Simplified Non-Empirical Excited States Calculations

Part II. Interpretation of the Electronic Transitions in the Vacuum-UV Spectrum of Ethylene

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The simple non-empirical method for calculating excited electronic states that we have presented recently has been applied on Rydberg states of ethylene. All kinds of ns, np and nd series have been studied using a Gaussian basis set including s, p and d functions. Calculated values of energy, oscillator strengths and other properties have been compared with the experimental spectrum. Assignments of all the observed series have been proposed.

Die vor kurzem von den Verfassern entwickelte Methode zur Berechnung von angeregten elektronischen Zuständen wird auf Rydberg-Zustände angewendet. Alle ns-, np- und nd-Serien werden unter Benutzung eines Gaußschen Basissatzes mit s-, p- und d-Funktionen untersucht. Die errechneten Energiewerte, Oszillatorstärken und sonstigen Eigenschaften werden mit dem experimentellen Spektrum verglichen und den beobachteten Serien zugeordnet.

1. Introduction

The far UV spectrum of ethylene has been carefully investigated experimentally [1]. The vibrational structure of the bands corresponding to the different electronic transitions is generally well understood and the geometry of the resulting excited states has been established in some detail. However, the correlation of the experimentally found Rydberg series with group-theoretical symbols or semi-united atom orbital symbols is rather incomplete and somewhat ambiguous. Most theoretical calculations on excited states of ethylene, for example Refs. [2–7], have been concerned with the $\pi \rightarrow \pi^*$ excited $T\,^3B_{1u}$ and $V\,^1B_{1u}$ states. Assignments of some Rydberg transitions were recently proposed by Buenker et al. [8], using a very elaborate combined SCF and CI method, and by Betts and McKoy [9], using a semiempirical model potential method. However, neither of these calculations is quite complete, as no basis functions of d-type were employed, though some of the Rydberg series obviously have this symmetry, and as no transition probabilities were computed.

We have recently suggested a new simplified non-empirical method for excited state calculations [10] and applied it on the ns and $np\sigma$ Rydberg series of ethylene. We have now found it warranted to perform similar calculations on the remaining p and d Rydberg series of this molecule to further contribute to the interpretation of the spectrum.

The method is based on describing excited states by mixing singly excited configurations. By using the frozen core approximation combined with the natural orbital transformation [11, 12], the excited state wavefunctions can actually be referred to single configurations with one electron transferred from a ground state orbital – in this study of ethylene, a π-orbital – to an excited state natural orbital. Besides transition energies, also oscillator strengths and some properties of the excited states may easily be computed.

In Section 2 we present the details of the basis sets used and the ground state calculations. Section 3 describes the results of the excited state calculations on the $nd\sigma$, $nd\delta$, $np\pi$ and $nd\pi$ Rydberg series. In Section 4 our results are compared with the experimental spectrum and with earlier assignments.

2. Computational Details

As discussed in Ref. [10] it is possible to divide the Gaussian function basis set in a natural way into two parts, the normal state basis functions, NGTF's, and the Rydberg state basis functions, RGTF's. These two sets seem to be rather independent [10].

The basis sets adopted in the present study were similar to the basis used previously [10]. As before, the NGTF's were chosen as the ethylene-optimized set of 56 Gaussians, determined by Schulman et al. [13]. The RGTF's however were chosen somewhat differently. Among the diffuse Gaussians centered at the molecular midpoint, the s-type functions were replaced by d-type functions. The orbital exponents of these functions were chosen three times as large as those of the corresponding s-type functions of Ref. [10] in order to keep the maximas of the radial distributions at the same distance from the midpoint. For all seven Rydberg series investigated here, a total of 46 RGTF's is needed if the accuracy is to be comparable with that of Ref. [10]. Inclusion of all these functions would lead to an inadmissible computational time for the ground state SCF-MO part of the calculation. This part was carried out with the IBMOL program version 4 [14]. As pointed out in Ref. [10], much higher efficiency may be reached if separate calculations are performed for particular classes of excited states. Accordingly, three separate SCF-MO calculations with different RGTF subsets were accomplished, cf. Table 1.

Table 1. Diffuse basis functions (RGTF's) added to the normal state basis functions in the different calculations on Rydberg states of ethylene

Rydberg orbitals	Types and numbers of RGTF's per center															Total number of RGTF's
	C				H	Molecular midpoint										
	s	p_x	p_y	p_z	s	s	p_x	p_y	p_z	$d\sigma$[a]	$d\delta'$[a]	d_{xy}	d_{xz}	d_{yz}	$3s$	
$s, p\sigma$[b]	2	–	–	1	1	4	–	–	4	–	–	–	–	–	–	18
$d\sigma, d\delta'(a_g)$	2	–	–	1	1	–	–	–	–	4	4	–	–	–	4	22
$p\pi_y, d\pi_y$	–	–	1	–	1	–	–	4	–	–	–	–	–	4	–	14
$p\pi_x, d\pi_x, d\delta''(b_{1g})$	–	1	–	–	–	–	4	–	–	–	–	4	4	–	–	14

[a] $d\sigma = d_{2z^2 - x^2 - y^2}$, $d\delta' = d_{x^2 - y^2}$. [b] Calculations carried out in Ref. [10].

