positions of the first bands of the R-N systems on the number of alkyl substituents had first been noted by Carr and Stücklen;⁹⁵ arguing from this dependence, and from the fact that the system in ethylene itself was known to be Rydberg, they proposed a Rydberg assignment for the bands of the alkylethylenes.¹⁰⁴⁻¹⁰⁶ Since the first IP's

have subsequently been found to show the same dependence on the number of substituents, we can now be certain of the Rydberg assignment. This is because, provided that the effective principal quantum number n^* for the Rydberg MO is not changed by alkyl substitutions, the difference between the ionization limit and the energies of the Rydberg states must always be the same.

Of course, by the arguments of Figure 12, we expect that n^* will be slightly different in an alkyl derivative from what it is in ethylene itself, since, with the increased size of the molecule, the Rydberg MO must be modified to some extent by the presence of the alkyl groups; actually, however, the IP of ethylene lies only just off the line for the derivatives in Figure 19, so that this difference in n^* is small. Exactly why it is so small is an interesting theoretical question which deserves further study. The reason for the steady decrease of the IP with increasing number of substituent groups can be understood partly in terms of hyperconjugation and partly of charge transfer from the alkyl groups to the double-bond carbon atoms.^{106a}

(ii) A second line of evidence is that the vibrational structures of the R-N systems of ethylene^{14a} and the alkylethylenes^{101,107} are very sensitive to pressure. Because the Rydberg MO is so large we must expect it to be very considerably squeezed and distorted when the molecule is placed in a condensed phase or in a gas at high pressure. Robin, *et al.*,^{14a} have demonstrated clearly how the sharp vibrational structure of the first Rydberg transition of ethylene is smeared out in spectra taken with 150 atm of added N_2 , and Evans¹⁰⁷ has shown that the same effect occurs for the R-N bands of tetramethylethylene and cyclohexene. Figure 20 gives the actual spectra observed: what happens is that on adding a high pressure of nitrogen the vibrational structure is pretty much washed out, and the whole transition moves to shorter wavelengths. On the other hand, the V-N transition is not affected by the presence of added nitrogen. Much the same effect has been noticed¹⁴ in spectra of a low-temperature thin film of tetramethylethylene. As before, the R-N system is flattened out (see Figure 21), but the V-N system is less affected.

The R-N bands disappear altogether when the alkylethylenes are dissolved in a rigid glass of isopentane and 3-methylpentane at 77°K.¹⁰¹ Figures 17 and 18 show the comparison between the room-temperature spectra of the solution and the spectra of the cold glass for trimethylethylene and tetramethylethylene. The cold glass is 22% denser than the solution at room temperature,¹⁰⁸ so that this seems to be another instance of the effect described by Evans: it is probable that the Rydberg transition moves a long way toward higher frequencies in a condensed phase, so that it becomes hidden under the V-N transition. In its place are seen some much weaker bands, with molar absorptivity ϵ around 0.3 to 3, which may be a triplet transition (see below); these can be identified with the very weak bands which are seen to the red of the R-N system at room temperature (see above), but shifted like the R-N bands to shorter wavelengths.

(iii) Where the vibrational structures of the R-N systems of alkylethylenes can be arranged into regular progressions, it is found that the frequency occurring is usually about 1400 cm^{-1} ,

(93) E. P. Carr and M. K. Walker, *J. Chem. Phys.*, **4**, 751 (1936).

(94) E. P. Carr and G. F. Walter, *ibid.*, **4**, 756 (1936).

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(96) E. P. Carr and H. Stücklen, *J. Am. Chem. Soc.*, **59**, 2138 (1937).

(97) J. T. Gary and L. W. Pickett, *J. Chem. Phys.*, **22**, 599 (1954).

(98) D. Semenow, A. J. Harrison, and E. P. Carr, *ibid.*, **22**, 638 (1954).

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(102) R. Bralsford, P. V. Harris, and W. C. Price, *Proc. Roy. Soc. (London)*, **A258**, 459 (1960).

