

## THE RYDBERG STATES OF TRANS-BUTADIENE FROM GENERALIZED VALENCE BOND AND CONFIGURATION INTERACTION CALCULATIONS\*

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Self-consistent ab initio generalized valence bond (GVB) and configuration interaction (CI) calculations are presented for the Rydberg states of *trans*-1,3-butadiene. Five Rydberg series were identified, three optically allowed ( $np_z$ ,  $np_x$  and  $nf_x$ ) and two optically forbidden ( $ns$  and  $nd_x$ ). It is shown that, except for the  $\tilde{A}$  and  $\tilde{F}$  bands (which correspond to the non-valence  $1^1B_u$  and the valence  $2^1A_g$  states, respectively) all the transitions observed in the ultra-violet (UV) and electron-impact (EI) spectra, and in the two-photon spectra, can be assigned to members of these Rydberg series.

### 1. Introduction

Because of the role of particular polyenes in the photochemistry of vision there have recently been numerous experimental studies of the excited states of various polyenes [1-18].

However, there is still considerable uncertainty in both the nature and the assignment of even the smaller polyenes such as 1,3-*trans*-butadiene and 1,3,5-*trans*-hexatriene (hereafter referred to as butadiene and hexatriene, respectively).

In a previous publication (hereafter referred to as paper I) [19], we presented results of extensive ab initio generalized valence bond (GVB) and configuration interaction (CI) studies for the valence states of butadiene and hexatriene molecules. In this paper we present calculations for the Rydberg states of butadiene.

Some of the results for hexatriene have been published [20], but a more complete description of the calculations will be presented in another publication. These studies are used to assign the observed one- and two-photon spectra of butadiene and hexatriene.

The  $^1B_u$  ( $\pi \rightarrow \pi^*$ ) states are more complicated. These states involve Rydberg and valence character and in addition a correct description requires inclusion of electron correlation in the  $\sigma$  system. For these reasons a discussion of these states is postponed to a later paper.

### 2. Geometry and basis set

We used the ground state geometry as determined experimentally by electron diffraction techniques [21]. The basis set consisted of the Dunning valence double zeta basis [22] augmented with diffuse basis functions of 3s, 3p <sub>$\sigma$</sub> , 3p <sub>$\pi$</sub>  and 3d <sub>$\pi$</sub>  character (as described

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herein) in order to provide an adequate description of the Rydberg excited states.

### 3. Butadiene Rydberg states

In this section we describe the calculations performed for the Rydberg states of the butadiene molecule.

To understand the symmetry of the states being described recall that:

(a) a simple molecular orbital (MO) description of butadiene leads to four  $\pi$  MO's,  $1a_u$ ,  $1b_g$ ,  $2a_u$ , and  $2b_g$ , in order of increasing energy; thus the ground state corresponds to the electronic configuration  $(1a_u)^2(1b_g)^2$ ; and

(b) the molecular designation of the atomic orbitals in butadiene is  $ns = a_g$ ;  $np = a_u$ , two  $b_u$ ;  $n_d =$  three  $a_g$ , two  $b_g$ ; and  $nf =$  four  $a_u$ , three  $b_u$ .

The Rydberg states have overall symmetries  $B_g(1b_g \rightarrow ns, nd\sigma)$ ,  $A_u(1b_g \rightarrow np_\sigma, nf_\sigma)$ ,  $A_g(1b_g \rightarrow nd_\pi)$ , and  $B_u(1b_g \rightarrow np_\pi, nf_\pi)$ . Transitions to the  $^1A_u$  and  $^1B_u$  states are optically allowed while transitions to the  $^1A_g$  and  $^1B_g$  states are forbidden.

#### 3.1. Basis sets

In order to describe the  $\sigma$  Rydberg excited states, we augmented the valence basis set with 12 diffuse basis functions of  $3s$ ,  $3p_x$ , and  $3p_y$  character ( $\xi_{3s} = 0.023$ ,  $\xi_{3p} = 0.021$ ) centered at each carbon atom. An IVO calculation [23] with this basis (referred to as basis A) provides an adequate description of the  $3s$ ,  $3p_\sigma$ ,  $3p_\sigma$ ,  $3d_\sigma$ ,  $3d_\sigma$ , and  $3d_\sigma$  Rydberg orbitals.

In solving self-consistently (and also at the CI level) for the Rydberg states of butadiene it is desirable to reduce the size of the basis set without sacrificing the accuracy of the results. To this purpose we performed several calculations at the IVO level as summarized in table 1.

From table 1 we see that excluding the  $3p$  basis functions (basis B) reduces the number of diffuse basis functions to four but at the sacrifice of serious errors in the  $3p_\sigma$  orbitals. On the other hand, from the plots of the  $3s$ ,  $3p_\sigma$ , and

$3p_\sigma$  orbitals in fig. 1(a, c, e) it appears that four off-center  $3s$ -like basis functions might adequately describe these states. Choosing appropriate coordinates (see table 1) for the  $3s$ -like basis functions (basis C) leads to adequate results for the first four Rydberg states. Fig. 1(b, d, f) shows the first three Rydberg states obtained from the calculation with basis C [compare with fig. 1(a, c, d)].

An alternative approach is to use both  $3s$  and  $3p_\sigma$  basis functions but to center them at the  $C_1$ - $C_2$  and  $C_3$ - $C_4$  bond midpoints. This basis (D) has half the diffuse basis from basis A but leads to an excellent description of the first five Rydberg orbitals. This approach was used for the calculations on the hexatriene molecule, and we recommend this approach for similar calculations on larger polyenes.

For the  $\pi$  Rydberg states we considered a basis augmented by one  $3p_\pi$  basis on each carbon atom (basis E) and a basis with two  $3p_\pi$  basis functions at each carbon atom plus a set of  $3d_\pi$  basis functions at the  $C_1$ - $C_2$  and  $C_3$ - $C_4$  bond midpoints. From table 1 we see that while basis E is quite accurate for describing the  $3p_\pi$ ,  $3d_{xy}$  and  $4f_x^3$  Rydberg orbitals, the second  $3d_\pi$  ( $3d_{xz}$ ) and the  $4f_{xz^2}$  orbitals are off by 0.25 eV and 0.4 eV, respectively (compare with the basis E).