Table 2. Ground state energies and π-orbital energies (in a.u.) of the different calculations

Rydberg orbitals	Total number of RGTF's	Ground state energy	π-orbital energy
—	0	-77.90830 [a]	-0.3914 [a]
$s, p\sigma$	18	-77.91451 [b]	-0.38728 [b]
$d\sigma, d\delta'(a_g)$	22	-77.91501	-0.38665
$p\pi_y, d\pi_y$	14	-77.91035	-0.39610
$p\pi_x, d\pi_x, d\delta''(b_{1g})$	14	-77.90985	-0.39449

[a] Values from Ref. [13].   [b] Values from Ref. [10].

All calculations were carried out with the experimental ground state equilibrium geometry as given by Allen and Plyler [15]. With this geometry the ethylene molecule belongs to the point group D_{2h}. The coordinate system was chosen according to the recommendation by Mulliken [16], the molecule lying in the yz plane with CC bond and z-axis collinear.

Total energies and π-orbital energies obtained in the three different calculations are listed in Table 2, which also includes the corresponding results obtained previously [10, 13]. As mentioned in Ref. [10], the effect of different RGTF sets on the ground state properties is of minor significance. This is also borne out by the present results, cf. Table 2.

3. Results

3.1. B_{3u} and B_{2u} States – $nd\sigma$ and $nd\delta$ Rydberg Series

Excitations from the occupied π-orbital ($1b_{3u}$) and belonging to the B_{3u} species are of the type $1b_{3u} \rightarrow ma_g$, $m \geq 4$. There are three kinds of semi-united atom orbitals (UAO) belonging to a_g in the D_{2h} group notation, i.e. ns, $nd\sigma$ and $nd\delta'$ ($nd_{x^2-y^2}$). Thus, the assignment of excited states as belonging to Rydberg series of specified symmetry may be somewhat intricate when mixing of configurations is allowed. This fact was observed and discussed already in [10], where the ns series was considered. In the present study, a mixing of thirteen $1b_{3u} \rightarrow ma_g$, $m = 4, \ldots, 16$, configurations resulted in eight singlets and eight triplets below the ionization limit, 10.521 eV, calculated according to Koopmans' theorem. By inspecting the natural orbitals corresponding to the singlets it was possible to classify the lowest of these states as originating from the $\pi \rightarrow 3s$ excitation. The excitation energy was found to be 7.52 eV, the same as obtained in Ref. [10]. The fact that this state is comparatively well described here although no s-type Gaussian centered at the molecular midpoint has been explicitly included, is probably due to the presence of three equivalent $d\sigma$-functions. Their sum, $d_{x^2} + d_{y^2} + d_{z^2} = r^2 e^{-\alpha r^2}$, is a radial function, more similar to a $3s$ orbital than the usual s-type Gaussians, $e^{-\alpha r^2}$. For this reason it has been included in Table 1 under the heading $3s$. The classification of the higher states was less straight-forward. It was of some guidance to study the contours of the natural
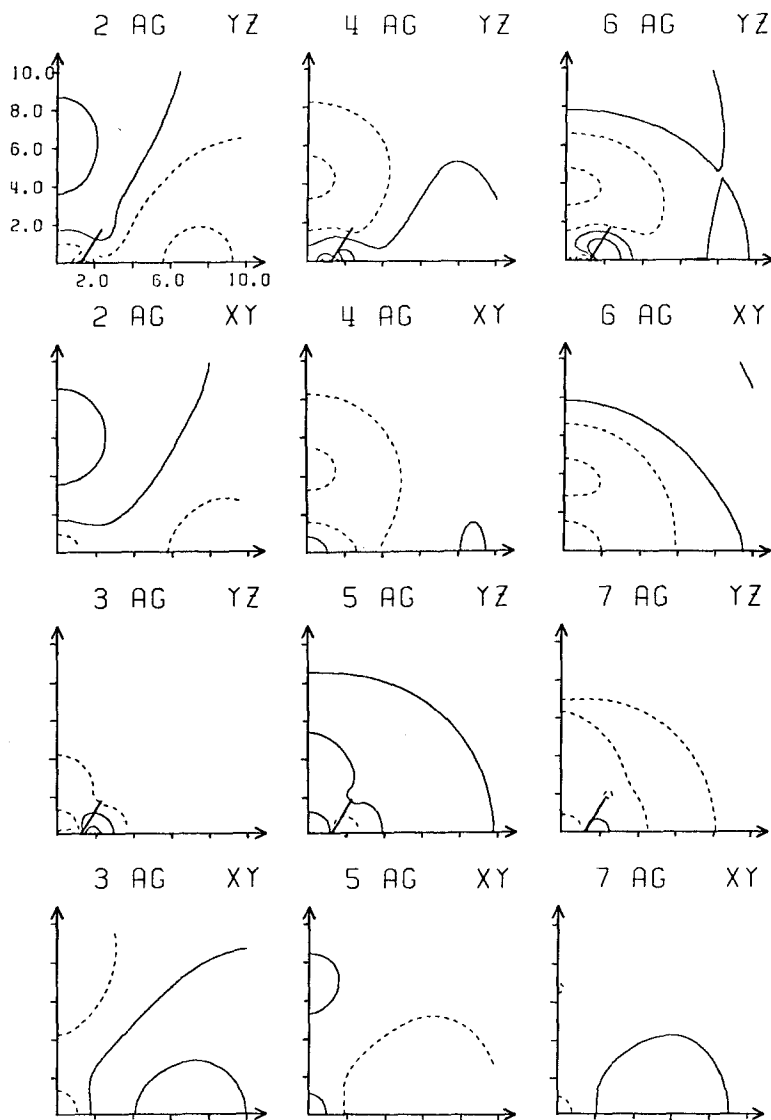
Fig. 1. Contours of a_g natural orbitals of $d\sigma$ and $d\delta'$ types in the molecular yz-plane and in the perpendicular xy-plane. The vertical axis is the y-axis in all cases. Solid lines indicate positive loops and broken lines negative loops. In the yz-plane the CH-bonds are indicated. Orbitals numbered 2, 4, 6 were assigned as $4d\sigma$, $5d\sigma$, $6d\sigma$. Orbitals numbered 3, 5, 7 were assigned as $3d\delta'$, $4d\delta'$, $5d\delta'$.
(Length scale in a.u.)