(103) V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, and Ye. L. Frankevich, "Bond Energies, Ionization Potentials and Electron Affinities," Edward Arnold, London, 1966.

(104) E. P. Carr and H. Stücklen, *J. Chem. Phys.*, **7**, 631 (1939).

(105) E. P. Carr, L. W. Pickett, and H. Stücklen, *Rev. Mod. Phys.*, **14**, 260 (1942).

(106) E. P. Carr, *Chem. Rev.*, **41**, 293 (1947).

(106a) Very recently, R. McDiarmid, *J. Chem. Phys.*, **50**, 1794 (1969), has confirmed that the R-N systems of *cis*- and *trans*-butene-2 are the first members of Rydberg series leading to the first IP's.

(107) D. F. Evans, *Proc. Chem. Soc.*, 378 (1963).

(108) W. J. Potts, *J. Chem. Phys.*, **21**, 191 (1953).

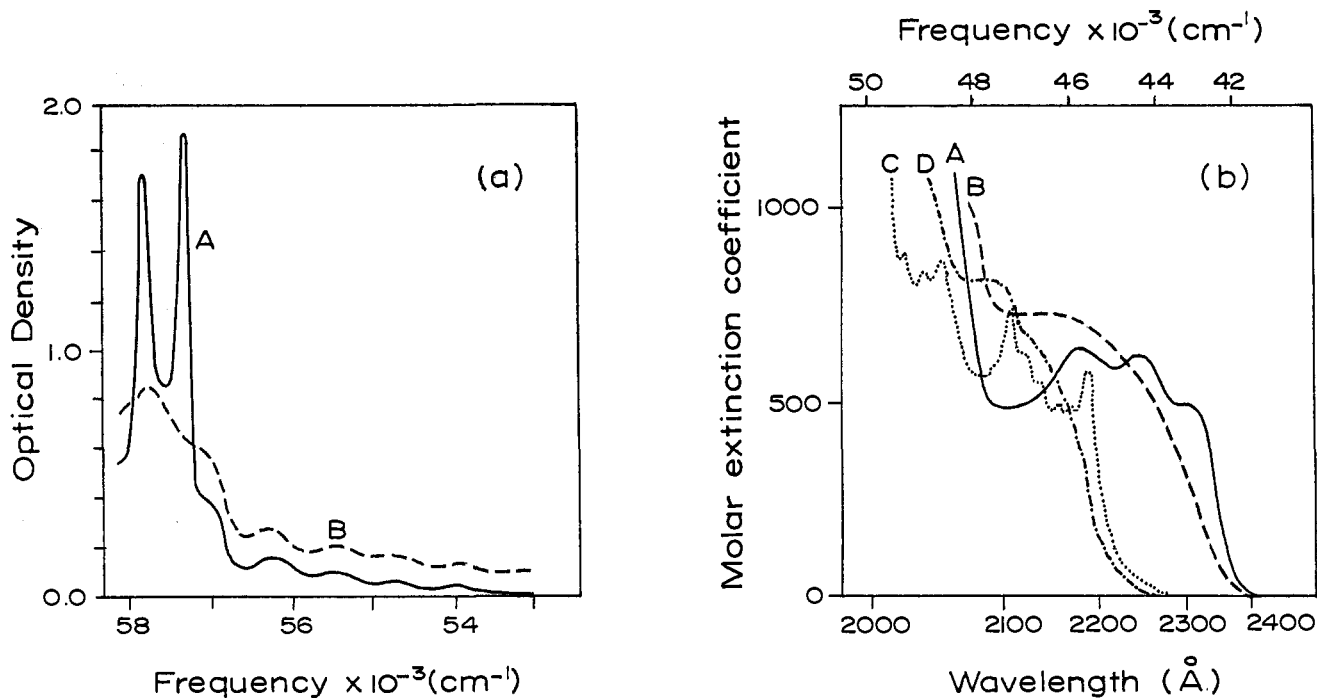


Figure 20. (a) Absorption spectrum of ethylene at room temperature (A) and in the gas phase (B) on adding 150 atm of nitrogen (spectrum displaced upwards for clarity), after Robin, *et al.*^{14a} (b) Absorption spectra of (A) tetramethylethylene vapor, (B) tetramethylethylene vapor + 133 atm of nitrogen, (C) cyclohexene vapor, (D) cyclohexene vapor + 133 atm of nitrogen (D. F. Evans, *Proc. Chem. Soc.*, 378 (1963)).