#### 3.2. Character of the Rydberg orbitals

Although these orbitals have the overall characteristics expected from the designated names ( $3s$ ,  $3p$ ,  $3d$ , etc.), there are clear effects due to the influence of the molecule.

In fig. 1(a, c, e) we show the first three  $\sigma$  Rydberg orbitals (using basis A). These orbitals can be easily associated with  $3s$  (a) and the two  $3p_\sigma$  (c, e) atomic orbitals. Because the  $3s$  orbital must be orthogonal to the bonding orbitals of the molecule, its shape (in the molecular plane) is modified from spherical symmetry to an ellipse with the major axis elliptical along the line joining the  $C_1$ - $C_4$  carbon atoms (the  $\bar{z}$  axis). The two  $3p_\sigma$  orbitals are less distorted but are oriented parallel ( $\bar{z}$  axis) and perpendicular ( $\bar{y}$  axis) to the molecular coordinate system. Using

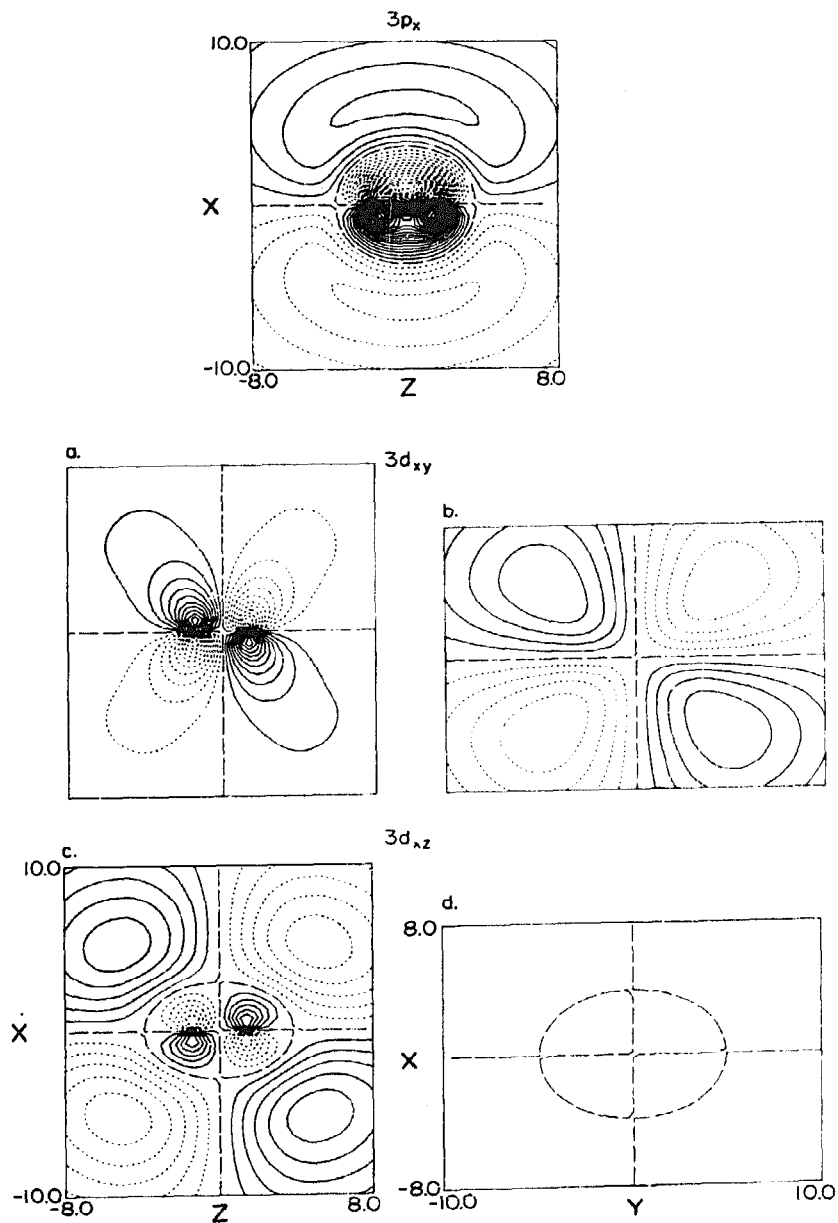


Fig. 3.  $3p_\sigma$  and  $3d_\sigma$  Rydberg orbitals of butadiene using basis set E (table 1). Amplitudes as in fig. 1.

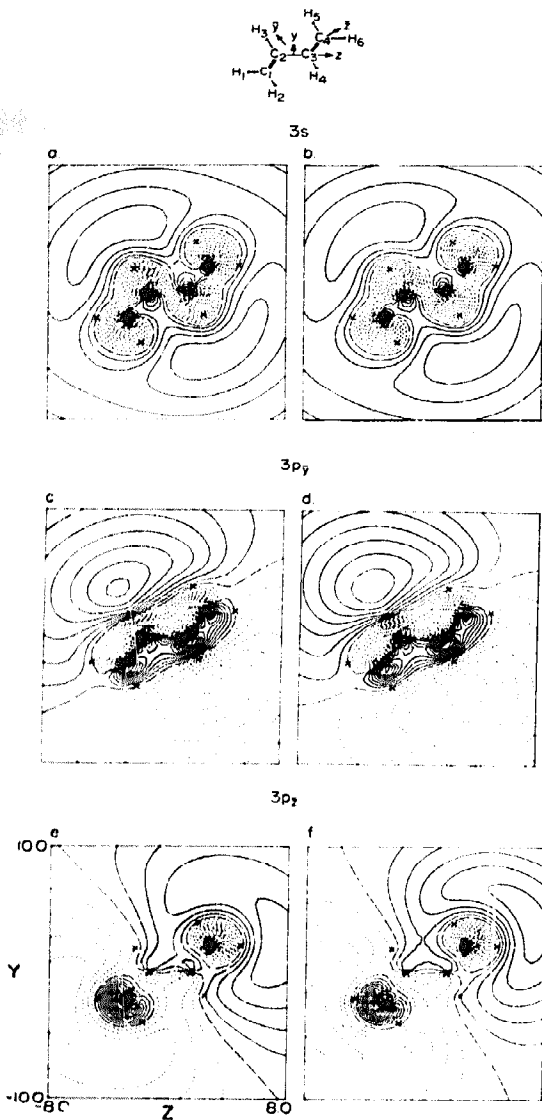


Fig. 1.  $3s$  and  $3p$  Rydberg orbitals of butadiene. Orbitals a, c, e using basis set A (table 1). Orbitals b, d, f using basis set C (table 1). Long dashes indicate zero amplitude, solid lines and short dashes indicate positive and negative amplitudes, with a spacing of 0.005 atomic units between the contours.