Rydberg orbitals corresponding to the various states. In Fig. 1 contours of the natural orbitals corresponding to the six next higher singlets are presented both in the molecular yz-plane and in the perpendicular xy-plane. The natural Rydberg orbitals numbered 2, 4 and 6 in the figure were assigned as $4d\sigma$, $5d\sigma$ and $6d\sigma$ respectively, while the orbitals denoted 3, 5 and 7 were assigned as $3d\delta'$, $4d\delta'$ and $5d\delta'$. No assignment was made for the eighth B_{3u} state obtained in this calculation.

Table 3. Some lower B_{3u} (13 conf.) and B_{2u} (4 conf.) states of ethylene. (Energies in eV)

Rydberg orbital	Singlet vertical transition energy	Singlet-triplet splitting	$(n-\delta)^2$	δ	r_{max} of the outermost loop (a.u.)	Oscillator strength	IP-adjusted singlet energy
B_{3u} $4d\sigma(a_g)$	8.992	0.009	8.90	1.02	7	10^{-4}	8.98[a]
$5d\sigma$	9.633	0.024	15.32	1.08	18	0.002	9.62[a]
$6d\sigma$	9.904	0.057	22.05	1.3	30	0.013	9.89[a]
B_{3u} $3d\delta'(a_g)$	9.036	0.048	9.16	-0.03	7	0.016	9.03[a]
$4d\delta'$	9.684	0.027	16.29	-0.04	20	0.010	9.67[a]
$5d\delta'$	9.985	0.015	25.38	-0.04	35	0.006	9.98[a]
B_{2u} $3d\delta''(b_{1g})$	9.271	0.019	9.29	-0.05	7	0.019	9.04[b]
$4d\delta''$	9.907	0.009	16.43	-0.05	20	0.009	9.68[b]
$5d\delta''$	10.204	0.005	25.62	-0.06	35	0.005	9.98[b]

[a] $E(IP) = 10.521$.   [b] $E(IP) = 10.734$.

Excitations from the occupied π-orbital and belonging to the B_{2u} species are of the type $1b_{3u} \rightarrow mb_{1g}$, $m \geqq 1$. No orbital of the b_{1g} symmetry is obtained from the valence basis set. The virtual molecular orbitals belonging to this species are linear combinations of the four d_{xy} RGTF's centered at the molecular midpoint. No assignment problems were thus encountered. The principal quantum number of the lowest orbital in the $nd\delta''$ series must be $n = 3$ since no core ancestor is present. This principal quantum number value is also confirmed by a study of the orbital radial density along the $x = y$, $z = 0$ line, as no node except those at origo and infinity is present.

Some properties calculated for the Rydberg $nd\sigma$ and $nd\delta$ states are collected in Table 3. The singlet-triplet splittings are very small as anticipated for Rydberg states.