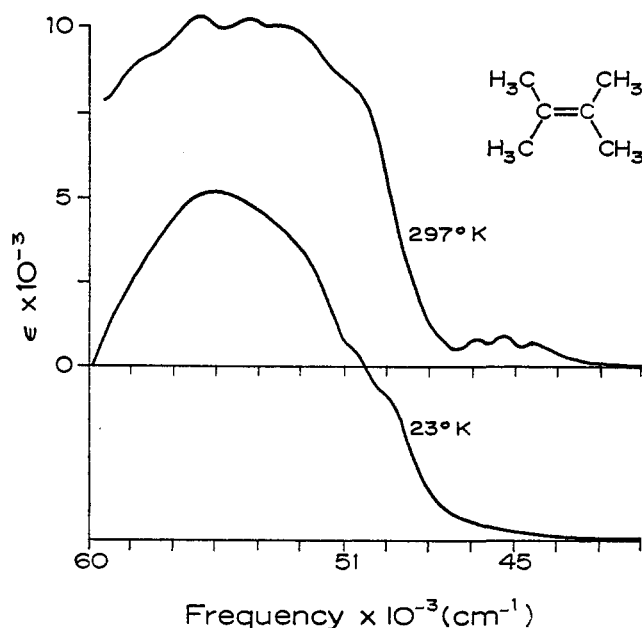


Figure 21. (Upper) The spectrum of tetramethylethylene vapor at 298° K. (Lower) The spectrum of a thin film of tetramethylenethylene at 23° K (M. B. Robin, R. R. Hart, and N. A. Kuebler, *J. Chem. Phys.*, 44, 803 (1966)).

which is close to the observed value of 1370 cm^{-1} for the C-C stretching vibration in the R-N system of ethylene itself. This presumably means that the ethylenic double bond stretches approximately the same amount in the R-N transition irrespective of whether the substituents on the ethylenic carbon atoms are alkyl groups or hydrogen atoms. The R-N system

of tetramethylethylene (Figure 18) shows particularly clear vibrational structure,⁹⁶ with intervals of 1340 and 1370 cm^{-1} , though in trimethylethylene the bands are less well resolved.

Having presented the evidence for the Rydberg nature of the R-N systems, we must now consider the assignments for the very weak longer wavelength portions of the spectra. The R-N systems are fairly intense (ϵ 500–1000), and, as we have already noted, the absorption drops very rapidly to the red of the 0,0 band. The next absorption is the very weak structureless system found in liquid⁶³ or solution¹⁰¹ spectra, which in the low-temperature glass spectra probably appears as the weak banded system a little further to the violet (see, for example, Figure 18). Although there is the danger that contamination by impurities is the reason for the appearance of such weak bands, it is likely that these bands revealed in the low-temperature glass spectra may represent transitions to the triplet Rydberg states T_R ; these *must* exist (though they are not seen in ethylene itself), and should lie less than 1 eV below the singlet Rydberg states.¹⁰⁹ There are two reasons for this assignment. In the low-temperature glass spectra the weak continua near $35,000$ – $40,000 \text{ cm}^{-1}$ have moved to shorter wavelengths, which is the behavior found for the singlet Rydberg systems, and also they show vibrational structure not unlike the singlet Rydberg systems (Figure 18). However, the observed intensities, although very low, are rather stronger than one might have expected for triplet Rydberg transitions.

There is now the problem of where the T-N (triplet $\pi^* \leftarrow \pi$) systems of the alkylethylenes are. Itoh¹¹⁰ has recently investigated the spectra of various alkylethylenes in the presence of added oxygen, in an attempt to clarify the situation, and has

(109) R. S. Mulliken, *J. Chem. Phys.*, 33, 1596 (1960).