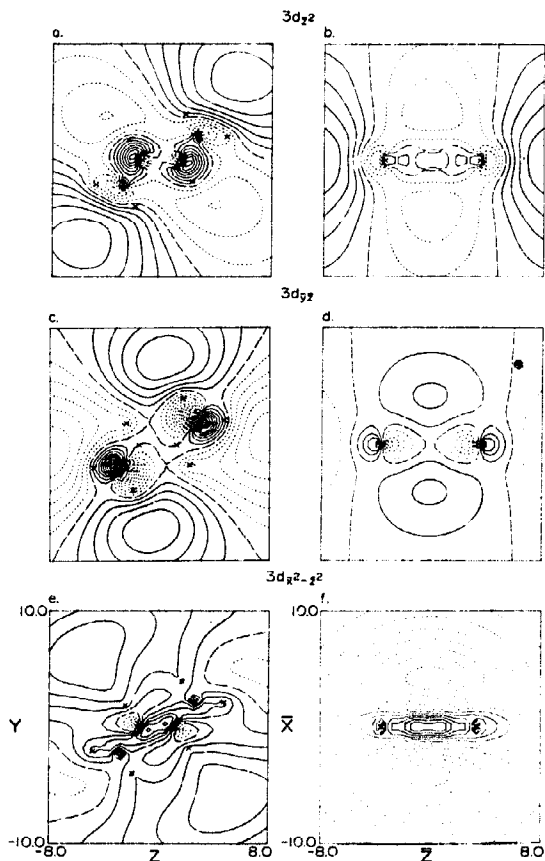


Fig. 2.  $3d$  Rydberg orbitals of butadiene using basis set A (table 1). Orbitals a, c, e are plotted in the molecular plane. Orbitals b, d, f are plotted in the plane perpendicular to the molecule with abscissa along the long axis of the molecule ( $\bar{X}\bar{Z}$  plane of fig. 1). Amplitudes as in fig. 1.

### 3.3. Hartree-Fock and GVB calculations

In this section we will describe the calculations performed on the Rydberg states at the Hartree-Fock (HF) and GVB levels.

#### 3.3.1. ${}^1B_g$ and ${}^1A_u$ states

The  ${}^1B_g$  and  ${}^1A_u$  Rydberg states correspond to excitations out of the  $1b_g(\pi)$  orbital to the  $3s$

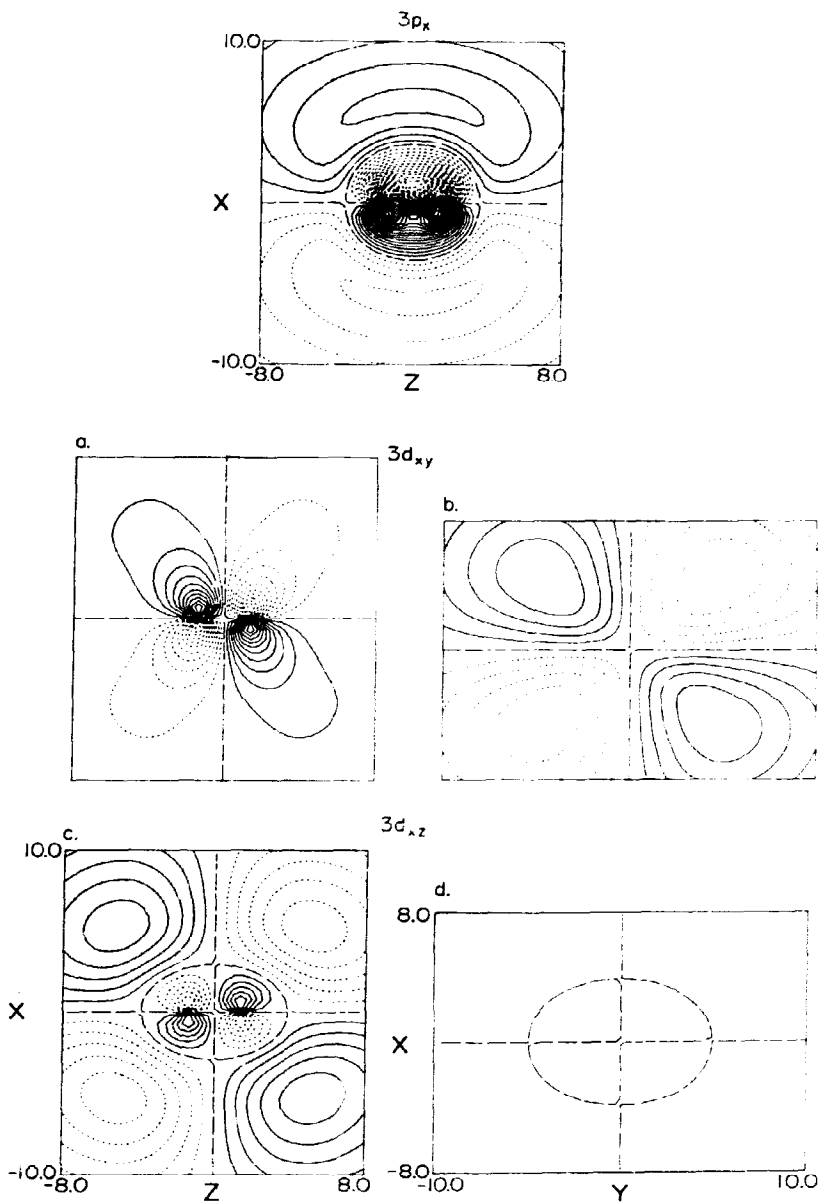


Fig. 3.  $3p_{\pi}$  and  $3d_{\pi}$  Rydberg orbitals of butadiene using basis set E (table 1). Amplitudes as in fig. 1.

