Theoret. chim. Acta (Berl.) 27, 243—264 (1972)

Vibrational Analysis of the Electronic Spectrum of Ethylene Based on *ab initio* SCF-CI Calculations

Sigrid D. Peyerimhoff
Institut für physikalische Chemie, Johannes Gutenberg Universität, 65 Mainz, Germany

Robert J. Buenker
Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68508

Received June 22, 1972

Ab initio calculations for CH_2 twisting and CC stretching vibrational wavefunctions and energy levels are reported for various electronic states of ethylene C_2H_4. Electronic transition moments between these states are also obtained to allow a calculation of the oscillator strengths for vibrational transitions involved in various electronic band systems; from this study it is concluded that the *vertical electronic* energy difference ΔE_e may differ significantly from the energy of the absorption maximum $\Delta E_{\max}$ with which it is often equated. In particular it is found in the case of the $\pi \rightarrow \pi^*$ singlet-singlet excitation of ethylene that the ΔE_e value overestimates the most probable vibrational transition energy (7.89 eV) by some 0.4 eV, thereby offering an explanation for the fact that previous attempts to predict the location of the $V-N$ Franck-Condon absorption maximum have consistently obtained substantially higher results than the 7.66 eV value actually observed. Similar calculations for various Rydberg species and for the $N-T$ transition are also found to obtain a quite consistent representation of the electronic spectrum of this system.

Mit Hilfe von *ab initio*-Methoden werden Energieniveaus und Wellenfunktionen für die CH_2-Rotation und CC-Streckschwingung des Äthylens in einer Reihe von Elektronenzuständen berechnet. Aus den elektronischen Übergangsmomenten zwischen diesen Zuständen werden die Oszillatorenstärken der Schwingungsübergänge in den einzelnen Elektronenbanden erhalten. Die Untersuchungen führen zu dem Schluß, daß die Energiedifferenz für *vertikale* Anregung, berechnet als Unterschied der *Elektronenenergie* ΔE_e der entsprechenden Zustände, ganz erheblich von der Energie für maximale Absorption abweichen kann, wenn sie auch dieser oft gleichgesetzt wird. Insbesondere stellt sich heraus, daß bei der Singulett-Singulett $\pi \rightarrow \pi^*$-Anregung im Äthylen der Wert von ΔE_e ungefähr um 0,4 eV über dem entsprechenden Wert für den wahrscheinlichsten Schwingungsübergang (7,89 eV) liegt; dadurch läßt sich wohl die Tatsache erklären, daß frühere Versuche zur Berechnung des $V-N$ Franck-Condon-Absorptionsmaximums immer einen beträchtlich höheren Wert ergaben als wirklich beobachtet worden ist (7,66 eV). Ähnliche Berechnungen für die verschiedenen Rydberg-Banden und den $N-T$-Übergang führen ebenfalls zu einer durchaus konsequenten Beschreibung des Elektronenspektrums des C_2H_4-Moleküls.

1. Introduction

For the past forty years and continuing into the present there have been numerous theoretical calculations which have attempted to obtain agreement with the experimental details of the electronic spectrum of ethylene. Most of this work has centered around the so-called $T \leftarrow N$ and $V \leftarrow N$ transitions, characterized by Mulliken [1, 2] as being *valence* $\pi \rightarrow \pi^*$ excitations. The observed absorption maxima for these two band systems have almost invariably been attributed to *vertical* transitions between the N ground state and the respective excited states in question, in accordance with the Franck-Condon Principle [3].

Nevertheless the results of *ab initio* calculations[1] (through 1970) are not found to be entirely consistent with such an interpretation of the ethylene spectrum, since they indicate that the lowest excited $\pi \rightarrow \pi^*$ singlet state possesses a considerable amount of diffuse character, and yield a *vertical* transition energy for the $V \leftarrow N$ system which exceeds that of the experimental Franck-Condon maximum by a considerable margin.

Given the apparent lack of success on the part of previous calculations on this subject, more recent theoretical treatments have attempted to improve the situation either by enlarging the scope of the earlier calculations (by upgrading the level of CI undertaken [5–7], for example) or by utilizing substantially different methods, such as the RPA approximation [8]. These later calculations have led to some conflicting results concerning the *degree* of diffuse character of the $\pi \rightarrow \pi^*$ singlet and also with respect to the *magnitude* of the vertical transition energy to this state; yet the basic findings that 1) the singlet is calculated to exhibit substantially less valence character than the corresponding triplet and 2) that the vertical transition energy obtained by subtracting the total energies of ground and excited states (for the equilibrium geometry of the ground state) exceeds that of the $V \leftarrow N$ absorption maximum by from 0.3 to 0.6 eV remain unchanged.

The apparently exceptional nature of the transition to the $\pi \rightarrow \pi^*$ singlet is further emphasized by the fact that the calculated results for the corresponding $\pi \rightarrow \pi^*$ triplet seem to be totally consistent with the earlier interpretation of the spectrum; these calculations also find good agreement with the experimental excitation energies to the various low-lying Rydberg states of ethylene [4, 5]. As a result it has been speculated that the measured absorption maximum in the $V \leftarrow N$ bands might actually correspond to a non-vertical transition, whose energy is significantly *lower* than that of the true vertical species. Additional support for this interpretation has been provided by the finding that in the twisted C_2H_4 nuclear arrangement the $\pi \rightarrow \pi^*$ singlet state of planar geometry correlates with the $2\,{}^1B_1$ rather than the lowest state of this symmetry; at the same time the $\pi \rightarrow \pi^*$ state for the *antiplanar* CH_2 conformation is found to correlate with the $\pi \rightarrow 3p_y$ Rydberg species of the planar molecule. Consequently the calculations indicate that the potential curves for CH_2 twist are significantly different for the $\pi \rightarrow \pi^*$ singlet state than for the corresponding triplet and hence suggest that these two states quite possibly exhibit radically different vibrational characteristics.

Ultimately a complete characterization of the electronic spectrum of ethylene must necessarily involve consideration of the vibrational motion which accompanies the transitions between various electronic states. To this end potential curves for both CC stretch and CH_2 twist in the ground and various excited states of ethylene have been obtained in earlier work [5] in order to effect the necessary vibrational analysis for the electronic transitions of this molecule.

2. Outline of the Theoretical Method

The potential curves for ethylene as a function of the CH_2 twisting angle θ and the CC separation R reported previously [5] have been obtained using the

---

[1] A survey of this work may be found in Ref. [4].

Born-Oppenheimer approximation. Accordingly the total wavefunction of the system is defined as the product of the electronic function ψ_e obtained from the CI treatment and a vibrational function ψ_v, which in this treatment is assumed to depend only on the nuclear coordinates R and θ. In addition the assumption is made that the stretching and twisting vibrations are completely separable[2], leading to the following expression for the total wavefunction:

$$\Psi = \psi_e(\boldsymbol{r}_i; R, \theta) \cdot \psi_v(R) \cdot \psi_v(\theta) \tag{1}$$

where the $\boldsymbol{r}_i$ are the coordinates of the electrons of the system.

The vibrational wavefunctions are obtained by an expansion technique. The expression for the stretching mode is taken to be:

$$\psi_v(R) = \sum_n c_n R^{n-1} \exp(-\alpha R^2) \tag{2}$$

with $\alpha = \frac{1}{2}\sqrt{k\mu}$, the harmonic oscillator value (k being the stretching force constant and μ the associated reduced mass with each CH_2 group treated as a point mass). The twisting vibration, in turn, is described by:

$$\psi_v(\theta) = \sum_n a_n \sin 2n\theta \quad \text{or} \quad \sum_n b_n \cos 2n\theta\,. \tag{3}$$

Standard formulas for the kinetic energy [9] are used in constructing the Hamiltonian operators for the two types of nuclear motion. Corresponding potential energy functions are obtained from Fourier series representations of the aforementioned Born-Oppenheimer potential curves. For CC stretch a polynomial in R is employed, while a linear combination of functions of the form $\cos 2n\theta$ is used to represent the CH_2 twisting potential; the number of terms in a given fitting is always taken to be equal to the number of data points available (i.e. four to six for CC stretch and nine to eleven for CH_2 twist [5]).

For a given Hamiltonian the set of vibrational wavefunctions is obtained by energy minimization with respect to the appropriate expansion coefficients. In the representation of $\psi_v(R)$ a total of 16 terms was normally employed but it was found that increasing the size of this basis and/or varying the exponent α from its harmonic oscillator value by $\pm 20\%$ had no significant effect on the position of at least the first ten calculated energy levels. The highest order terms in $\psi_v(\theta)$ are $\sin 60\theta$ and $\cos 60\theta$ respectively; again it was found that inclusion of higher order terms had essentially no effect on the location of the important low-lying vibrational levels. Because the potentials under consideration are of period π, the solutions obtained are necessarily either pure cosine or pure sine series, as indicated in Eq. (3).