(110) M. Itoh, private communication.

succeeded in finding the T-N bands of propene, 2-methylpropene, and *trans*-butene-2, with faint indications of vibrational structure similar to that seen for ethylene in Figures 7 and 8. He has not obtained any further information about the possible triplet Rydberg bands, because of a structureless oxygen-induced contact charge-transfer absorption which masks this region.

In 1963 Berry,¹¹¹ noting that the first absorption system in the isoelectronic molecule formaldehyde is the intravalency shell $\pi^* \leftarrow n$ transition, supposed that the corresponding transition $\pi^* \leftarrow \text{CH}$ in the alkylethylenes is responsible for these very weak bands. The principal experimental foundations on which this suggestion was based were Snow and Allsopp's "shoulder" in the ethylene spectra⁶² at 2000–2200 Å, and the supposed electron-impact peak^{69–71} at 6.5 eV (1910 Å), but, as we saw in the discussion of ethylene, both these have been shown to be erroneous by more recent work. The main support for Berry's assignment has come from theoretical calculations of orbital energies^{12,13} rather than experimental studies. In ethylene this particular transition is forbidden by the electric dipole selection rules, being



It should therefore also be forbidden in tetramethylethylene, but not in trimethylethylene, where with the lower symmetry all transitions are allowed. Yet, as we can see in Figures 17 and 18, there is little difference between the bands of these two molecules.

Berry¹¹¹ was referring to the bands with ϵ about 0.1 to 1.0, but Robin, Hart, and Kuebler¹⁴ seemed to think he was discussing the R-N systems, and unfortunately clouded the issue by referring to the R-N bands as "mystery bands." It seems that they have mistaken the weakness of the R-N bands compared to the V-N bands (ϵ 500 compared to ϵ 10,000) for the intrinsic weakness of the bands with ϵ 0.1–1. In addition they failed to realize that the Rydberg 3s MO ($4a_g$) is the same MO as the first CH antibonding MO (though, in a later paper,^{14a} Robin, *et al.*, have corrected this error). This reference to CH* and 3s as if they were two different actual MO's is a confusion that often arises in a discussion of Rydberg states.⁸⁸ For example, as we have explained in connection with Figure 1, the T and V states of H₂ have the valence-shell configuration $(1\sigma_g)(1\sigma_u) \approx (\sigma_g 1s)(\sigma_u 1s)$ at medium R values, but at small R values the $1\sigma_u$ MO goes over to the UAO form $2p\sigma$, so that the T and V states become Rydberg states.^{111a} We use the 3s Rydberg description for the $4a_g$ MO rather than CH*, since the photoelectron results^{11,89} indicate the predominance of the former so clearly. Robin, *et al.*¹⁴ have therefore merely reaffirmed the Rydberg character of the R-N systems.

Table VI summarizes the spectroscopic and photoionization data for ethylene and the methyl-substituted ethylenes. The spectroscopic frequencies given are all for the Franck-Condon maxima, corresponding to "vertical transitions"; the IP data are from the photoionization work of Bralsford, Harris, and Price.¹⁰² We have already remarked that the IP's drop quite quickly with increasing numbers of alkyl substitu-

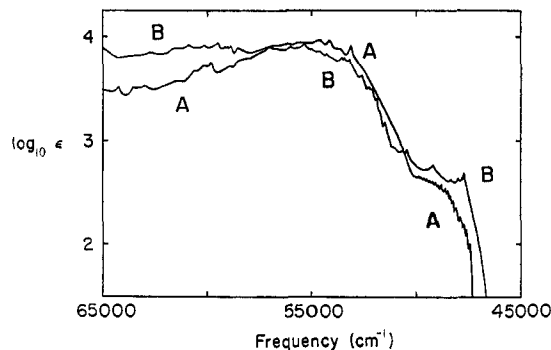


Figure 22. Vapor-phase absorption spectra of (A) cyclopentene and (B) cyclohexene, after Pickett, *et al.*¹¹³

Table VI

Observed Vertical Frequencies and Term Values for the V-N and R-N Systems of C₂H₄ and Its Methyl-Substituted Derivatives^a