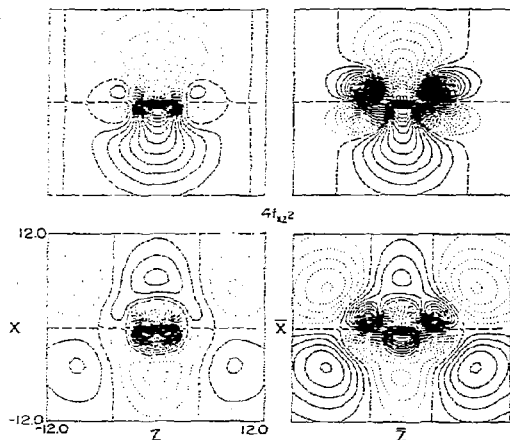


Fig. 4.  $4f_{\pi}$  Rydberg orbitals of butadiene using basis set E (table 1). Amplitudes as in fig. 1.

and  $3p_y$ ,  $3p_z$  orbitals. These transitions add one more electron to the  $\sigma$  space. We have not correlated the  $\sigma$  valence orbitals in the SCF calculations (in order to avoid any additional constraints that might affect various Rydberg states differently).

Using the IVO's obtained with basis set C (table 1) as starting guesses for the excited orbitals, we solved self-consistently, at the HF level, for the  ${}^1B_g[1b_g(\pi) \rightarrow 3s]$  and  ${}^1A_u[1b_g(\pi) \rightarrow 3p_{\sigma}]$  Rydberg states.

### 3.3.2. ${}^1B_u$ and ${}^1A_g$ states

The  ${}^1A_g$  and  ${}^1B_u$  Rydberg states correspond to excitations out of the  $1b_g(\pi)$  orbital to the  $3d_{\pi}$  and  $3p_{\pi}$  orbitals, respectively. Since they are both  $\pi$  states, we do not expect that correlating the  $\sigma$  valence orbitals will cause any constraints on the description of these states.

Using the IVO's obtained with basis set E (table 1) as starting guesses for the excited orbitals ( $3p_{\pi}$  and  $3d_{\pi}$ ), we constructed GVB(3/PP) $^{\ddagger}$  wavefunctions for both the  ${}^1A_g$

$^{\ddagger}$  The GVB calculations were carried out with the Bobrowicz-Wadt-Goddard GVB TWO program. See ref. [24].

and  ${}^1B_u$  states. These wavefunctions correspond to correlating the three  $(C-C)_{\sigma}$  bonds.

Because the  ${}^1A_g[1b_g(\pi) \rightarrow 3d_{\pi}]$  Rydberg state is not the lowest state of this particular symmetry, the GVB(3/PP) wavefunction will not represent the "pure" Rydberg state. Nevertheless, the self-consistent orbitals generated will be adequate to describe a diffuse open-shell state. The final description of this Rydberg state is obtained as a higher root of a CI calculation. It is very easy to distinguish, in the CI calculations, the Rydberg  ${}^1A_g$  state from the valence  $X{}^1A_g$  and  $2{}^1A_g$  states, as will be discussed in the next sections.

The  ${}^1B_u[1b_g(\pi) \rightarrow 3p_{\pi}]$  Rydberg state has the same symmetry as the strong dipole-allowed  ${}^1B_u$  state observed experimentally (peak) at 5.95 eV. Using the ground state geometry and eschewing electron correlation of the  $\sigma$  electrons, the lowest  ${}^1B_u$  state is of Rydberg character. From table 1 we can see that the Rydberg states corresponding to the same atomic  $l$  quantum number occur close to each other. Of course, in a "central field" they would be degenerate. Since the transitions to the  $3p_{\sigma}$  states can be unambiguously assigned and since the  $\pi$  IVO state always occurs in the same region of the two  $3p_{\sigma}$  states, this  $\pi$  state is assigned as the  $3p_{\pi}$  Rydberg transition. After solving for these states self-consistently, carrying out CI calculations leads to final states that also occur in the same region of the spectrum.

### 3.4. Full $\pi$ -CI calculations.

The first set of CI calculations\* was performed using the respective HF of GVB wavefunctions obtained in the previous section.

For the  ${}^1B_g(3s)$  Rydberg states the  $\pi$  space was formed by the eight HF  $\pi$  MO's. To the diffuse self-consistent  $3s$  orbital we added three more  $\sigma$  orbitals, obtained from the IVO calculations, properly reorthogonalized to the occupied  $\sigma$  orbitals. Using these 12 orbitals ( $8\pi + 4\sigma$ ) we performed a full  $\pi$ -CI while simultaneously allowing the  $\sigma$  electrons to

\* The CI calculations were carried out with the Caltech spin-eigenfunction program. See ref. [24].

Table 2  
Transition moments and spatial extension of the Rydberg orbitals of butadiene

Orbital <sup>a)</sup>	Transition moments (au)		Component	Second moments <sup>d)</sup>		
	$\langle\phi_{\text{IVO}} r \pi_2(1b_g)\rangle^b$	$\langle S r X^1A_g\rangle^c$		$\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle z^2 \rangle$
$\pi_1(1a_u)$				2.436	2.277	4.487
$\pi_2(1b_g)$				2.463	3.451	6.721
3s	0.5883	1.0384	$\langle xy \rangle$	15.138	22.057	23.133
	1.2163	2.0701	$\langle xz \rangle$			
3p <sub>y</sub>	0.0257	0.0737	$\langle x \rangle$	12.859	33.095	24.371
3p <sub>z</sub>	0.3429	0.4684	$\langle x \rangle$	17.315	31.745	47.192
3p <sub>x</sub>	0.7863	0.6065	$\langle y \rangle$	27.898	13.827	16.257
	0.7948	0.7590	$\langle z \rangle$			
3d <sub>z<sup>2</sup></sub>	0.2180		$\langle xy \rangle$	12.578	29.270	53.010
	0.1566		$\langle xz \rangle$			
3d <sub>yz</sub>	0.3284		$\langle xy \rangle$	14.928	55.963	45.454
	0.0925		$\langle xz \rangle$			
3d <sub>x<sup>2</sup>-y<sup>2</sup></sub>	0.7531		$\langle xy \rangle$	18.394	35.346	23.453
	1.3187		$\langle xz \rangle$			
3d <sub>xy</sub>	1.4438		$\langle yz \rangle$	30.816	32.224	15.059
3d <sub>yz</sub>	0.2717		$\langle yz \rangle$	37.754	13.418	38.540
4f <sub>x<sup>3</sup></sub>	1.0866		$\langle y \rangle$	20.014	8.177	9.434
	0.9729		$\langle z \rangle$			
4f <sub>xz<sup>2</sup></sub>	0.4851		$\langle y \rangle$	32.51	32.630	38.777
	0.4619		$\langle z \rangle$			

<sup>a)</sup> Orbitals  $\pi_1(1a_u)$  and  $\pi_2(1b_g)$  are from ground state wavefunction. Rydberg orbitals are from IVO calculations using basis sets A and E of table 1.