The $(n - \delta)^2$ values were found from the relation [17]:

$$E_n = E(IP) - \frac{R}{(n-\delta)^2}. \tag{1}$$

They lead to quantum defects, δ, which are reasonably constant within the $nd\sigma$ series and almost exactly constant within the two $nd\delta$ series. The values of $E(IP)$, the ionization potentials used in Eq. (1), were obtained from Koopmans' theorem, which is consistent with our method of calculating the transition energies, cf. Ref. [10]. It should be pointed out that we assume the first member of the $nd\sigma$ series to have the principal quantum number $n = 4$, since in agreement with Merer and Mulliken [1] we interpret the $3a_g$ MO of the ground state as the $3d\sigma$ UAO, cf. [10]. This interpretation is at variance with the assignment of Buenker et al. [8], who correlate the $3a_g$ MO with the $3s$ UAO and consequently assume the Rydberg $nd\sigma$ series to start with $n = 3$. Such an assignment would of course lead to δ-values very different from those of Table 3. Our δ-values seem however to be consistent with experiments, see Table 6 below. The high values may be understood as a result of the strong penetration of the $nd\sigma$ orbitals into the molecular core. The penetration is obviously much lower for the $nd\delta$ orbitals.
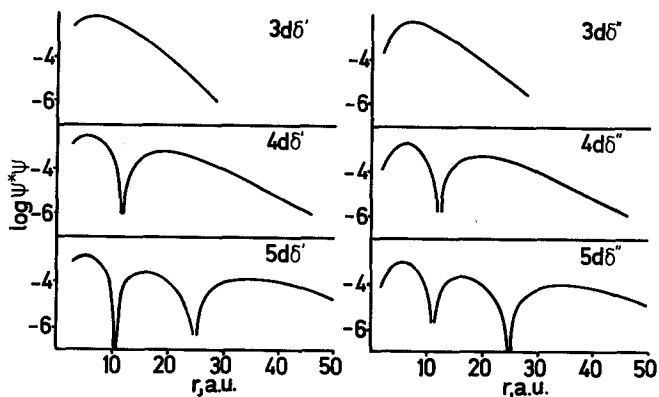
Fig. 2. Logarithm of charge density vs. distance from the molecular midpoint along the z-axis (CC-axis) for $nd\delta'$ and $nd\delta''$ natural orbitals

According to Mulliken [17] the $(n - \delta)^2$ values should be equal to the distance between origo and the position of maximum radial density of the outermost loop, r_{max} in Table 3. The r_{max} values were estimated from density plots similar to those of Fig. 2. The agreement with Mulliken's formula is moderately good. The $^1A_g \rightarrow {}^1B_{3u}$ and $^1A_g \rightarrow {}^1B_{2u}$ transitions are symmetry allowed and the oscillator strengths were computed using dipole transition moments.

It should be stressed that the $nd\sigma$ and $nd\delta'$ series on the one hand and the $nd\delta''$ series on the other have been computed using different ground state calculations, cf. Section 2. Therefore a comparison between the energy values of these series cannot be made until all values have been related to a common reference point. Since Rydberg states are closely connected with ionized states and since our method of calculation parallels Koopmans' theorem, we have chosen to refer the calculated excitation energies to a common value of the ionization potential. Thus, from the primarily computed excitation energies, listed in the second column of Table 3, we have subtracted the difference between the E(IP)-value from Koopmans' theorem and the experimental value, 10.51 eV [18]. These IP-adjusted energies are given in the last column of Table 3. After the adjustment, the near degeneracy of the $d\delta$ levels becomes clear. This result can be theoretically justified as follows. The levels are degenerate in the iso-electronic oxygen molecule. Since the high density regions of these particular Rydberg orbitals do not interfere with the molecular skeleton, the exchange of an oxygen atom for a CH_2 group should only have a minor influence. The radial density plots for both types of $nd\delta$ orbitals are shown in Fig. 2. It should be noted that not only the positions of maximal density for all the loops fall at the same distance from the molecular midpoint, but even the form of the curves is extremely alike.

3.2. A_g and B_{1g} States − $np\pi$ Rydberg Series

The semi-united atom $p\pi$ orbitals belong in ethylene to the symmetry species b_{3u} and b_{2u} for π_x and π_y respectively. No other s, p or d UAO belongs to any of these irreducible representations of the D_{2h} group and thus no assignment

Table 4. Some lower A_g (6 conf.) and B_{1g} (7 conf.) states of ethylene. (Energies in eV)

	Rydberg orbital	Singlet vertical transition energy	Singlet-triplet splitting	$(n-\delta)^2$	δ	r_{max} of the outermost loop (a.u.)	IP-adjusted singlet energy
A_g	$3p\pi_x(b_{3u})$	8.645	0.324	6.51	0.45	6	8.42[a]
	$4p\pi_x$	9.669	0.104	12.76	0.43	16	9.44[a]
	$5p\pi_x$	10.092	0.050	21.19	0.40	29	9.86[a]
	$6p\pi_x$	10.328	0.048	33.5	0.2	43	10.10[a]
B_{1g}	$3p\pi_y(b_{2u})$	8.298	0.048	5.49	0.66	5	8.03[b]
	$4p\pi_y$	9.581	0.016	11.37	0.63	14	9.31[b]
	$5p\pi_y$	10.071	0.008	19.24	0.61	25	9.80[b]
	$6p\pi_y$	10.313	0.005	29.3	0.6	42	10.04[b]