No. of methyl groups	IP of π MO	Observed system maxima			Orbital term values	
		V-N	R-N	T _{R-N}	$1b_{2g}(\pi^*)$	$4a_g(3s)$
0	10.51	7.58	7.15		2.93	3.36
1	9.73	7.15	6.72	(5.49)	2.58	3.01
2 (1,1)	9.23	6.68	6.19		2.55	3.04
2 (1,2- <i>cis</i>)	9.13	7.10	6.03		2.03	3.10
2 (1,2- <i>trans</i>)	9.13	6.97	6.09	(5.30)	2.16	3.04
3	8.68	6.75	5.74	(4.88)	1.93	2.94
4	8.30	6.61	5.40	(4.57)	1.69	2.90

^a Values in electron volts.

ents, and that the R-N system energies, which are tied to the IP's, in consequence drop faster than the V-N system energies. The term values of the V and R states (which are the differences between the IP and the V-N and R-N system energies, respectively) show this quite well. The term values of the R states are nearly constant, though that of ethylene itself is larger than the others, but the term values of the V states decrease rather strongly with increasing substitution. Although the T_{R-N} spectra are uncertain, some tentative values are included in Table VI for completeness.

B. CYCLIC MOLECULES

When the substitution of the ethylene molecule is more elaborate than simply putting in an alkyl group, the spectra of the resulting compounds show approximately the same general features, but some quite big modifications in the details often occur. Cyclopentene and cyclohexene are essentially disubstituted ethylenes (though, to be sure, in the form of rings), and their spectra should be similar^{65,112,113} to that of *cis*-butene-2. Figure 22 shows the spectra of these molecules. The R-N systems, in the region 2000–2200 Å, are readily recognized, and it is seen that the vibrational structure is quite well resolved. In cyclohexene this structure is clearly the expected progression in the C-C stretching vibration, with a frequency of about 1485 cm⁻¹, but in cyclopentene it takes the form of 20 narrow bands, separated from one another¹¹² by about

(111) R. S. Berry, *J. Chem. Phys.*, **38**, 1934 (1963).

(111a) Qualitatively, $\sigma_u 1s$ and $2p\sigma$ are similar but not identical. $1\sigma_u$ can be expressed as a linear combination of these (and small amounts of other) expressions, in which the $\sigma_u 1s$ component disappears as the internuclear distance approaches zero, and is already small at the equilibrium distance of state N and even of state V. Similarly $4a_g$ in ethylene can be expressed as a linear combination of CH* and 3s (and small amount of other) forms.

(112) E. P. Carr and H. Stücklen, *ibid.*, **6**, 55 (1938).

(113) L. W. Pickett, M. Muntz, and E. M. McPherson, *J. Am. Chem. Soc.*, **73**, 4862 (1951).

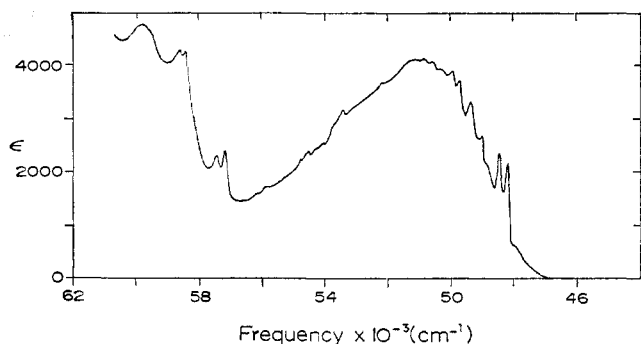


Figure 23. Absorption spectrum of norbornene vapor (M. B. Robin and N. A. Kuebler, *J. Chem. Phys.*, **44**, 2664 (1966)).