<sup>b)</sup> Transition moments using IVO orbitals.

<sup>c)</sup> Transition moments using full  $\pi$ -CI wavefunctions.

<sup>d)</sup> Second moments from IVO orbitals.

readjust in the full  $\sigma$  space. The first CI root of this calculation corresponds to the 3s Rydberg state and the second one to the first 3d <sub>$\sigma$</sub>  Rydberg state. Table 3 shows the results of this calculation and compares them with other results obtained at the same level.

The  $^1A_u(3p_\sigma)$  states were obtained by a similar calculation using the appropriate orbitals. The results are also shown in table 3.

For the  $^1A_g(3d_\pi)$  Rydberg states we started from the GVB(3/PP) wavefunction described above. From our augmented basis set we obtain 12  $\pi$  MO's. To these orbitals we added six  $\pi$  IVO's properly reorthogonalized to the occupied  $\pi$  MO's. Using this space (18  $\pi$  MO's) we performed a full  $\pi$ -CI calculation. Four CI roots were obtained from this calculation in order to project out the ground state and the first valence excited  $^1A_g$  states. These can be clearly distinguished from the Rydberg states.

The first root is dominantly a closed-shell valence state, while the second one is dominantly a double excited valence state. The next two roots correspond to dominantly single excited diffuse configurations and represent the Rydberg states. The results obtained for these Rydberg states are also shown in table 3.

For the  $^1B_u$  states we proceeded in an analogous way. Starting with the 12  $\pi$  MO's from the GVB(3/PP) calculation on the  $^1B_u$  state, we added six  $\pi$  IVO's properly orthogonalized to the occupied  $\pi$  MO's and performed a full  $\pi$ -CI among the 18  $\pi$  MO's. The results of this calculation are shown in Table 3.

### 3.5. All-valence CI calculations

In this second set of CI calculations we allowed all but the carbon 1s-like orbitals to participate in the CI treatment.

Table 3  
Results of full  $\pi$ -CI calculations for the 1,3-*trans*-butadiene molecule<sup>a)</sup>

State <sup>b)</sup>	Present results	Shih et al. <sup>c)</sup>
X $^1A_g$	-154.92796 h	-154.9181 h
1 $^1B_g(3s)$	6.30 eV	6.24 eV
2 $^1B_g(3d_{xz})$	7.33	7.31
1 $^1A_u(3p_y)$	6.63	6.50
2 $^1A_u(3p_x)$	6.80	6.76
$^1B_u(3p_x)$	6.79	6.60
$^1B_u(4f_x)$	8.16	7.98
$^1B_u(4f_{xz})$	9.00	
3 $^1A_g(3d_{xy})$	7.73	7.79
4 $^1A_g(3d_{zz})$	7.84	

<sup>a)</sup> Ground state in hartrees. Transition energies in eV.

<sup>b)</sup> State assignments from present calculations.

<sup>c)</sup> Ref. [29].

In these calculations the CI matrices are considerably larger than the ones generated in the previous calculations. Because of this we limited ourselves to lower levels of CI excitations. In so doing, we follow exactly the same strategy as used in paper I, where we examined  $\sigma$  effects on the valence states. Here we also used both localized and delocalized descriptions of these states.

The localized description calculation was designed to detect any flow of charge along the bonds in the  $\sigma$  space resulting from the redistribution of charge in the  $\pi$  space. To obtain the localized description of these states, one should have to solve, in principle, for at least a GVB(9/PP) wavefunction for each one of the states. Since Rydberg states correspond to excitation of an electron to an orbital that is in general much larger than the dimensions of the molecule, one can look at these states as being composed of one electron plus a residual positive core. Since all the Rydberg states with which we are dealing result from excitations out of the same  $\pi(1b_g)$  orbital, the remaining  $N-1$  electron core will be similar for all these states. This positive core corresponds basically to the  $^2B_g$  ion. Consequently, we solved for a GVB(9/PP) wavefunction for the  $^2B_g$  ion state. The first natural orbitals from this latter cal-

ulation were then projected onto the occupied HF  $\sigma$  core of each one of the Rydberg states. The second natural orbitals were projected onto the virtual (unoccupied) HF space of each one of the Rydberg states. In this way we obtained a localized representation of the HF  $\sigma$  space nearly identical to the one that we would have obtained from the first natural orbitals of a full GVB solution. In addition, we obtained a good approximation to the correlating (second natural) orbitals that would have been obtained from the full GVB calculations.

Once the localized description was obtained, we proceeded in exactly the same way as in paper I. We started from the full  $\pi$ -CI configuration lists of each one of the states and selected all the configurations contributing an energy lowering of 0.001 h or more. From these we allowed all single excitations in the  $\pi$  space times all single excitations in the full  $\sigma$  space. To these new lists we added the respective configuration lists corresponding to the full  $\pi$ -CI's described in the previous section. With these final lists we performed the CI calculations. The results of these calculations are shown in table 4. We did not find any special  $\sigma$ - $\pi$  mixed effect, but again, as in the case of the valence states (paper I), all the important configurations involving  $\sigma$  excitations came from excitations within the (CC)  $\sigma$  subspace. Comparing tables 3 and 4, one notices that the results of the full  $\pi$ -CI calculations do not differ appreciably from the present simplified CI, particularly for the first roots of each symmetry.