The transition moment $\boldsymbol{R}_{e'v'e''v''}$ between vibrational levels of the ground and excited electronic states respectively is then given by the expression

$$\begin{aligned} \boldsymbol{R}_{e'v'e''v''} = \int \cdots \int \psi_{e'}^{*}(\boldsymbol{r}_i; R, \theta) \\ \cdot \psi_{v'}^{*}(R)\, \psi_{v'}^{*}(\theta) \Big(\sum_i \boldsymbol{r}_i\Big)\, \psi_{e''}(\boldsymbol{r}_i; R, \theta)\, \psi_{v''}(R)\, \psi_{v''}(\theta) \cdot d\boldsymbol{r}_i\, dR\, d\theta\,. \end{aligned} \tag{4}$$

---

[2] Explicit SCF and CI calculations indicate that these two types of nuclear motion are only slightly dependent on one another so that this assumption seems quite justified.

In this equation and hereafter primed subscripts refer to the electronic excited state, doubly-primed to the electronic ground state. Within the Born-Oppenheimer Approximation this expression reduces to:

$$\boldsymbol{R}_{e'v'e''v''} = \int\int \psi_{v'}^{*}(R)\, \psi_{v'}^{*}(\theta)\, \boldsymbol{R}_{e'e''}(R,\theta)\, \psi_{v''}(R)\, \psi_{v''}(\theta)\, dR\, d\theta \tag{5}$$

where the electronic transition moment, defined as

$$\boldsymbol{R}_{e'e''}(R,\theta) = \int \cdots \int \psi_{e'}^{*}(\boldsymbol{r}_i; R,\theta) \left(\sum_i \boldsymbol{r}_i\right) \psi_{e''}(\boldsymbol{r}_i; R,\theta)\, d\boldsymbol{r}_i\,, \tag{6}$$

depends only parametrically on the nuclear coordinates. Analogous formulas for the transition moments based on the dipole velocity operator ($\boldsymbol{V}_{e'v'e''v''}$) are obtained similarly.

In the usual assumption $\boldsymbol{R}_{e'e''}$ is treated as a constant vector, leading to what is commonly referred to as the Franck-Condon Principle [3]. Explicit calculation of $\boldsymbol{R}_{e'e''}$ for the various states of ethylene show, however, that $\boldsymbol{R}_{e'e''}$ generally depends quite strongly on θ, although only to a much smaller extent on R, and thus in what follows the electronic transition moment is assumed to be a function of θ but to be independent of R. As a result the contribution to the total transition moment due to CC stretch is made strictly in terms of the vibrational overlap of the two corresponding wavefunctions, while the part caused by the twisting vibration is obtained more directly. The final expression used is thus:

$$\boldsymbol{R}_{e'v'e''v''} = \int \psi_{v'}(R)\, \psi_{v''}(R)\, dR \cdot \int \psi_{v'}(\theta)\, \boldsymbol{R}_{e'e''}(\theta)\, \psi_{v''}(\theta)\, d\theta\,. \tag{7}$$

This equation is then evaluated by inserting a Fourier representation of $\boldsymbol{R}_{e'e''}$. Corresponding oscillator strengths for a given vibrational transition have subsequently been obtained as:

$$f_{e'v'e''v''} = \tfrac{2}{3}\, \Delta E\, |\boldsymbol{R}_{e'v'e''v''}|^2 \tag{8}$$

or

$$f_{e'v'e''v''} = \tfrac{2}{3}\, |\boldsymbol{V}_{e'v'e''v''}|^2 / \Delta E \tag{9}$$

where ΔE is the transition energy between the vibrational levels involved[3]. The *total* oscillator strength for a given electronic transition is then obtained as the sum of all $f_{e'v'e''v''}$ values between the ground state vibrational level of $\psi_{e''}$ (that is, ignoring the possibility of thermally excited vibrations in the electronic ground state) and *all* the vibrational states of the electronically excited species.

3. Transition Probabilities to the $\pi \rightarrow \pi^*$ States in Ethylene

A) Vibrational Wavefunctions and Energy Levels

The potential curves used in the treatment of the vibrational characteristics of the electronic spectrum of ethylene are those of the CI-1 calculation reported earlier [5, 10]. The ground state CH_2 twisting potential curve is given in Fig. 1 and has been obtained by means of pointwise calculation of the total energy for 11 different values of θ between 0° and 90° inclusively ($R = 1.35$ Å). The vibrational levels calculated for this potential are also shown in Fig. 1; successive

---

[3] All values are in atomic units.

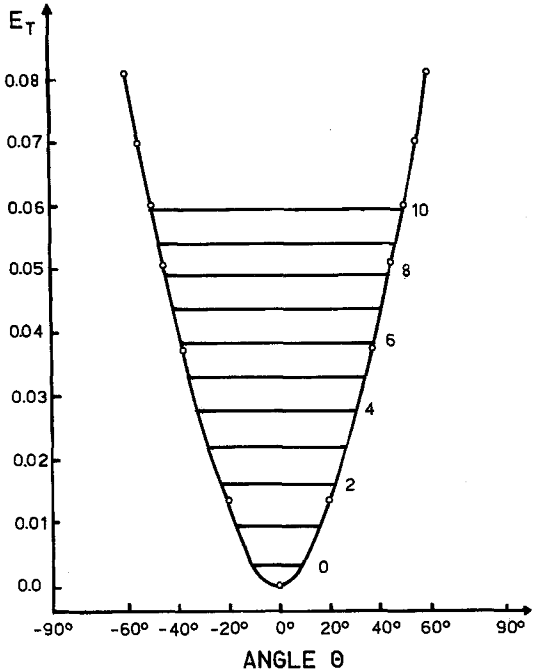

Fig. 1. CH_2 twisting potential curve for the ground state of ethylene obtained from the CI-1 treatment ($R_{CC} = 1.35$ Å). Calculated vibrational levels for $v_4'' = 0$ to $v_4'' = 10$ are also included. In this paper all energy values, unless specified otherwise, are given in hartrees

energy differences between even levels[4] are found to decrease with increasing vibrational quantum number, levelling off to a value of approximately 1100 cm^{-1}, as compared to the experimental [11] result of 1023 cm^{-1}. The corresponding vibrational wavefunctions for the lowest three states of even quantum number are plotted in Fig. 2.

The ground state CC stretch potential curve was obtained for a planar arrangement of CH_2 groups and the resulting optimum value of R (1.35 Å) and the calculated stretching force constant (9.9 mdyn/Å) are in good agreement with the experimental values of 1.338 ± 0.003 Å [11] and 9.305 mdyn/Å [12, 13] respectively. Since the CC stretch normal coordinate is actually a mixture involving some CH stretch and ∢ HCH bending (a_g species), however, the calculated frequency of 1100 cm^{-1} obtained by using the pure CC stretch potential curve considerably underestimates the observed spectral frequency (1623 cm^{-1}) [11]. The three lowest energy vibrational wavefunctions for the pure stretching motion are plotted in Fig. 3.

Previous calculations [5] have shown that in the planar molecule the $\pi \rightarrow 3py(^1B_{1g})$ state possesses a lower energy than the $\pi \rightarrow \pi^*(^1B_{1u})$, a result which is of great interest since both of these states transform according to the same $(^1B_1)$ irreducible representation in the reduced symmetry of the twisted molecule.

---

[4] The selection rules for the (a_u) twisting vibration are such that only the even (cosine) levels of the upper electronic state can combine with the lowest vibrational level of the ground state.