[a] $E(IP) = 10.734$.   [b] $E(IP) = 10.778$.

problems caused by the mixing occur for these orbitals. The $1b_{3u} \rightarrow mb_{3u}$, $m \geq 2$, transitions generate states of A_g symmetry. Mixing six configurations of this type, with $m = 2, \ldots 7$, gave four singlets and triplets below the ionisation limit, 10.734 eV. The $1b_{3u} \rightarrow mb_{2u}$, $m \geq 2$ transitions generate states of B_{1g} symmetry. Four singlets and triplets below the ionization limit, 10.778 eV, were obtained by mixing seven configurations with $m = 2, \ldots, 8$.

Transitions to these states from the ground state are only quadrupole allowed and the dipole oscillator strengths are thus zero. Some properties calculated for the B_{1g} and A_g excited states are summarised in Table 4. A comparison of un-corrected energy values indicates the $B_{1g}(np\pi_y)$ states to be throughout lower than the corresponding $A_g(np\pi_x)$ states. Further, previously studied $B_{2g}(np\sigma)$ states [10] seem to lie below both kinds of $np\pi$ states. After an IP-adjustment, the order of increasing energy becomes instead $\pi_y < \sigma < \pi_x$ for every value of n. Singlet-triplet splittings are very small for the π_y series but rather large for the π_x series. This might have been expected since the considerable overlap between the ground state occupied π-orbital and the Rydberg π_x orbitals leads to sub-stantial values of the exchange integrals between these orbitals. The quantum defects are rather constant within the series. The lowest δ-values are found in the $np\pi_x$ series, which obviously has the smallest penetration into the core. Mulliken's relation between $(n - \delta)^2$ and r_{max} is fulfilled moderately well also here; r_{max} is always found to be larger for the $np\pi_x$ than for the $np\pi_y$ orbitals in agreement with this relation. The general appearance of the orbital radial densities is rather similar and resembles also the curves for the $np\sigma$ orbitals [10].

3.3. A_u and B_{1u} States – $nd\pi$ Rydberg Series

The semi-united atom $d\pi$ orbitals belong in ethylene to the symmetry species b_{2g} and b_{3g} for $d\pi_x$ and $d\pi_y$ respectively. The $1b_{3u} \rightarrow mb_{3g}$, $m \geq 2$ transitions generate states of A_u symmetry. Seven configurations of this type were mixed resulting in three pairs of states (singlets and triplets) below the ionization limit.

The states were assigned as corresponding to the Rydberg orbitals $4d\pi_y$, $5d\pi_y$ and $6d\pi_y$. The first member of the series has the principal quantum number $n = 4$, because the core orbital $1b_{3g}$ correlates with the $3d\pi_y$ UAO. The $^1A_g \rightarrow {}^1A_u$ transitions are strictly forbidden and the transition probabilities are thus zero.

The $1b_{3u} \rightarrow mb_{2g}$, $m \geq 1$, transitions generate states of B_{1u} symmetry. Mixing seven configurations of this type with $m = 1, \ldots, 7$ led to four pairs of states below the ionization limit. However, the lowest pair of these states, with configuration $(1b_{3u})^1 (1b_{2g})^1$, is not of Rydberg type but represents the spectroscopic V and $T(\pi \rightarrow \pi^*)$ states. The unadjusted energies of these states are 8.85 eV and 3.68 eV respectively. The T state is presumably described rather satisfactorily, the too low energy compared with experiment being caused by the difference in correlation energy. The description of the V state on the other hand is probably rather deficient, as its computed energy is about 1 eV too high. The basis set used in this study is supposedly not flexible enough and besides, the reorganisation energy, approximately counterweighting the correlation change for Rydberg states, may be rather large for the V state. The oscillator strength computed for the $N^1A_g \rightarrow V^1B_{1u}$ transitions is 0.47. An interesting feature shown by the natural orbital of π^* type, corresponding to the V state, is a lack of a maximum in the radial density curve outside the molecular frame, which clearly distinguishes this orbital from the higher excited natural orbitals of b_{2g} symmetry.