To study the effect of higher excitation levels, we recombined the natural orbitals to obtain a set of symmetry orbitals. In so doing we reduced considerably the number of configurations and that allowed us to increase the level of excitation.

With the delocalized description we first considered the same type of CI described above. From the full  $\pi$ -CI calculations, using the delocalized description, we selected all the configurations contributing an energy lowering of 0.0002 h or more. From these selected configuration lists we allowed all single excitations in the  $\pi$  space times all single excitations



Table 4  
All-valence CI results for the Rydberg states of butadiene<sup>a)</sup>

State <sup>b)</sup>	Present results	Buenker et al. <sup>c)</sup>
$\infty$ $^1A_g$	-155.01537	-155.1900
1 $^1B_g(3s)$	6.29	6.20
2 $^1B_g(3d_{yz})$	7.29	7.29
1 $^1A_u(3p_y)$	6.61	6.53
2 $^1A_u(3p_x)$	6.78	6.72
$^1B_u(3p_x)$	6.67	6.67
$^1B_u(4f_x^2)$	7.97	7.96
$^1B_u(4f_{xz}^2)$	8.91	
3 $^1A_g(3d_{xy})$	7.68	7.53
4 $^1A_g(3d_{xz})$	7.79	7.78

<sup>a)</sup> Ground-state energies in hartrees. Transition energies in eV.

<sup>b)</sup> State assignments from present calculations.

<sup>c)</sup> Ref. [26].

in the full  $\sigma$  space. To these new lists of configurations we added the respective configuration lists corresponding to the full  $\pi$ -CI calculations. With these final lists we performed the CI calculations. No appreciable changes were found relative to the previous CI's, using the localized description. The next CI calculations were designed to investigate the effect of double excitations in the  $\sigma$  space. We started once more from the full  $\pi$ -CI configuration lists and selected those configurations contributing an energy lowering of 0.001 or more. From these configurations we allowed single excitations in the  $\pi$  space configurations and we allowed single excitations in the  $\pi$  space times (S+D) excitations in the  $\sigma$  space. To the new lists of configurations we added the respective lists of configurations corresponding to the full  $\pi$ -CI calculations. Again, no appreciable changes occurred and practically all the configurations including double excitations in the  $\sigma$  space involved the (C-C)  $\sigma$  subspace.

From these calculations one can conclude that the Rydberg states of butadiene can be very well represented at a full  $\pi$ -CI level. While not shown in table 3, it is also true that the first states of each symmetry can be well represented at intermediate levels of excitation in the  $\pi$

space. Another conclusion that results from these calculations is that the  $\sigma$  effects can be well established using only the (CC)  $\sigma$  subspace.

#### 4. Discussion

We now proceed to discuss the results of the calculations comparing our results with the experimental spectra and other theoretical calculations. As will be apparent from the discussion, most of the spectra of butadiene can be explained in terms of a few valence states plus a series of Rydberg transitions.

Except for the  $1^1B_u$  state experimentally observed at 5.95 eV (peak) [4], our present calculation provides assignments for all of the observed transitions. Table 5 shows our results (including the valence states) and compares them with experimental results. (A recent ab initio calculation [25] leads to generally similar assignments.)

The transitions observed experimentally at  $\approx 3.2$  eV and  $\approx 4.9$  eV can be unambiguously assigned to the two lower triplets  $^3B_u$  and  $^1A_u$  states, corresponding to the  $\bar{a}$  and  $\bar{b}$  bands.

The next transition, observed experimentally at  $\approx 5.95$  eV [4, 26] and assigned to the  $1^1B_u$  state ( $\bar{A}$  band system), constitutes the most serious challenge to the theoretical description of the electronic states of polyenes. The results obtained so far provide evidence that the peak in the observed transition has significant contributions from distorted geometries. Our best estimate locates this transition at 6.12 eV and that corresponds to a "state" with all C-C bond distances equal to 1.40 Å and with the (C-C) terminal bonds symmetrically bent 0.8 degrees relative to the ground-state geometry. We believe that a more detailed investigation of the symmetric stretched geometries will provide the final answer to the problem.

We assigned the system band  $\bar{B}\ddagger$  observed at  $\approx 6.27$  eV to the  $^1B_g(3s)$  Rydberg state. This transition has recently been observed in a two-photon absorption experiment [7, 17]. While no

$\ddagger$  This state designation is used by Herzberg [27].

polarization studies were performed, on the basis of the present calculation this transition can be unambiguously assigned to the  $1^1B_u(3s)$  Rydberg state, since no other parity-forbidden states were predicted in this region. This assignment also agrees with the results of Buenker et al. [26].

In the region between 6.0 eV and 7.0 eV two more transitions have been observed experimentally, one at 6.64–6.66 eV [3, 4] and another at 6.80–6.81 eV [3, 4]. In the same region our calculations predicted three states, namely, the  $1^1A_u(3p_y)$  at 6.61 eV, the  $1^1B_u(3p_x)$  state at 6.67 eV, and the  $2^1A_u(3p_x)$  state at 6.78 eV. The transition at 6.80–6.81 eV can be assigned to the  $2^1A_u(3p_x)$  Rydberg state but the transition at 6.64–6.66 eV could be assigned equally to the  $1^1A_u(3p_y)$  state or the  $1^1B_u(3p_x)$  state. At this point the assignment has to be decided in terms of the relative intensities of the transitions. For this purpose we calculated oscillator strengths for all three transitions at the full  $\pi$ -CI level. We found  $f$  values of 0.0026 for the  $1^1A_u$  state, 0.1096 for the  $2^1A_u$  state and 0.3410 for the  $1^1B_u(3p_x)$  state. From these results it is quite reasonable to assume that the  $1^1A_u(3p_y)$  may not be observed. So we assigned the transition observed at 6.64–6.66 eV ( $\bar{C}$  band) [27] to the  $1^1B_u(3p_x)$  Rydberg state. The transition at 6.80–6.81 eV ( $\bar{D}$  band) [27] we assign to the  $2^1A_u(3p_x)$  Rydberg state. Our assignments in this region differ from the ones by Buenker et al. since they do not assign any transition corresponding to the  $\bar{D}$  band.

Several transitions are observed experimentally in the region between 7.0 eV and 8.0 eV [3, 4]. These were designated as  $\bar{E}$ ,  $\bar{F}$ , and  $\bar{G}$  band systems by Herzberg [27].