130 cm^{-1} . Some discussion of these is required. In the ground state of cyclopentene the five carbon atoms are not all coplanar; the double bond holds four of them in a plane, but the fifth lies out of the plane at equilibrium, and there is a double minimum potential function in the ring-puckering vibration.¹¹⁴⁻¹¹⁶ The first 12 levels of this vibration have been observed in the far-infrared spectra¹¹⁴ and are found to be very closely spaced. This feature must complicate the electronic spectrum enormously, because there must be strong sequence bands arising from several ground-state vibrational levels. In addition, the torsional frequency (386 cm^{-1} in the ground state^{117,118}) must be considerably lower in the excited state, rather as in ethylene, and there is also the possibility of a double minimum in its coordinate. The detailed analysis will obviously be an extremely difficult problem. In view of the observed band intervals of 130 cm^{-1} , it is interesting that the separation of the zero-point level and the level $v = 2$ of the puckering vibration in the ground state is 128.0 cm^{-1} , since this interval is expected to be prominent in the electronic spectrum. There is no sign in the cyclopentene spectrum of band intervals corresponding to the C-C stretching vibration, and they are probably disguised by structure due to the torsion and ring puckering vibrations. The R-N bands of cyclohexene behave like those of tetramethylethylene in the presence of high pressures of nitrogen¹⁰⁷ or in a low-temperature glass.¹⁰¹

It is difficult to make constructive comments about the more complicated molecules, since the spectra are very different from those of the simple olefins and are mainly quite poorly resolved. In norbornene,^{119,120} for example, strong absorption starts near 2100 Å (as in *cis*-butene-2), but the maximum molar absorptivity of the first system is about 4000, compared to 500-1000 for the R-N system and 10,000 for the V-N system of a simple olefin. The first sharp peaks, at 48,000 cm^{-1} , probably represent the beginning of a Rydberg transition, and the peaks at 57,000 cm^{-1} are possibly part of another. The norbornene spectrum¹²⁰ is shown in Figure 23.

Three Rydberg transitions have been identified in the electronic spectrum of tricyclo[3.3.0.0^{2,6}]oct-3-ene.^{14a}

The ultraviolet spectra of cyclopropene¹²¹ and cyclobutene¹²² are anomalous, as one might expect from the considerable strains in these molecules. The spectra are weaker than those of the simple dialkylethylenes and are shifted to shorter wavelengths. Spectra of 1-methylcyclobutene and methylenecyclobutane have also been observed.¹²² None of these shows much vibrational structure.

When the compounds considered are optically active, there are further possibilities. Attempting to determine the nature of the first strong absorption systems, Robin, *et al.*,¹⁴ have measured the optical rotatory dispersion (ORD) of α -D-pinene, and Mason and Vane¹²³ have studied the circular dichroism (CD) of 1-isopropylene-3-methylcyclopentane. ORD is the variation of the angle of rotation of plane polarized light across an absorption system of an optically active compound, and CD is the difference between its absorption spectra measured in left- and right-handed circularly polarized light. Both experimental methods determine the relative sizes of the electric dipole and magnetic dipole contributions to the strength of an absorption transition; the results are quoted in terms of the dissymmetry parameter, g , defined as four times the magnetic dipole strength divided by the electric dipole strength for the transition. If there is a considerable magnetic dipole contribution to the intensity, as in the 3000-Å bands of formaldehyde, the parameter g can be as high as 0.3, but if the electric dipole contribution is strongly predominant, g is very small.¹²⁴ In both the olefins studied the first strong absorption transition turns out to have a very small value of g , thus confirming its primarily electric dipole character. The compound studied by Mason and Vane¹²³ is essentially a tetraalkylethylene; the first transition, which lies at 44,000 cm^{-1} , with ϵ 400, is a typical R-N system (see Figure 18). The spectrum of α -D-pinene is peculiar¹⁴ but bears some resemblance to that of norbornene.¹²⁰

In a recent paper, Yaris, Moskowitz, and Berry¹²⁵ have concluded from examination of ORD and CD for the twisted cyclic olefin *trans*-cyclooctene that the data give evidence not only for $V \leftarrow N$ and $R \leftarrow N$ transitions, but also for a low-lying electric-quadrupole-allowed transition to a state corresponding to the ${}^1B_{1g}$ state at 7.45 eV shown for ethylene in Figure 14.

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