Calculated properties of the $B_{1u}(nd\pi_x)$ and $A_u(nd\pi_y)$ states are summarized in Table 5. The energies of the $nd\pi_y$ states are distinctly lower than the $nd\pi_x$ energies, and consequently the difference in quantum defects is quite large. However, it is not unlikely that the present description of the whole $nd\pi_x$ series is inferior to that of the other Rydberg series. The reason for this is the unsatisfactory description of the first, non-Rydberg member of the series, the V state. As already mentioned, its energy was computed 1 eV too high. Since the higher members of the series must be orthogonal to this first member, the whole series may be pushed to too high energy levels, implying somewhat too small δ-values. The penetration of the $nd\pi_y$ orbitals is obviously large since their loops point in almost the same direction as the C–H bonds. Low singlet-triplet splitting for

Table 5. Some lower B_{1u} (7 conf.) and A_u (7 conf.) states of ethylene. (Energies in eV)

	Rydberg orbital	Singlet vertical transition energy	Singlet-triplet splitting	$(n - \delta)^2$	δ	r_{max} of the outermost loop (a.u.)	Oscillator strength	IP-adjusted singlet energy
B_{1u}	$4d\pi_x(b_{2g})$	9.657	0.320	12.62	0.45	13	0.158	9.43[a]
	$5d\pi_x$	10.071	0.128	20.49	0.47	26	0.061	9.84[a]
	$6d\pi_x$	10.332	0.106	33.75	0.2	38	0.071	10.10[a]
A_u	$4d\pi_y(b_{3g})$	9.310	0.010	9.27	0.94	7	——	9.04[b]
	$5d\pi_y$	9.955	0.005	16.53	0.93	20	—	9.67[b]
	$6d\pi_y$	10.251	0.003	25.9	0.9	35	—	9.98[b]

[a] $E(\text{IP}) = 10.734$.   [b] $E(\text{IP}) = 10.778$.

these states is quite obvious too; with their special form, the exchange integrals between them and the occupied π-orbital must be extremely low. On the other hand, the $nd\pi_x$ orbitals have high density in the same part of space as the core π-orbital, resulting in a larger singlet-triplet splitting than for other Rydberg states. In accordance with Mulliken's relation, the larger $(n-\delta)^2$ values in the $nd\pi_x$ series are accompanied by larger r_{max} values, *i.e.* larger diffuseness of the orbitals. $^1A_g \rightarrow {}^1B_{1u}$ transitions are fully allowed and their oscillator strengths were computed. The $\pi \rightarrow 4d\pi_x$ transition is predicted to be very strong, even stronger than $\pi \rightarrow 3s$, the first Rydberg transition. It should be remembered, however, that no estimate of the Franck-Condon integral has been made within the present computational scheme. This integral may change the relative oscillator strengths by a considerable factor. In particular, the integral is likely to be much larger for a bonding Rydberg orbital, e.g. $3s$, than for an antibonding, e.g. $4d\pi_x$. Hence, the above comparison between the strength of different transitions must not be considered as conclusive.

4. Discussion of the Spectrum

The higher Rydberg states in ethylene have been studied experimentally by Price and Tutte [19], who discovered several transitions belonging to one Rydberg series and two transitions belonging to other series. Wilkinson [20] identified several other transitions belonging to four Rydberg series in all. He even suggested assignments of most of the vibrational bands. Wilkinson also found some bands that he did not assign, conjecturing that they might belong to a fifth Rydberg series.

In previous theoretical investigations [8,9] attempts have been made to assign group-theoretical symbols and semi-united atom Rydberg orbital symbols to the series, by Wilkinson named nR, nR', nR'', nR'''.

In the present investigation we are also concerned with this problem. For which reason, the results of the present calculations and of our previous ones [10] are listed together in Table 6 in order of increasing energy. The IP-adjusted values have been given since they are most suitable for a direct comparison between different calculations, cf. the above discussion. Oscillator strengths f and quantum defects δ are also listed. The experimental material included in Table 6 has been taken from Wilkinson [20], Merer and Schoonveld [21] and Ross and Lassettre [22]. The latter authors have found a forbidden transition at 7.45 eV. The values of $v_{vertical}$, r_0 and δ, reported as experimental, have been estimated by us from the information given in Refs. [20–22]. The r_0-values are not the same as in Ref. [20] since we have used another ground-state value, *i.e.* $r_0 = 1.339$ Å.

The assignment we propose here are obvious from our tabular setup. They coincide with previous assignments in several cases. There is no doubt that the nR series originates from $\pi \rightarrow ns$ transitions, the $2R$ band at 7.11 eV from the transition to the $3s$ Rydberg orbital, the $3R$ band at 8.90 eV to the $4s$ orbital and the $4R$ band at 9.62 eV to the $5s$ orbital. These assignments agree with those of previous authors [1, 8, 9, 20], the only diversity being a difference in principal quantum number, advocated by Buenker *et al.* [8]. This point was discussed in

Table 6. Calculated properties of the lower singlet Rydberg states of ethylene compared with experiments. Energy values in eV