The first of these bands ( $\bar{F}$ ) is observed at 7.07–7.08 eV [3, 4]. McDiarmid [3] assigns this transition to the first member ( $n=3$ ) of a p-allowed Rydberg series (series 2). More recently, Wiberg et al. [12] from a comparative study of the vibrational structures of the UV and photoelectron spectra (PE) also assigned this transition as the origin of a Rydberg series. We do not find any Rydberg transitions in this region. On the contrary, we find the  $2^1A_g(\pi \rightarrow$

$\pi^*)$  valence state at 7.06 eV and another recent ab initio calculation [26] also finds this state in the same region (7.02 eV). As discussed above, from the three possible  $\pi p$  series, one is probably not observed ( $1^1A_u(3p_y)$ ) and the first members of the two other series were identified with the  $\bar{C}$  and  $\bar{D}$  bands ( $3p_\pi$  and  $3p_\sigma$ , respectively). Since the higher members of McDiarmid series 2 can be accounted for in terms of our Rydberg series, we assign the 7.06 eV transition to the  $2^1A_g(\pi \rightarrow \pi^*)$  valence state. (Of course, this transition is made optically allowed because of vibronic coupling.) In addition, the spectrum of solid butadiene shows the presence of a weak absorption in this region, providing supporting evidence for the identification of this transition with a valence state.

The UV absorption in the 7.27–7.86 eV region was originally assigned to a  $X \rightarrow \bar{E}$  band system [27] and is by far the most complicated structure of the spectrum. From the McDiarmid [3] analysis of the UV spectrum and from the electron-impact (EI) results of Mosher et al. [4], it is quite clear that this  $\bar{E}$  band has several components. Transitions are observed at 7.27, 7.47, 7.63, 7.79, and 7.85 eV in the UV spectrum [3] and at 7.28, 7.48, 7.60, and 7.80 eV in the EI spectrum [4]. We find several Rydberg transitions in this region. In table 5 we list the components of the  $\bar{E}$  band system as predicted by our calculations. The first three observed transitions (7.33, 7.47, and 7.65 eV) are assigned to parity-forbidden transitions that can be made vibronically allowed. The last two transitions (7.79 and 7.85 eV) correspond to higher members of the dipole-allowed Rydberg series  $\pi p_x$  and  $\pi p_z$ . These assignments are consistent with the fact that the first three transitions are very weak, while the last two are relatively more intense. The  $3^1B_g(3d_{yz})$  Rydberg state at 7.40 eV does not result from the CI calculations. From table 1 we can see that our basis set (basis C) cannot represent well the second  $3d_\sigma$  orbital. But we can still make a good estimate of the transition energy in the following way. From table 1 we have an estimate of the transition energies for both  $3d_\sigma$  Rydberg orbitals, and from table 4 we have the

Table 5  
Excited electronic states of the butadiene molecule

State	Theoretical results <sup>a)</sup> (eV)	McDiarmid <sup>b)</sup> UV absorption	Experimental results (eV)	
			Flicker et al. <sup>c)</sup> electron-impact	others
$\tilde{A}1 \ ^3B_u$	3.35		3.22	3.22 <sup>d)</sup> , 3.3 <sup>e)</sup>
$\tilde{B}1 \ ^3A_g$	5.08		4.91	4.9 <sup>d)</sup>
$\tilde{A}1 \ ^1B_u$	6.12		5.76, 5.92 (peak), 6.05	(5.75, 5.92, 6.09) <sup>d)</sup> , (5.71–0.29)
$\tilde{B}1 \ ^1B_g(3s)$	6.29	6.27		6.26 <sup>d)</sup>
$\tilde{C} \ ^1B_u(3p_x)$	6.67	6.66	6.64	
$\tilde{D}2 \ ^1A_u(3p_z)$	6.78 <sup>i)</sup>	6.81	6.80	
$\tilde{F}2 \ ^1A_g$	7.06	7.07	7.08	
$\tilde{E}$	$2 \ ^1B_g(3d_{z^2})$	7.29	7.27, 7.33	7.28
	$3 \ ^1B_g(3d_{xz})$	7.40 <sup>k)</sup>	7.47, 7.48	7.48
	$4 \ ^1B_g(4s)$	7.65	7.63, 7.64	7.60
	$3 \ ^1A_g(3d_{xy})$	7.68		
$\tilde{G}$	$1 \ ^1B_u(4p_x)$	7.79	7.79	7.80
	$4 \ ^1A_u(4p_z)$	7.82	7.85	
$\tilde{H}$	$1 \ ^1B_u(4f_{z^3})$	7.97	8.00	8.00
	$1 \ ^1B_u(5p_x)$	8.23	8.18	8.18
$\tilde{I}$	$1 \ ^1A_u(5p_z)$	8.26	8.25	
	$1 \ ^1B_u(5f_{z^3})$	8.33	8.36	8.39
	$1 \ ^1B_u(6p_x)$	8.45	8.41	
	$1 \ ^1A_u(6p_z)$	8.48	8.47	
	$1 \ ^1B_u(6f_{z^3})$	8.52	8.50	8.54
	$7p_x, 7p_y, 7f_x^3$	8.60, 8.63	8.65	
$8p_x, 8p_y, 8f_x^3$	8.68, 8.70	8.67	8.69	
$9p_x, 9p_y, 9f_x^3$	8.74, 8.75	8.77		
$10p_x, 10p_y, 10f_x^3$	8.78	8.78		
$11p_x, 11p_y, 11f_x^3$	8.80, 8.81	8.85		
$12p_x, 12p_y, 12f_x^3$	8.82, 8.83	8.89	8.90	

<sup>a)</sup> Results for the valence states from paper I.

<sup>b)</sup> Ref. [3]. <sup>c)</sup> Ref. [4]. <sup>d)</sup> Ref. [30]. <sup>e)</sup> Ref. [32]. <sup>f)</sup> Ref. [33].

<sup>g)</sup> Ref. [26]. <sup>h)</sup> Ref. [27]. <sup>i)</sup> Refs. [7, 31].

<sup>j)</sup> The  $1 \ ^1A_u(3p_z)$  state calculated at 6.61 eV is probably not observed ( $f=0.0026$ ). See text for discussion.