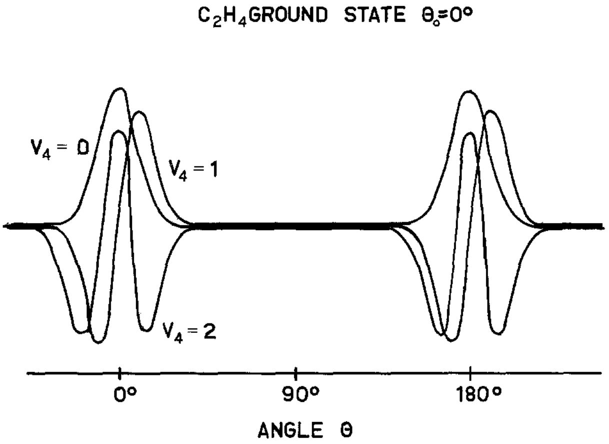

Fig. 2. Calculated vibrational wavefunctions for the CH_2 twisting mode in the C_2H_4 ground state obtained from the potential curve in Fig. 1

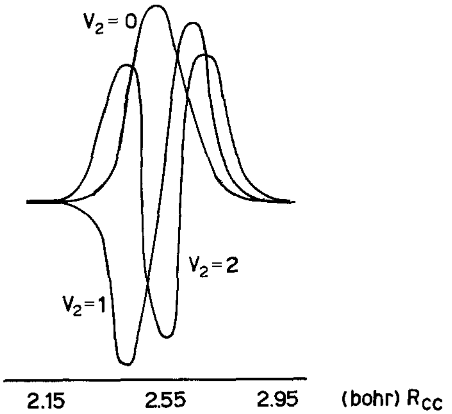

Fig. 3. Calculated vibrational wavefunctions for the CC stretching mode in the ground state of ethylene

Consequently application of the non-crossing rule for these two states leads to a quite sharp avoided crossing, as can be seen from the calculated CH_2 twisting potential curves given in Fig. 4 ($R = 1.35$ Å in both cases). In other words, according to the calculations the valence $\pi \rightarrow \pi^*$ singlet species for $\theta = 90°$ (lowest $^1B_1$ state at this angle) does not correlate with the more diffuse $\pi \rightarrow \pi^*$ singlet found for the planar molecule; such a situation has not been anticipated in the earlier analysis by Mulliken [1, 2, 11] and others. Because there is reason to believe that *both* $^1B_1$ states are responsible for the $V \leftarrow N$ absorption in the ethylene spectrum, the more stable of these species will hereafter be referred to as the V_g, the less stable as the V_u state; the respective subscripts refer to the inversion symmetry characteristics of each species in the planar nuclear arrangement.

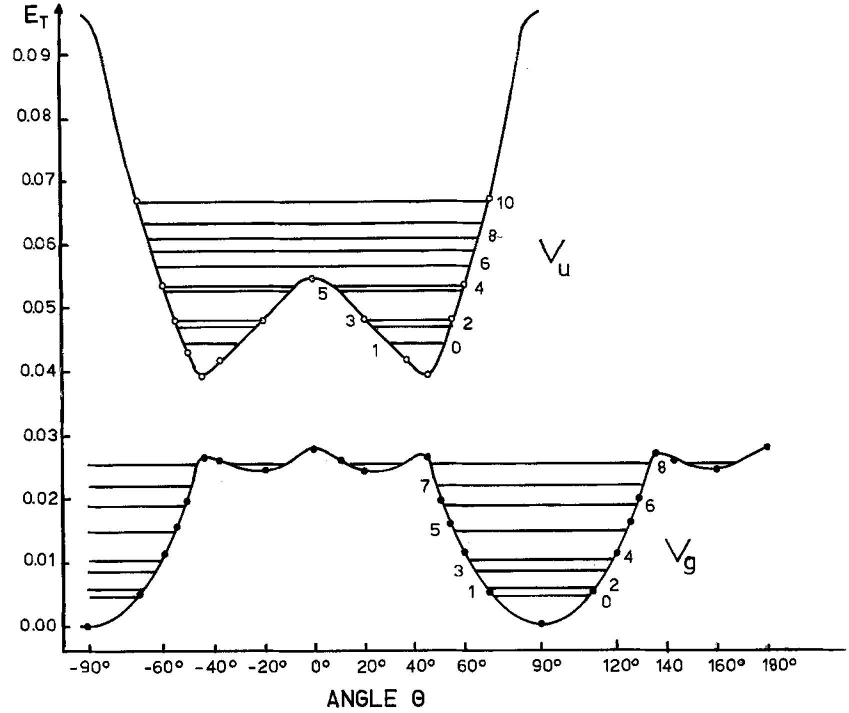

Fig. 4. CH$_2$ twisting potential curves for the $({}^1B_{1g} - 1\,{}^1B_1 - {}^1B_2)V_g$ and the $({}^1B_{1u} - 2\,{}^1B_1 - {}^1A_2)V_u$ excited states of ethylene obtained from the CI-1 treatment ($R_{CC} = 1.35$ Å). The lowest calculated vibrational levels are also indicated

Vibrational levels calculated for both states are also indicated in Fig. 4. In the upper V_u state one observes a characteristic doubling of levels, which is expected in view of the double-minimum nature of the corresponding twisting potential curve ($\theta_0 = \pm 42.5°$). Vibrational levels for the V_g state are also doubled but to a lesser extent than for the V_u species. The V_g state possesses two types of energy minima, one corresponding to the valence $\pi \rightarrow \pi^*$ region, the other to the more Rydberg-like region of the potential. The optimum bond distances for the V_g and V_u states are calculated to be nearly equal (1.39 Å) and, perhaps more importantly, are found to differ by a relatively small amount from the ground state equilibrium value, in sharp contrast to the behavior predicted for the V state in previous work [11].

B) Electronic Transition Moments

In the present theoretical treatment calculation of the electronic transition moment $\boldsymbol{R}_{e'e''}$ is complicated by the fact that the electronic wavefunctions obtained for ground and excited states are expanded in configurations based on *different* sets of MO's, due to the nature of the CI(PCMO) method employed[5]. In order to take advantage of the computional simplifications arising from the use of the

---

[5] In these calculations the SCF MO's of a given state (parent configuration) are used in its own CI expansion; details of this procedure are given elsewhere [10].

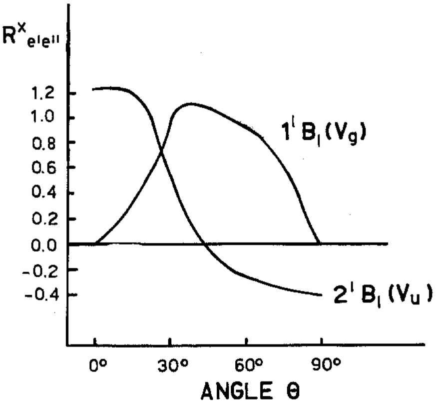

Fig. 5. Variation of the x-component of the electronic transition moment $R_{e'e''}$ between the ground state and the two states of ${}^1B_1$ symmetry [obtained in the CI(GSMO) treatment] as a function of the CH_2 twisting angle θ

same set of MO's in the CI expansions for $\psi_{e'}$ and $\psi_{e''}$, additional CI calculations have been carried out which employ the ground state SCF MO's as the basis in the treatment for each excited state [CI(GSMO) method]; in addition the ground state wavefunction has also been obtained by using the SCF MO's of various of the excited states.

The variation with θ of the electronic transition moment $R_{e'e''}$ between the ground state and each of the two ${}^1B_1$ excited states obtained from the CI(GSMO) treatment is shown in Fig. 5. (Only the x-component is non-zero.) Transitions to the V_u state are allowed for the planar geometry and hence $R^x_{e'e''}$ for this species begins with a non-zero value at $\theta = 0^0$ but decreases quite rapidly beyond $\theta = 20°$, reaching a negative value for $\theta = 90°$ ($2\,{}^1B_1$ correlates with a ${}^1A_2$ state in D_{2d} symmetry, to which transitions from the ${}^1B_1$ ground state are also allowed). In contrast the corresponding curve for the V_g state is zero[6] at $\theta = 0°$ and $\theta = 90°$ and has a maximum around 38°. In both cases the transition moments are far from constant with twisting, contrary to what is often assumed in connection with the application of the Franck-Condon Principle.

From the $R^x_{e'e''}$ curve for the V_u state it is clear that simple changes in the valence character of excited states are not sufficient to explain even the most rudimentary aspects of the transition moment behavior upon CH_2 twist since the observed increase in valence character for this state with increasing θ would ordinarily be expected to lead to an *increase* rather than to the decrease actually calculated. A factor of greater importance is the relative orientation of initial and final orbitals in such electronic transitions; thus the fact that these two MO's in the case of the $N - V_u$ transition possess their respective charge density maxima in rapidly diverging coordinate planes as CH_2 twist prodeeds is largely responsible for the calculated decrease in transition moment. These observations emphasize quite strongly that the degree of valence character for an excited state is far from

---

[6] Transitions from the ${}^1A_g$ to the ${}^1B_{1g}$ in D_{2h} and from ${}^1B_1$ to ${}^1B_2$ in D_{2d} symmetry are forbidden under the dipole selection rules.

the sole determining factor in the probability of its transitions from the ground state and thus that calculations of quantities such as $\langle x^2 \rangle$ and $\langle z^2 \rangle$, which are a measure almost exclusively of the diffuseness of the upper state, can be quite misleading.