State	Calculations				Experiments [20–22]				
	Rydberg orbital MO(UAO)	Energy (IP-adj.)	f	δ	Label	ν_{00}	$\nu_{vert}^a - \nu_{00}$	r_0^a	δ^a
$^1B_{3u}$ [b]	$4a_g(3s)$	7.49	0.05	0.9	$2R$	7.11	0.2	1.41	1.0
$^1B_{1g}$	$2b_{2u}(3p\pi_y)$	8.03	0	0.7	—	7.45	—	—	0.9
$^1B_{2g}$ [b]	$3b_{1u}(3p\sigma)$	8.19	0	0.6	$3R'$	8.26	0	1.44	0.5
^1A_g	$2b_{3u}(3p\pi_x)$	8.42	0	0.5					
$^1B_{3u}$	$5a_g(4d\sigma)$	8.98	10^{-4}	1.0	$4R'''$	9.05	0.1	1.39	0.9
$^1B_{3u}$	$6a_g(3d\delta')$	9.03	0.02	-0	} $3R''$	8.62	0.3	1.41	0.3
$^1B_{2u}$	$1b_{1g}(3d\delta'')$	9.04	0.02	$-0.$					
^1A_u	$2b_{3g}(4d\pi_y)$	9.04	0	0.9					
$^1B_{3u}$ [b]	$7a_g(4s)$	9.06	0.02	0.9	$3R$	8.90	0.1	1.39	1.1
$^1B_{1g}$	$3b_{2u}(4p\pi_y)$	9.31	0	0.6					
$^1B_{2g}$ [b]	$4b_{1u}(4p\sigma)$	9.38	0	0.5	$4R'$	9.36	0.1	1.47	
$^1B_{1u}$	$2b_{2g}(4d\pi_x)$	9.43	0.16	0.5	—	9.11	—	—	0.9
^1A_g	$3b_{3u}(4p\pi_x)$	9.44	0	0.4					
$^1B_{3u}$	$8a_g(5d\sigma)$	9.62	0.002	1.1					
^1A_u	$3b_{3g}(5d\pi_y)$	9.67	0	0.9					
$^1B_{3u}$	$9a_g(4d\delta')$	9.67	0.01	-0	} $4R''$	9.51	—	1.49	0.3
$^1B_{2u}$	$2b_{1g}(4d\delta'')$	9.68	0.01	-0					
$^1B_{3u}$ [b]	$10a_g(5s)$	9.74	0.003	0.8	$4R$	9.62	0	—	1.1

[a] Values estimated by the present authors.   [b] Values from Ref. [10].

our precedent paper [10]. In the nR series our calculated values are seen to lie 0.1–0.2 eV above our appraisal of vertical transition energies. Our assignment of the forbidden transition at 7.45 eV is also in harmony with previous suggestions [1, 8].

The nR' series is observed to be weaker than the nR series [20], the strength of the first member, $3R'$, being lower than that of $3R$, yet slightly larger than that of $4R$. For the nR' series, different assignments have been suggested previously. Betts and McKoy assigned it as a $nd\sigma$ series, $n = 4$, 5, ... Buenker et al. [8] discussed the possibility of $3R'$ being either $3d\delta$ or $3d\sigma$. Our assignment is $3p\sigma$. This might seem questionable since the transition to the $^1B_{2g}$ state is not dipole allowed. However, it is well known that both the ion and the Rydberg states do not have planar equilibrium conformations but are somewhat twisted [1, 7, 20, 21]. By arbitrarily twisting the molecule the point group D_{2h} is transferred into the group D_2 where transitions to all B-states are allowed. To evaluate the effect of twisting on the oscillator strengths we have carried out calculations on the Rydberg ns and $np\sigma$ series with a twisted conformation (cf. Merer and Schoonveld [21]):

$$r(\text{C–C}) = 1.41\,\text{Å}, \quad r(\text{C–H}) = 1.11\,\text{Å}, \quad \angle\,\text{CCH} = 120°,$$

and the dihedral angle $= 25°$. The same basis set as in Ref. [10] was used. Some results from calculations within the frozen core approximation are displayed in

Table 7. Some lower singlet $B_{3(u)}$ and $B_{2(g)}$ states of ethylene with twisted conformation, see text for details. Results from frozen core approximation. Energy values in eV

Rydberg orbital	Vertical transition energy in D_2 geometry	Transition energy to D_2 state from D_{2h} ground state[a]	Vertical transition energy in D_{2h} geometry[b]	Oscillator strengths for vertical transitions	
				D_2	D_{2h}[b]
$3s$	6.72	7.33	7.52	0.029	0.045
$4s$	8.28	8.89	9.09	0.016	0.022
$5s$	8.97	9.58	9.77	0.002	0.003
$3p\sigma$	7.41	8.02	8.22	0.005	0
$4p\sigma$	8.60	9.21	9.41	0.001	0
$5p\sigma$	9.06	9.67	9.86	10^{-4}	0

[a] $E_0(D_{2h}) = -77.91451$ a.u., $E_0(D_2) = -77.89211$ a.u.
[b] Values from Ref. [10].