<sup>k)</sup> Estimated from IVO calculations plus CI corrections. See text for discussion.

#### CI correction for the $3d_{xz}$ Rydberg state.

Assuming the same CI corrections for both states, we obtain the  $3d_{xz}$  state at 7.40 eV. The observed transition at 7.63–7.64 eV [3] can be correlated with either the  $4 \ ^1B_g(4s)$  state or the  $3 \ ^1A_g(3d_{xy})$  state. We expect the transition to correspond most probably to the  $3d_{xy}$  state since the first member of the  $ns$  series is very weak. Our assignments of the components of the  $\tilde{E}$  band system differ appreciably from the ones by Buenker et al. [25]. Recently, Wiberg et al. [12] proposed that all the transitions in this

region are vibrational components of a single Rydberg transition with the origin at 7.06 eV.

The next two observed transitions correspond to bands  $\tilde{G}$  and  $\tilde{H}$  at 8.0 eV and 8.18 eV, respectively [3, 4]. We assign these transitions to the  $1 \ ^1B_u(4f_{z^3})$  and  $1 \ ^1B_u(5p_x)$   $\pi$ -Rydberg states.

In order to understand the many transitions converging to the first IP, we examined the various Rydberg series for which our calculations provided the first members.

Table 6 shows the results of our studies on five different Rydberg series. The other possible

series were discarded because their first members showed very low intensity or because their first members cannot be well represented by our basis set. One example of the former is the  $np_z$  ( $n^1A_u$ ) series whose first member ( $3p_z$ ) is very weak ( $f = 0.0026$ ). An example of the latter is the  $nf_{xz^2}$  series.

Typical quantum defects ( $\delta$ ) for molecular spectra are [28]  $\delta_s \approx 1.0$ ,  $\delta_p \approx 0.6$ ,  $\delta_r \approx 0.1$ , and  $\delta_t \approx 0.0$  with deviations of  $\pm 0.2$  units.

From table 6 we can see that:

(a) the quantum defects obtained are in the range expected for each type of series. The fact that the  $\delta f_{xz^2}$  are larger than expected can be attributed to a possible strong coupling between those states and the  $np_x$  states since they both have the same symmetry;

(b) for  $n \geq 9$  all the series are practically degenerate;

(c) the optically allowed  $np_x$  ( $^1B_u$ ),  $np_z$  ( $^1A_u$ ) and  $nf_{xz^2}$  ( $^1B_u$ ) Rydberg series can account for all the transitions observed in this region.

The disagreement between our calculated transitions and the ones observed for larger  $n$ 's is certainly because our series converges to a lower ionization potential.

This region of the butadiene spectrum has been recently analyzed by McDiarmid [3] and

Ellison [15] using UV absorption spectroscopy and by Johnson [7] using multi-photon absorption spectroscopy. In Ellison's analysis [15] he finds a single Rydberg series with the first member ( $n = 3$ ) at 7.06 eV. McDiarmid [3] analyzes this region in terms of four Rydberg series. She assigns two of the series to p-allowed series and the other two to d or f series. Johnson [7] proposes the existence of three Rydberg series in the molecule with two of them almost degenerate. He proposes an  $n(p, f)^1B_u$  series with a very strong f component, an  $n(p, f)^1A_u$  series, and another  $n(p, f)^1A_u$  series with strong p character.

From our analysis we conclude that the transitions in this region can be explained in terms of an  $np_x^1B_u$  series, an  $nf_{xz^2}^1B_u$  series, and an  $np_z^1A_u$  series. We also expect an  $nf_{\sigma}^1A_u$  series to be present in this region. Because our basis set cannot describe adequately  $f_{\sigma}$  states, we do not present any results for this series. But we expect, as in the case of the  $np_x$  and  $np_z$ , that both f series will be nearly degenerate even for small  $n$ .

Finally, the transitions observed at 9.53 eV and 11.04 eV in the electron-impact spectrum [4] may correspond to  $\sigma \rightarrow \pi^*$  transitions. In *trans*-hexatriene we found  $\sigma \rightarrow \pi^*$  transitions in these regions of the spectrum. It also could correspond to excitations out of the inner  $\pi$  ( $1a_u$ ) orbital.

Table 6.  
Rydberg series for the butadiene molecule<sup>a)</sup>

$n$	$ns(^1B_u)$ $\delta = 0.76$	$np_z(^1A_u)$ $\delta = 0.52$	$np_x(^1B_u)$ $\delta = 0.58$	$nd_{xz^2}(^1A_u)$ $\delta = 0.18$	$nf_{xz^2}(^1B_u)$ $\delta = 0.36$
3	6.29 <sup>b)</sup>	6.78 <sup>b)</sup>	6.67 <sup>b)</sup>	7.29 <sup>b)</sup>	
4	7.65	7.82	7.79	8.02	7.97 <sup>b)</sup>
5	8.18	8.26	8.23	8.35	8.33
6	8.44	8.48	8.45	8.53	8.52
7	8.58	8.60	8.60	8.64	8.63
8	8.67	8.68	8.68	8.71	8.70
9	8.73	8.74	8.74	8.75	8.75
10	8.77	8.77	8.77	8.78	8.78
11	8.80	8.80	8.80	8.81	8.81
12	8.82	8.82	8.82	8.83	8.83
$\infty$	8.95	8.95	8.95	8.95	8.95

<sup>a)</sup> All energies in eV.

<sup>b)</sup> First members of each series represents calculated values. Other members are predicted values based on the quantum defects.

## 5. Summary

In this final section we summarize the main conclusions of our calculations.

(a) The spectrum of the butadiene molecule can be understood in terms of a few valence states plus a series of Rydberg states.

(b) While the  $2^1A_g$  valence states and the *non-vertical*  $^1B_u$  transition require the inclusion of  $\sigma$  correlation effects to correctly describe them, the remaining Rydberg states can be accurately described at the  $\pi$ -CI level.

(c) The effects of  $\sigma$  correlation on these states can be well established using only the subspace of the (C-C)  $\sigma$  orbitals.

(d) In the description of the  $\sigma$  Rydberg states the size of the basis set can be considerably reduced without loss of accuracy by using appropriate off-center basis functions.

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