C) Transition Probabilities

Oscillator strengths for transitions between the vibrationless ($v''_2 = v''_4 = 0$) ground state and the $2\,^1B_1(V_u)$ excited state, as calculated from Eq. (8) using the electronic transition moments discussed above, are contained[7] in Table 1. These results show the most probable vibrational transition to the V_u upper state to correspond to an excitation energy of 7.894 eV, despite the fact that the *vertical* transition energy (calculated as the difference between the electronic energies of ground and excited state for the equilibrium geometry of the former) is considerably larger [5], namely 8.250 eV. The upper vibrational state in question is characterized by $v'_2 = 0$ (pure stretching) and $v'_4 = 2$ (torsional vibration); the "vertical" transition, on the other hand, corresponds most closely to either $v'_4 = 8$ (on the basis of the 8.275 eV ΔE value of Table 1) or to $v'_4 = 6$ (based on the results in Fig. 4)[8]. In other words, these calculations find that the most probable transition is markedly non-vertical, as has been speculated earlier [4, 5].

The cause of this non-verticality can be qualitatively understood from the form of the vibrational wavefunctions given in Fig. 6. Since the potential curve

Table 1. Tabulation of transition energies ΔE and oscillator strengths f for the $2\,^1B_1(V_u)$ state of C_2H_4. All results are obtained relative to the lowest vibrational level of the (^1A_g) ground state ($v''_2 = v''_4 = 0$). The corresponding calculated electronic vertical transition energy is 8.250 eV

v'_4	f	ΔE (eV)	f	ΔE (eV)	f	ΔE (eV)
	$v'_2 = 0$		$v'_2 = 1$		$v'_2 = 2$	
0	0.0005	7.813	0.0001	7.925	0.0000	8.036
2	0.1405	7.894	0.0239	8.005	0.0009	8.116
4	0.0109	8.049	0.0019	8.160	0.0001	8.271
6	0.0644	8.154	0.0109	8.265	0.0004	8.376
8	0.0157	8.275	0.0027	8.387	0.0001	8.497
10	0.0081	8.427	0.0014	8.539	0.0001	8.650
12	0.0035	8.580	0.0006	8.692	0.0000	8.803
14	0.0014	8.749	0.0002	8.861	0.0000	8.972
16	0.0006	8.924	0.0001	9.035	0.0000	9.146
18	0.0002	9.093	0.0000	9.205	0.0000	9.316
20	0.0001	9.249	0.0000	9.360	0.0000	9.471
$\sum_{v'_4}$	0.2459	—	0.0418	—	0.0016	—
$\sum_{v'_2} \sum_{v'_4} f = 0.289$						

---

[7] The notation for the vibrational quantum numbers used in this paper is essentially that of Herzberg [14], except that in the present work ν_2 refers to a pure CC stretch motion rather than to a normal coordinate (see Sect. 3 A).

[8] The uncertainty as to which of these values for v'_4 most closely corresponds to the condition of verticality is a reflection of the rather large difference between the zero point energies of the N and V_u states respectively.

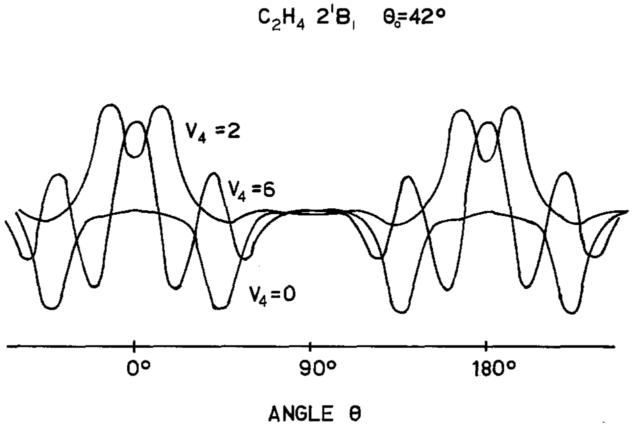

Fig. 6. Calculated important vibrational wavefunctions for the CH_2 twisting mode in the $2\,^1B_1(V_u)$ excited state obtained from the corresponding potential curve in Fig. 4

Table 2. Vibrational overlaps $S(v_4', v_4'')$ and electronic transition moments $R^x_{e'v'e''v''}$ between various $2\,^1B_1(V_u)$ twisting vibrational wavefunctions and that of the lowest vibrational level ($v_4''=0$) of the ground state

v_4'	v_4''	$S(v_4', v_4'')$	$R^x_{e'v'e''v''}$	$R^x_{e'v'e''v''}/S(v_4', v_4'')$
0	0	0.045	0.053	1.164
	2	0.762	0.923	1.211
	4	0.206	0.255	1.238
	6	0.503	0.615	1.223
	8	0.253	0.302	1.194
	10	0.184	0.215	1.168
	12	0.121	0.140	1.157
	14	0.074	0.087	1.183
	16	0.046	0.056	1.219
	18	0.028	0.036	1.254
	20	0.019	0.024	1.279

of the V_u state has its minimum at $\theta = 42°$, there is as expected practically no overlap between the $v_4' = 0$ function with its maximum at this angle and the $v_4'' = 0$ function with its maximum at $\theta = 0°$ (Fig. 2). Nevertheless, the equilibrium angles for the N and V_u states are sufficiently close to one another to enable the vibrational wavefunction for $v_4' = 2$ to have the greatest overlap with the $v_4'' = 0$ function of any of the upper state twisting species (see Table 2), even though its maxima occur for a distinctly non-planar conformation of the CH_2 groups (see Fig. 6). One finds that of the two species to which transitions could be called vertical, the $v_4' = 8$ function has only a relatively small overlap with the vibrationless ground state, while that for the $v_4' = 6$ function is quite substantial; in the latter case the Franck-Condon factor (S^2) is still only 0.25, however, as compared to the corresponding value of 0.58 for the $v_4' = 2$ species. Moreover, the fact that the so-called vertical transitions are not found to be the most probable does not actually constitute a violation of the Franck-Condon Principle, which merely states that the ratio between the transition moment $\boldsymbol{R}_{e'v'e''v''}$ and the corresponding vibrational overlap is very nearly constant (see Table 2).

These results serve to emphasize the need for unequivocal evidence (experimental or theoretical) concerning the relative location of the V_g state, since it is obvious from the present treatment that the presence of this state below the V_u has a dramatic effect upon the description of the absorption bands in the 7.5 to 8.5 eV region of the electronic spectrum of ethylene. In addition, since the validity of the Born-Oppenheimer approximation depends critically upon the magnitude of the energy difference between neighboring states, it is clear that an accurate estimate of the closest approach of the twisting potential curves for the V_g and V_u species is also required (in the present treatment this energy difference is calculated to be 0.3 eV; see Fig. 4). In the absence of the V_g state the V_u potential curve would be very similar to that of the $\pi \rightarrow \pi^*$ triplet state, namely with a minimum occurring for $\theta = 90°$, as has been assumed in earlier interpretations.

In order to determine to what extent the results given in Tables 1 and 2 depend on the specific nature of the calculated potential curves and electronic transition moment data, a number of additional calculations have been carried out. A limited CI(GSMO) calculation has been employed in the treatment of the important $^1B_1$ excited states, but this method is clearly not as reliable, primarily because it leads to an excessively diffuse wavefunction [5] for the $\pi \rightarrow \pi^*$ singlet in the planar geometry. As a result not only is the absolute energy of this state $(2\,^1B_1)$ substantially higher than in the CI(PCMO) treatment but also the curvature of its twisting potential curve is much less pronounced in the neighborhood of $\theta = 0°$[9]. Consequently the fact that the non-verticality of the most probable transition is not as pronounced in this case (absorption maximum at 8.09 eV after correcting for the difference in vertical electronic transition energy) is not at all surprising; indeed, since more extensive calculations [6, 7] indicate *more* rather than less valence character for the planar $\pi \rightarrow \pi^*$ singlet than has been found in the present CI(PCMO) treatment, it seems likely that the actual non-verticality of the observed $V \leftarrow N$ transition is even *greater* than that indicated by the results of Table 1.

An alternative method has also been used to calculate the electronic transition moment $\boldsymbol{R}_{e'e''}$. If the curves in Fig. 5, which result from the use of the ground state SCF MO's are replaced by those obtained from a CI calculation in which the excited state SCF MO's are used for all species (including the ground state), the essential features of the vibrational structure of the $N - V_u$ transition remain unchanged; in particular, the most probable transition is again found to occur at an energy of 7.894 eV.