Table 7. Nine configurations were used for the B_3 states and ten for the B_2 states. Calculations mixing all singly excited configurations were also performed (extended CI of Ref. [10]) including thirtyeight B_3 and forty B_2 configurations. The deviation between these two rather different CI-treatments in no case exceeded 0.01 eV, although the $\sigma - \pi$ separability is lost by twisting. In agreement with previous, more elaborate studies we found that all Rydberg states were stabilized by twisting, cf. columns three and four of Table 7. Oscillator strengths obtained with twisted (D_2) and planar (D_{2h}) conformations are compared in the last two columns. It is noticeable that the strength obtained for the $B_2(3p\sigma)$ state is even larger than for the $4R(5s)$ state, thus supporting our assignment. The experimental energy values of the nR' series, 8.26 eV and 9.36 eV, are rather close to the energies calculated for the transitions to the $B_2(3p\sigma)$ and $B_2(4p\sigma)$ states, i.e. 8.19 eV and 9.38 eV respectively (cf. Table 6). Furthermore, the comparatively large values of r_0 indicate that the nR' Rydberg orbitals are likely to be antibonding. Experimental and theoretical δ-values are also in good accord and of a magnitude typical for Rydberg np states. On the other hand, the previous assignments of the Rydberg orbital of $3R'$ as $3d\delta$ [8] or $4d\sigma$ [9] are not supported by our results. We obtained energy values for both these states close to 9 eV, i.e. 0.7 eV above the experimental value. In view of our good results for the nR series, it is rather unlikely that the nR' series should be so badly described by our model. It should also be noted that the previous treatments [8, 9] did not include d-functions in their basis sets.

The $3R''$ system consists of several strong, diffuse bands with maximum intensity at $3R''_{20}$ (8.96 eV), 0.34 eV above the 00-band. Its unusual appearance led us to consider that it might be composed of two superimposed transitions of almost equal energy. Since our calculations of IP-adjusted energies indicate that the $B_{3u}(3d\delta')$ and $B_{2u}(3d\delta'')$ states are almost degenerate, we propose that both these states contribute to the $3R''$ system. A justification for this proposal is given by the fact that during twisting the B_3 and B_2 states will approach each other and finally become exactly degenerate in the D_{2d} (perpendicular) geometry. The calculated energies are found about 0.1 eV above the vertical transitions. The intensities as well as the small r_0-value of $3R''$ are in harmony with our

assignment. Our conclusion is in partial agreement with that of Betts and McKoy [9], who assigned $3R''$ as $3d\delta'(a_g)$ and an unassigned band at 8.92 eV as $3d\delta''(b_{1g})$. A different interpretation of $3R''$ was given by Buenker et al. [8]. As already mentioned these authors suggested that $3R''$ and $3R'$ may correspond to $3d\sigma$ and $3d\delta$, with some preference for $3R''$ being $3d\sigma$. As mentioned, none of these two investigations included d-functions in the basis sets. Both inter- pretations must therefore be considered as somewhat speculative.

Among the observed bands, not yet discussed here, the $4R'''$ system is by far the most important. This system is composed of several rather intense bands. Following a suggestion by Wilkinson, Betts and McKoy [9], as well as Buenker et al. [8], assigned the Rydberg orbital involved as $d\pi_x$, and presumably $4d\pi_x$. This assignment is supported by our result that the oscillator strength calculated for this transition is as large as 0.16. However, it is difficult to understand how the r_0-value of the $4R'''$ state (1.39 Å) could be compatible with an antibonding ($d\pi_x$) Rydberg orbital. This r_0-value should be compared to the CC-distance of the ion $C_2H_4^+$ which is found to be 1.41 ± 0.01 Å [21]. For this reason we tentatively assign $4R'''$ as $B_{3u}(4d\sigma)$ (accordant with r_0 and δ values, but not quite in harmony with the calculated oscillator strength) and the rather intense 9.11 eV transition as $B_{1u}(4d\pi_x)$, cf. Table 6. An interchange of these two assignments might be considered. A more definite conclusion would however require much more elaborate calculations. The most intense band of the $4R'''$ system is found very close to the 9.11 eV band [20]. In contrast, our energy values of the two states under discussion indicate a separation of 0.4 eV. However, as already mentioned, we expect all members of the $nd\pi_x$ series to be less adequately represented in our model than the other Rydberg series. Therefore, this deficiency is not a very serious argument against our assignments.

It should be pointed out that the order of the lowest states as computed with our method agrees completely with the results of Buenker et al. [8]. However, their very elaborate method does not easily allow either a description of the higher states or calculation of oscillator strengths. Both these things can easily be achieved by our method. In view of the simplicity of the method and its characteristic of being completely ab initio the results collected in Table 6 must be considered as very satisfactory and promising for continued application.

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