Use of the dipole velocity rather than the dipole length operator in the transition moment calculation leads to identical oscillator strengths according to Eqs. (8) and (9) respectively if the exact wavefunctions are employed. For the wavefunctions of the present treatment, however, oscillator strengths obtained using the dipole velocity operator are found to be considerably smaller than the

---

[9] The situation is entirely analogous to that found in formaldehyde [10], for which the limited CI(GSMO) predicts a planar geometry for the $n \rightarrow \pi^*$ excited states whereas the analogous CI(PCMO) treatment correctly finds the non-planar structure to be more favored.

corresponding dipole length values given in Table 1; thus while the total oscillator strength for the $N - V_u$ transition calculated using $\boldsymbol{R}_{e'e''}$ is 0.289, in good agreement with the experimental value [11] of 0.34, the value obtained by employing $\boldsymbol{V}_{e'e''}$ is only one-eighth as large[10]. Nevertheless despite the large disparity in the absolute magnitudes of the two types of oscillator strengths, it is still found that the prediction of the *relative* intensities of the various vibrational transitions in this system is essentially unaffected by the exchange of these two operators, especially in the identification of the most probable transition. In summary, while the uncertainty in the absolute intensity calculated for the $N - V_u$ system underscores the need for more accurate wavefunctions in this study, the observed stability in the relative transition probability results leaves little doubt that this calculated excitation should be identified with the experimental $V \leftarrow N$ absorption bands, at least in the region of the Franck-Condon maximum.

D) Importance of the V_g State

The indirect role of the $^1B_1(V_g)$ state in determining the shape of the CH_2 twisting potential curve for the $2\,^1B_1(V_u)$ species has already been discussed. The more direct influence of the V_g state upon the electronic spectrum of ethylene may be considered from the results of Table 3. The O—O transition is calculated to

Table 3. Tabulation of transition energies ΔE and oscillator strengths f for the $1\,^1B_1(V_g)$ state of C_2H_4. All results are obtained relative to the lowest vibrational level of the (^1A_g) ground state ($v_2'' = v_4'' = 0$). The corresponding calculated electronic vertical transition energy is 7.517 eV

v_4'	f	ΔE (eV)	f	ΔE (eV)	f	ΔE (eV)
	$v_2' = 0$		$v_2' = 1$		$v_2' = 2$	
0	0.00000	6.756	0.00000	6.886	0.00000	7.015
2	0.00009	6.786	0.00003	6.917	0.00001	7.046
4	0.00000	6.911	0.00000	7.042	0.00000	7.171
6	0.00000	7.140	0.00000	7.270	0.00000	7.400
8	0.00003	7.326	0.00001	7.456	0.00000	7.586
10	0.00011	7.393	0.00003	7.523	0.00001	7.653
12	0.00005	7.583	0.00002	7.713	0.00000	7.843
14	0.00116	7.728	0.00035	7.858	0.00007	7.988
16	0.00008	7.791	0.00002	7.922	0.00001	8.051
18	0.00026	7.997	0.00008	8.128	0.00002	8.257
20	0.00054	8.233	0.00016	8.364	0.00003	8.493
22	0.00132	8.469	0.00040	8.600	0.00008	8.729
24	0.00212	8.679	0.00064	8.809	0.00013	8.939
26	0.00098	8.886	0.00030	9.016	0.00006	9.145
28	0.00016	9.139	0.00005	9.270	0.00001	9.399
30	0.00000	9.425	0.00000	9.555	0.00000	9.684
$\sum_{v_4'}$	0.00690	—	0.00209	—	0.00043	—
$\sum_{v_2'} \sum_{v_4'} f = 0.00945$						

---

[10] In previous work fairly large discrepancies between $f(\boldsymbol{r})$ and $f(\boldsymbol{V})$ values have been noted in connection with near Hartree-Fock calculations [15, 16] and also for some rather limited CI treatments [17].

occur at an energy of 6.756 eV, and this result coupled with the more qualitative information that the potential minimum for this state corresponds to the $\pi \rightarrow \pi^*$ singlet species for the antiplanar CH_2 conformation leads one to associate this state with the experimental O–O transition of the $V-N$ bands. Such an assignment presupposes that what has heretofore been assumed to be a *single* electronic transition corresponds in realty to two such species, and in fact the rather irregular spacing of the vibrational levels found for both the V_g and V_u states and the near equality of their respective twisting force constants (V_g: $4.05 \cdot 10^{-11}$ erg/rad^2 and V_u: $3.07 \cdot 10^{-11}$ erg/rad^2) indicate that under these circumstances a complete resolution might indeed be difficult. The experimental value for the O–O energy of the $V-N$ bands is obtained from a long extrapolation of the (supposed) CH_2 twisting frequency of the upper state in this system and has been a matter of no little controversy, with values of 4.9 eV and 5.8 eV both having been proposed [11, 18]; at present the higher of these values seems to be the favored result [19]. In any event the calculated value in Table 3 appears to be too high and it thus appears likely that more extended CI treatments will find a lowering in the energy of the $\pi \rightarrow \pi^*$ singlet in the antiplanar CH_2 arrangement relative to that of the planar ground state.

The calculated transition probabilities for the V_g state show one fairly sharp and relatively weak line at 7.728 eV for $v'_4 = 14$ and a second broader maximum of greater intensity between 8.469 and 8.679 eV with $v'_4 = 22$ and 24 respectively ($v'_2 = 0$ is again most probable for the CC stretching vibration)[11]. Since the vertical *electronic* excitation energy to the V_g state is 7.52 eV [5], the first of these maxima can be said to correspond roughly to a vertical transition. From the vibrational wavefunctions plotted in Fig. 7 it can qualitatively be seen that this species has by far the greatest overlap with the vibrationless ground state

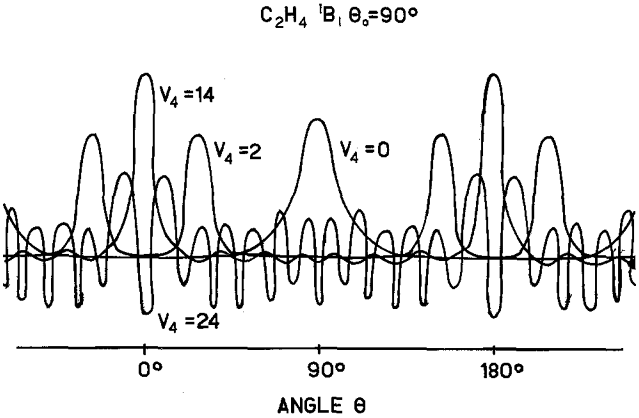

Fig. 7. Calculated important vibrational wavefunctions for the CH_2 twisting mode in the $^1B_1(V_g)$ excited state obtained from the corresponding potential curve in Fig. 4

---

[11] If a deeper potential minimum for the V_g state is assumed for better agreement with the experimental O–O transition energy while the $\theta = 0°$ region of this potential curve is left unaltered, only rather small changes in the location of the probability maxima occur, with a general shift towards larger wavelengths.

Table 4. Vibrational overlaps $S(v_4', v_4'')$ and electronic transition moments $R^x_{e'v'e''v''}$ between various $^1B_1(V_g)$ twisting vibrational wavefunctions and that of the lowest vibrational level ($v_4''=0$) of the ground state

v_4''	v_4'	$S(v_4', v_4'')$	$R^x_{e'v'e''v''}$	$R^x_{e'v'e''v''}/S(v_4', v_4'')$
0	0	0.0000	0.0000	0.496
	2	0.0555	0.0270	0.486
	4	0.0003	0.0001	0.456
	6	0.0024	0.0010	0.419
	8	0.0355	0.0143	0.403
	10	0.0747	0.0295	0.395
	12	0.0587	0.0201	0.342
	14	0.9226	0.0918	0.099
	16	0.0067	0.0243	3.627
	18	0.0704	0.0423	0.600
	20	0.1123	0.0604	0.537
	22	0.1796	0.0932	0.519
	24	0.2308	0.1168	0.506
	26	0.1620	0.0788	0.486
	28	0.0725	0.0314	0.433
	30	0.0242	0.0057	0.235

(Fig. 2) but at the same time it is obvious from Table 4 that the ratio between the electronic transition moment and vibrational overlap is far from constant for this system, reflecting of course the nominal (dipole) forbiddenness of the $N-V_g$ transitions. As a result the upper vibrational state with the greatest transition probability corresponds to $v_4'=24$, by virtue of the relatively delocalized characteristics of its wavefunction, even though its vibrational overlap with the ground state is actually quite small.

The sharp transition calculated at 7.728 eV could be characterized as a Rydberg species resulting from a $\pi \rightarrow (3py+3py)$ excitation, which in turn has been suggested by Merer and Mulliken [11] as being responsible for the 7.45 eV peak in the electron impact spectrum of ethylene found by Ross and Lassettre [20]. On the other hand another transition which seems equally likely to be associated with this experimental peak is the $\pi \rightarrow (3s-3s)$ species [11], which is also dipole forbidden but quadrupole allowed, and which has been calculated [4] to have very nearly the same vertical electronic excitation energy.

E) The $\pi \rightarrow \pi^*$ Triplet State

The complicating factors inherent in the description of the CH_2 twisting energy surface of the $\pi \rightarrow \pi^*$ singlet state of ethylene appear to have no counterpart in the case of the corresponding triplet T state; the angular potential curve obtained in the present treatment [5] is essentially equivalent to that predicted for this species earlier by Mulliken [1, 2]. Transitions to this state from the ^1A_g ground state are of course spin forbidden. Nevertheless it was decided to carry out oscillator strength calculations on the basis of the calculated T state potential curves (for CC stretch as well as CH_2 twist) under the assumption of a constant electronic transition moment in order to facilitate a comparison with the V_u and V_g state results. It is found that the vertical transition ($v'_2 = 4$ and $v'_4 = 8$) calculated at 4.04 eV is indeed most probable, as expected from the Franck-Condon Principle. This transition energy is somewhat lower than the vertical *electronic* transition energy (4.17 eV) obtained in the standard way; the small discrepancy is caused in large part by the differences in zero point energies for the N and T states.

Recent experimental studies [21] locate the maximum intensity in the $N-T$ bands at 4.22 eV, in quite good agreement with the present calculations[12]. The calculated O–O transition energy [5] (2.72 eV), however, is considerably lower than the T_0 value (3.6 eV) generally quoted on the basis of extrapolations of the CH_2 twisting frequency v'_4 of the T state. On the other hand, this experimental value seems to be in conflict with the established value of 2.83 eV (65 kcal/mole) for the barrier to internal rotation in the N state, since according to Hund's rules at $\theta = 90°$ the T state should be slightly more stable than the N state. The present calculation do in fact place the T state in antiplanar ethylene some 0.05 eV *below* the N state and furthermore represent the N-state barrier very well (2.764 eV). Merer and Mulliken [11] have recently estimated the actual T_0 value for this transition to be even smaller (~ 2.50 eV) than that presently calculated.

4. Vibrational Structure of the Rydberg Bands in Ethylene

A) The $\pi \rightarrow (3s+3s)$ Rydberg Bands

In order to further investigate the reliability of the foregoing analysis of the $\pi \rightarrow \pi^*$ transition of ethylene an analogous study has been carried out for the allowed Rydberg transitions in this spectrum. The lowest of these energy bands is the $N-R$ species with a T_0 value of 7.11 eV. It has been assigned by Wilkinson and Mulliken [22] as the $\pi \rightarrow 4a_g(3s+3s)$ transition, and earlier calculations by the authors [4, 5] are in complete agreement with this interpretation. The CH_2 twisting potential curve ($R = 1.35$ Å) for the upper state with associated calculated vibrational levels is shown in Fig. 8; the molecule is seen to be slightly non-planar in this state. Calculated equilibrium R_{CC} and θ values are 1.41 Å and 20° compared to the experimental data of 1.41 Å and 25° respectively. Although the calculated twisting barrier is comparatively small (0.0038 hartree) it still greatly overestimates the experimental value [23] of only 289 cm^{-1} or 0.0013 hartree; indeed the SCF treatment employed in these calculations finds a potential minimum for the planar geometry, i.e. no barrier *at all.*

The R state correlates with the degenerate ^1E species for the D_{2d} arrangement of CH_2 groups and as a consequence the twisting potential curve does not show a maximum with a horizontal tangent at odd multiples of $\theta = 90°$ but rather intersects at these points with the potential curve of the other component of the ^1E state. Merer and Schoonveld [23] have pointed out that this potential curve, with a period of 2π instead of π (as in the cases discussed above) requires in

---

[12] This experimental value is somewhat lower than the 4.4–4.6 eV range for this absorption maximum given previously [11].

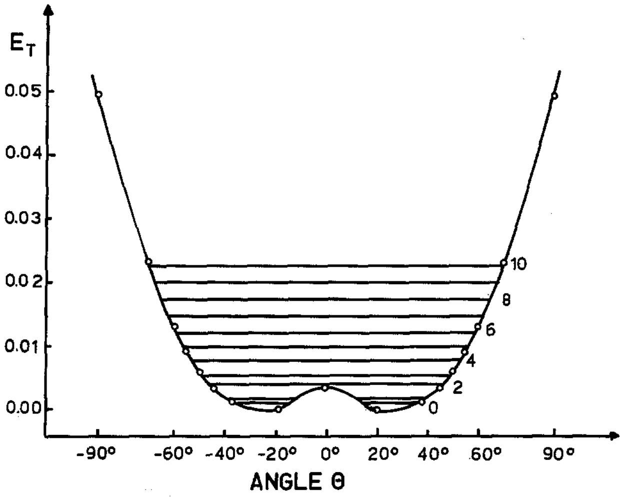

Fig. 8. CH_2 twisting potential curve for the $\pi \rightarrow (3s+3s)$ or R state of ethylene obtained from the CI-1 treatment ($R_{CC} = 1.35$ Å). The lowest calculated vibrational levels are also indicated

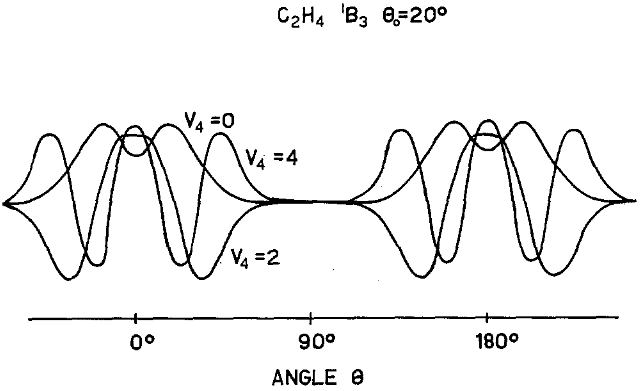

Fig. 9. Calculated important vibrational wavefunctions for the CH_2 twisting mode in the R state of ethylene obtained from the corresponding potential curve in Fig. 8

principle a more sophisticated treatment for obtaining the vibrational structure than has been outlined in Sect. 2. In practice, however, the more complicated treatment seems to have very little effect on the location of the *low-lying* twisting energy levels [23] and thus the results shown in Fig. 8 have been obtained in the same manner as the vibrational levels discussed previously (i.e. the potential is assumed to be periodic in π). The lowest energy vibrational wavefunctions of even quantum number obtained from this treatment are plotted in Fig. 9, from which it can be seen that a number of these species have appreciable overlap with the $v_4'' = 0$ ground state function (see Fig. 2).

The variation of electronic transition moment for the $R-N$ system with CH_2 twist is plotted in Fig. 10; there are two non-zero components for all angles

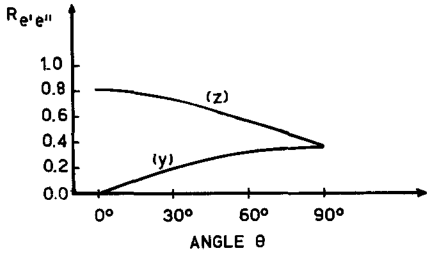

Fig. 10. Variation of the y- and z-components of the electronic transition moment $R_{e'e''}$ between the ground state of ethylene and the R state [obtained in the CI(GSMO) treatment] as a function of the CH_2 twisting angle θ

Tabelle 5. Tabulation of transition energies ΔE and oscillator strengths f for the $1\,^1B_3(R)$ state of C_2H_4. All results are obtained relative to the lowest vibrational level of the (^1A_g) ground state $(v_2''=v_4''=0)$. The corresponding calculated electronic vertical transition energy is 6.939 eV

v_4'	f	ΔE (eV)	f	ΔE (eV)	f	ΔE (eV)
	$v_2'=0$		$v_2'=1$		$v_2'=2$	
0	0.0192	6.645	0.0138	6.781	0.0060	6.916
2	0.0196	6.719	0.0141	6.856	0.0062	6.991
4	0.0091	6.819	0.0065	6.956	0.0029	7.091
6	0.0026	6.941	0.0019	7.077	0.0008	7.212
8	0.0008	7.078	0.0005	7.214	0.0002	7.350
10	0.0002	7.225	0.0002	7.362	0.0001	7.497
12	0.0001	7.381	0.0001	7.517	0.0000	7.652
14	0.0000	7.545	0.0000	7.681	0.0000	7.816
16	0.0000	7.713	0.0000	7.850	0.0000	7.985
$\sum_{v_4'}$	0.0516	—	0.0371	—	0.0162	—
$\sum_{v_2'}\sum_{v_4'} f = 0.114$						

except $\theta=0°$. The oscillator strengths for the various vibrational transitions present in this system (that is, those which involve either the CH_2 twisting or the CC stretch coordinates) calculated according to Eq. (8) on the basis of $R_{e'e''}$ data of Fig. 10 are listed in Table 5. Experimentally this transition appears as a progression of doublets [11, 24] in the stretching frequency ν_2', with this doubling of levels believed to be caused by the nearly equal strengths of transitions to the first two even twisting vibrational species of the upper state. This behavior is mirrored in the calculated results, with transitions to $v_4'=2$ being only slightly more probable than to the $v_4'=0$ level. In addition it appears from these calculations that high overlap with the $v_2''=0$ ground state function is possible for the first two or three stretching levels of the R state, in contrast to what has been observed for the $\pi \rightarrow \pi^*$ states discussed previously; the doublet corresponding to the lowest v_2' level, however, is calculated to be the most intense, in agreement with what is observed experimentally [1, 22, 23].

The calculated T_0 value is only 6.645 eV, smaller by nearly 0.5 eV than the experimental result. Most of this discrepancy appears to come from the calculation of the vertical electronic energy difference, as evidenced by the fact that this quantity *increases* from 6.94 eV in the CI-1 treatment [5] (used for the present analysis) to 7.11 eV in the more extended CI-2 calculation also carried out by the authors. The fact that the potential curve in Fig. 8 overestimates the rotational barrier is undoubtedly also responsible for some (but certainly not all) of the remaining discrepancy (0.30 eV) between calculated and experimental T_0 values; the shallowness of the double minimum indicates that no more than 0.05 to 0.10 eV of this difference can be attributed to this effect. The total oscillator strength obtained from this transition (0.114) is also somewhat at odds with the experimentally observed value of approximately 0.03, but again uncertainties of this magnitude in absolute intensities are not unexpected. In summary, the assignment of this $N-R$ transition as being $\pi \rightarrow (3s+3s)$ is unambiguously supported by the present calculations.

B) The $\pi \rightarrow 3d\sigma(3pz+3pz)$ Rydberg Bands

The next allowed Rydberg transition found in the present calculations involves the $5a_g$ MO as the upper orbital. It has been shown earlier [4] that this MO is basically a $3d\sigma$ semi-united atom species, despite the fact that it is constructed in the present basis almost exclusively from the in-phase combination of $3pz$ AO's on the carbons. The CC stretching and CH_2 twisting potential curves obtained for this excited state are almost wholly similar to those discussed for the $\pi \rightarrow (3s+3s)$ R state (see Fig. 8) and the corresponding vibrational oscillator strength calculations (Tables 5–6) also have a strong resemblance to one another, complete with the pattern of doublets caused by corresponding transitions to $v'_4=0$ and $v'_4=2$ respectively.

There are two transitions found experimentally (T_0 values of 8.257 eV and 8.618 eV) in the appropriate region of the ethylene spectrum, characterized by

Table 6. Tabulation of the transition energies ΔE and oscillator strengths for the $2\,^1B_3$ state of C_2H_4. All results are obtained relative to the lowest vibrational level of the (^1A_g) ground state ($v''_2=v''_4=0$). The corresponding calculated electronic vertical transition energy is 8.437 eV

v'_4	f	ΔE (eV)	f	ΔE (eV)	f	ΔE (eV)
	$v'_2=0$		$v'_2=1$		$v'_2=2$	
0	0.0054	8.153	0.0038	8.287	0.0018	8.418
2	0.0054	8.223	0.0038	8.357	0.0018	8.488
4	0.0022	8.324	0.0015	8.458	0.0007	8.590
6	0.0006	8.446	0.0004	8.580	0.0002	8.712
8	0.0002	8.584	0.0001	8.718	0.0001	8.849
10	0.0001	8.732	0.0000	8.865	0.0000	8.997
12	0.0000	8.889	0.0000	9.022	0.0000	9.154
14	0.0000	9.054	0.0000	9.188	0.0000	9.320
16	0.0000	9.224	0.0000	9.358	0.0000	9.490
$\sum_{v'_4}$	0.0139	—	0.0096	—	0.0046	—
$\sum_{v'_2}\sum_{v'_4} f=0.031$						

Wilkinson [24] as $N-R'$ and $N-R''$ respectively, which appear likely to be associated with this $\pi \rightarrow 3d\sigma$ excitation. Betts and McKoy [25] have reported model potential calculations which indicate the correct assignment should be $N-R'$ and indeed the present calculated T_0 value of 8.153 eV is found to be in better agreement with the corresponding experimental value for this transition than with that of the $N-R''$ system. Nevertheless the great similarity between the $\pi \rightarrow (3pz+3pz)$ and $\pi \rightarrow (3s+3s)$ species found to exist in the present treatment still makes identification of $\pi \rightarrow (3pz+3pz)$ with $N-R''$ a definite possibility[13]. The total oscillator strength calculated for this transition is 0.031, some three or four times smaller than that calculated for the lower-energy $N-R$ band system.

C) Other Rydberg Transitions for Ethylene

The AO basis set employed in the present calculations [4, 5] includes $3s$ and $3p$ but no $3d$ or more diffuse functions associated with higher principal quantum numbers. The observed transitions at 8.92 eV and 9.05 eV, which are assigned as $\pi \rightarrow (4s+4s)$ or $N-4R$ and $\pi \rightarrow (4px-4px)$ or $N-R'''$ respectively, are thus not expected to have any counterparts in the present theoretical treatment. The same conclusion must be made relative to the study of all other higher energy Rydberg species thus far identified beyond 9.05 eV.

Basis set deficiency also appears to be responsible for the inability of the present calculations to find a second allowed Rydberg transition (other than $\pi \rightarrow 3d\sigma$) in the neighborhood of 8.5 eV; in this case the main difficulty seems to be the failure to employ semi-united atom $3d\sigma$ functions. The aforementioned model potential calculations [25] suggest an assignment of the $N-3R''$ bands as $\pi \rightarrow 3d_{x^2-y^2}$, for example, and also indicate that another possible Rydberg species ($N-3R''''$) may correspond to $\pi \rightarrow 3d_{xy}$ transitions of only slightly higher energy. An earlier assignment [5] for the $N-R'$ system, namely as a (diffuse) *vertical* $\pi \rightarrow \pi^*$ transition, now seems ruled out on the basis of the present oscillator strength calculations, discussed in Sect. 3 C. Additional SCF-CI calculations to investigate the $\pi \rightarrow 3d\delta$ transitions are planned in future work.

5. Conclusion

The main conclusion resulting from the present theoretical study of the ethylene electronic spectrum is that the energy of maximum absorption $\Delta E_{\max}$, indicated by explicit calculation of the oscillator strengths for the various vibrational transitions within a given electronic system, may well differ significantly from the vertical *electronic* energy difference ΔE_e usually equated with this quantity. These points are best illustrated by a comparison of specific values for ΔE_e and $\Delta E_{\max}$ for various electronic transitions in ethylene (Table 7); for simplicity differences between these two quantities are hereafter referred to as

---

[13] The vertical electronic energy to the $\pi \rightarrow (3pz+3pz)$ state increases by 0.17 eV from the CI-1 to the CI-2 treatment (the same change observed for the $\pi \rightarrow (3s+3s)$ excitation) and the depth of the associated double minimum in the upper state potential curve also appears to be overestimated by slightly less than 0.10 eV. Hence it might be concluded that the calculations underestimate the respective T_0 values for these two transitions by roughly equal amounts.

Table 7. Comparison of experimental and calculated transition energies to various excited states of C_2H_4. Vertical electronic transition energies are denoted by ΔE_e whereas excitation energies for the most probable transitions between the vibrational levels of ground and excited states are denoted by $\Delta E_{\max}$

Upper state (D_2 notation)	ΔE_e (eV)			Vibrational correction (eV)		$\Delta E_{\max}$ (eV)		
	CI-1[a]	CI-2[a]	est. exact	CI-1[a]	est. exact	CI-1[a]	CI-2[a,b]	exptl.
$^3B_1$	4.17	4.19	4.35	−0.13	−0.13	4.04	4.06	$4.22(T)$[c]
$^1B_3$	6.94	7.10	7.31	−0.29	−0.20	6.65	6.81	$7.11(R)$[d]
$2\,^1B_1$	8.25	8.27	8.06	−0.36	−0.40	7.89	7.91	$7.66(V)$[e]
$2\,^1B_3$	8.44	8.61	8.46[f] 8.82[f]	−0.29	−0.20	8.16	8.32	$8.26(R')$[d,f] $8.62(R'')$[d,f]

[a] CI-1 and CI-2 refer to two different CI treatments, CI-2 being the more extensive, solving secular equations of the order of 500; details are given in Ref. [5].

[b] Entries in this column are obtained by adding the CI-1 vibrational corrections to the CI-2 values for ΔE_e.

[c] Ref. [21].

[d] The experimental number refers to T_0, Ref. [24].

[e] Ref. [22].

[f] Two results are given because of the uncertainty in assignment in this case (see Sect. 4 B).

vibrational corrections, since the origin of the discrepancies is so intimately associated with the effects of vibrational motion in the initial and final states of a given transition.

In the case of the $V-N$ absorption bands the results of Table 7 indicate that the upper state involved (at least at the Franck-Condon maximum) is indeed the $\pi \rightarrow \pi^*$ singlet (V_u) suggested by Mulliken and others, but that transitions to this electronic state are distinctly *non-vertical* in nature, with a calculated vibrational correction of −0.36 eV. The calculations indicate that the main reason for this non-verticality is the existence of the lower energy V_g state and the resultant avoided crossing between the twisting potential curve of this species and that of the upper V_u state. On this basis it has been concluded that the observed system in reality corresponds to *two* distinct electronic transitions, heretofore unresolved as a consequence of the great similarity between their respective vibrational manifolds.

The remaining discrepancy between the calculated $\Delta E_{\max}$ and the corresponding experimental value of 7.66 eV seems likely to be removed with improvements in the theoretical treatment since very elaborate calculations [6, 7] of more recent origin have found somewhat lower ΔE_e values and greater valence character for the $\pi \rightarrow \pi^*$ singlet of the planar molecule; the latter finding should lead to increased curvature for the CH_2 twisting potential curve of the upper state, thereby producing an even greater vibrational correction for this transition (see Table 7). At the same time it seems certain that the singlet $\pi \rightarrow \pi^*$ wavefunction (at least for planar ethylene) is still considerably more diffuse than that of the corresponding triplet. The most extensive calculation to date [7] yields a value for $\langle \pi^* | x^2 | \pi^* \rangle$ in the order of 27 bohr^2 (where π^* is the principal natural orbital)[14]; the corresponding value in the present CI-1 treatment is 32.0 bohr^2, while analogous results for the T state function fall consistently in the neighborhood of 10 bohr^2.

Transitions to the $T(^3B_1)$ state are found to be essentially vertical in character according to the present calculations, although the resultant vibrational correction is not negligible (Table 7). The calculated ΔE_{max} is somewhat lower than the experimental value [21], thereby suggesting that the exact ΔE_e result is approximately 4.35 eV. The calculations of Ryan and Whitten [6] do in fact yield a larger ΔE_e value (4.98 eV) than that obtained in the present work and elsewhere [26] but this value appears quite high in view of the most recent experimental information and also because it leads to a difference of ΔE_e values between the $\pi \rightarrow \pi^*$ singlet and triplet respectively of only 3.04 eV, compared to the 3.9 eV obtained for this quantity by Bender *et al.* [7] and the value of 4.08 eV of the present calculations.

A fairly large vibrational correction is also indicated for the allowed Rydberg transitions $\pi \rightarrow (3s+3s)$ and $\pi \rightarrow (3pz+3pz)$ respectively (Table 7). Even though this result is propably overestimated by about 0.1 eV in the present treatment (because the depths of the double wells in the associated CH_2 twisting potential curves appear to be overestimated by this margin) it still remains a sizeable effect. In retrospect the reason that earlier results [4, 5] based solely on ΔE_e values appear to find far better agreement with the experimental transition energies for the Rydberg species than for the $\pi \rightarrow \pi^*$ singlet-singlet excitation turns out to be a cancellation of errors in the fortuitous case, coupled with a reinforcement in the other.

In summary the treatment of the vibrational characteristics of the electronic transitions of ethylene illustrates the need for employing a more appropriate value than the vertical *electronic* energy difference ΔE_e in order to predict the location of a given maximum in absorption (ΔE_{max}). Further theoretical studies of electronic spectra should therefore not only continue to pursue more accurate treatments for the calculation of ΔE_e values but should also include the calculation of oscillator strengths for associated vibrational transitions in order to obtain a more accurate estimate of the vibrational corrections which must be applied. In addition in the case of the $V-N$ bands of ethylene such investigations should not be restricted to the $\pi \rightarrow \pi^*$ singlet (V_u) state but rather should include the study of the $\pi \rightarrow (3py+3py)$ V_g species since there seems little question at this point that it is the interaction between these two states which ultimately holds the key to the understanding of this important absorption system.

Acknowledgements. The authors wish to thank Dr. H. L. Hsu for her assistance in carrying out the calculations reported in this paper. They are indebted to Profs. R. S. Mulliken, A. J. Merer and I. Shavitt for several valuable discussions. They are also grateful to Profs. V. McKoy, J. H. Moore, H. F. Schaefer III and J. L. Whitten for communicating their results prior to publication. The services and computer time made available by the University of Nebraska and University of Mainz Computer Centers have been essential to this study. The financial support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

---

[14] Ryan *et al.* [6] have obtained a $\pi \rightarrow \pi^*$ singlet wavefunction with more valence character, but the corresponding total energy is approximately 0.10 hartree higher than in the calculation of Bender *et al.* [7]. In addition the degree of diffuse character in their representation of this state appears to have been arbitrarily minimized by the omission of basis functions with exponents smaller than 0.06, whereas a value of 0.02 has been found to be *optimum* in the present calculations [4].

References

1. Mulliken, R. S.: Physic. Rev. **41**, 751 (1932).
2. Mulliken, R. S.: Physic. Rev. **43**, 297 (1933).
3. Herzberg, G.: Molecular spectra and structure, Vol. I. Spectra of diatomic molecules, p. 200. Princeton, New Jersey: Van Nostrand 1966.
4. Buenker, R. J., Peyerimhoff, S. D., Kammer, W. E.: J. chem. Physics **55**, 814 (1971).
5. Buenker, R. J., Peyerimhoff, S. D., Hsu, H. L.: Chem. Physics Letters **11**, 65 (1971).
6. Ryan, J. A., Whitten, J. L.: A valence state description of the ethylene *V* state by configuration interaction theory; preprint communicated to the authors.
7. Bender, C. F., Dunning, T. H., Jr., Schaefer, H. F., III, Goddard, W. A., III: Multiconfiguration wavefunctions for the lowest ($\pi\pi^*$) excited states of ethylene; preprint communicated to the authors.
8. Rose, J., Tai-ichi Shibuya, McKoy, V.: Application of the equations-of-motion method to the excited states of N_2, CO and C_2H_4; preprint communicated to the authors.
9. Herzberg, G.: Molecular spectra and molecular structure II, Infrared and raman spectra of polyatomic molecules, p. 151. Princeton: D. Van Nostrand Company, Inc. 1966.
10. Buenker, R. J., Peyerimhoff, S. D.: J. chem. Physics **53**, 1368 (1970).
11. Merer, A. J., Mulliken, R. S.: Chem. Reviews **69**, 639 (1969).
12. Fletcher, W. H., Thompson, W. T.: J. molecular Spectroscopy **25**, 240 (1968).
13. Pulay, P., Meyer, W.: *Ab initio* calculation of the force field of ethylene, in Arbeitsbericht des Instituts für Theoretische Chemie der Universität Stuttgart, No. 18, p. 95.
14. Ref. [9], p. 107.
15. Huo, W. M.: J. chem. Physics **49**, 1482 (1968).
16. Popkie, H. E., Henneker, W. H.: J. chem. Physics **55**, 617 (1971); see also Schaefer, H. F., III: The electronic structure of atoms and molecules, p. 171. Addison-Wesley Publishing Company, Inc. 1972, for a discussion of this work.
17. Marchetti, M. A., La Paglia, S. R.: J. chem. Physics **55**, 1655 (1971).
18. Reid, C.: J. chem. Physics **18**, 1299 (1950).
19. McDiarmid, R.: J. chem. Physics **55**, 4669 (1971).
20. Ross, K. J., Lassettre, E. N.: J. chem. Physics **44**, 4633 (1966).
21. Moore, J. H., Jr.: An investigation of the low-energy singlet-triplet and singlet-singlet transitions in ethylene derivatives by ion-impact. Preprint communicated to the authors.
22. Wilkinson, P. G., Mulliken, R. S.: J. chem. Physics **23**, 1895 (1955).
23. Merer, A. J., Schoonveld, L.: Canad. J. Physics **47**, 1731 (1969).
24. Wilkinson, P. G.: Canad. J. Physics **34**, 643 (1956).
25. Betts, T., McKoy, V.: J. chem. Physics **54**, 113 (1971).
26. Dunning, T. H., Hunt, W. J., Goddard, W. A.: Chem. Physics Letters **4**, 147 (1969).

Prof. R. J. Buenker
Department of Chemistry
University of Nebraska
Lincoln, Nebraska 68508
USA

Prof. Dr. S. D. Peyerimhoff
Lehrstuhl für Theoretische Chemie
Universität Bonn
D-5300 Bonn
Federal Republic of Germany