Theoretical study of the low-lying states of *trans*-1,3-butadiene

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We present extensive *ab initio* calculations on the low-lying electronic states of *trans*-1,3-butadiene within the multireference configuration interaction (MRCI) framework by selecting the configurations with a perturbative criterion. The $X\ ^1A_g$ ground state and $1\ ^3B_u$, $1\ ^3A_g$, $2\ ^1A_g$, and $1\ ^1B_u$ valence excited states have been calculated at a fixed geometry. The results obtained are in good agreement with previous experimental and calculated values, and could help to understand polyene spectroscopy, photochemistry, and photophysics. The advantages of a MRCI method where the most important contributions to the total MRCI wave function, perturbatively selected, are treated variationally, and the remaining terms are evaluated by means of a perturbational approach, are also discussed. Furthermore, a criterion in order to build a correlation-consistent configuration interaction space is stated and, therefore, a reliable approximation to achieve accurate energy differences is obtained. Several monoelectronic molecular-orbital basis functions are tried in order to select the most adequate to describe each state.

I. INTRODUCTION

Conjugated polyenes have played an important role in the development of molecular quantum theory and they have served widely as models for biological chromophores. Their structure was thought to be rather simple, but this assumption has been revealed uncertain by recent experimental and theoretical findings.[1] The interpretation of the electronic spectra of polyenes is still an open question, in particular, the relative ordering and nature of the butadiene $2\ ^1A_g$ and $1\ ^1B_u$ states.[2–4] For longer all-*trans* polyenes, the $2\ ^1A_g$ state lies below the valence $1\ ^1B_u$. This last state falls, via a nonradiative decay, to the $2\ ^1A_g$ one. Since no emitting states have been observed in butadiene, it has been suggested that the above mechanism does not apply in this molecule.[5] However, the lack of fluorescence in butadiene could be explained by an internal conversion to the ground state from the $2\ ^1A_g$, if it were the lowest excited singlet state. This effect could be increased by the nonplanarity of the state.[4] Recent experimental results from multiphoton ionization and Raman spectroscopy[6] suggest the presence of the $2\ ^1A_g$ valence state below the $1\ ^1B_u$ in hexatriene and butadiene. There is no conclusive evidence, although it has been suggested that these excitations are actually nonvertical transitions.

The dominant feature in the optical[7–10] and electron impact spectra[11–16] of *trans*-1,3-butadiene is a broad intense band stretching from 5.7 to 6.3 eV, with the intensity maximum at 5.92 eV.[11] This band has been assigned to the lowest $\pi \rightarrow \pi^*$ transition, $1b_g \rightarrow 2a_u$ in C_{2h} symmetry, corresponding to a state of ^1B_u symmetry. No conclusions were obtained about the excited state equilibrium structure, potential surface, photochemistry, and photophysics. The interpretation of Frank–Condon analysis of absorption and Raman spectra for the $X\ ^1A_g \rightarrow 1\ ^1B_u$ transition[8,17] had led to the conclusion that the $1\ ^1B_u$ state is essentially planar. However, most recent revisions[2] bring serious doubts on the planarity of $1\ ^1B_u$ state, based on an interpretation of

the vibrational structure, and support the idea of a twisting of the terminal CH_2 group for this state. Electron impact[11–16] and two- and three-photon ionization spectroscopy[18,19] have failed to reveal any hint of a low-lying state $2\ ^1A_g$ state below the $1\ ^1B_u$, although an ion-impact study of substituted dienes[20] and a resonance Raman study[6,21] suggest the presence of such state. The transition to the $2\ ^1A_g$ state is one-photon forbidden, and the original assignment of this state was around 7.3 eV.[11,14] The absence of any emission from these states has complicated the understanding of all butadiene spectroscopy. Table I shows the most important experimental results for the absorption spectrum of *trans*-1,3-butadiene and the initial assignments of the transitions and states.

A large number of theoretical studies has been performed on the low-lying states of the butadiene. Table II presents one selection of the most recent *ab initio* results. It is to point out the relative agreement of the experimental and calculated data for the triplet states and the difficulty in determining the transitions to the $1\ ^1B_u$ and $2\ ^1A_g$ states. The calculated values for the $1\ ^1B_u$ state range from 6.2 to 7.7 eV, far from the experimental value of 5.92 eV. Some authors have suggested that the valencelike feature at 6.0 eV is probably due to a nonvertical transition. Therefore, geometry relaxation effects have been studied[3,4,22–25] with several methodologies. The twisting of the terminal CH_2 groups has been identified as the accepting vibration mode in the rapid nonradiative decay of the $1\ ^1B_u$ electronic state. A recent analysis suggests the $1\ ^1B_u$ state decays by crossing a small CH_2 twist barrier to another unknown state, twisted around the double bonds, and that state could be the unidentified $2\ ^1A_g$ state.[2] No definitive conclusions can be drawn from the experimental point of view about the geometry of these states, although the theoretical methods have found minima of C_{2h} and C_s symmetry for both states[3,4,25] and C_2 and S_2 for $2\ ^1A_g$.[4]

The aim of this work is to calculate as accurately as possible the five low-lying valence states of *trans*-1,3-

TABLE I. Experimental results on low-lying valence states of *trans*-1,3-butadiene.

Herzberg notation[a]	State (C_{2h})	Vertical[b] energies (eV) from the $X\ ^1A_g$ state						
		Reference						
		41	42	11	12	20	21	6
a	$1\ ^3B_u$	3.2	3.3	3.22[c]				
b	$1\ ^3A_g$	4.9	4.8	4.93				
	$2\ ^1A_g$		5.8–6.1	7.27[d]	5.7	6.1–6.7	5.40–5.87	5.7
A	$1\ ^1B_u$	6.2		5.76–5.92–6.09[e]				

[a] Reference 39.
[b] The transitions to the $1\ ^1B_u$ state, with 5.92 eV as intensity maximum and to $2\ ^1A_g$ below 6.0 eV, could be nonvertical.
[c] Reference 40.
[d] References 7 and 14.
[e] References 7, 14, and 43.

butadiene using multiconfigurational self-consistent field (MCSCF) and configuration interaction (CI) methods. We present a set of calculations where we show a computationally viable and inexpensive way to carry out multireferencial CI (MRCI) calculations. The main purpose in this procedure is to select the most important MRCI contributions by a perturbative criterion in order to be computed in a fully variational way and estimate the remaining ones by perturbative techniques. The reference wave function is perturbed, according to the Epstein–Nesbet definition of the unperturbed Hamiltonian, using the Rayleigh–Schrödinger perturbative expansion. In this way, the size of the space computed variationally is highly reduced by including in it only the most important contributions to the first-order wave function, selected using the configuration interaction by perturbation selected iterative process (CIPSI) program.[26,27] This perturbation-selected MRCI scheme, MRCI-PS, has been successfully used in a great variety of systems.[28–30] We present calculations of the vertical energy differences between the butadiene low-lying states using different molecular-orbital basis sets to test their influence on the results, including also complete active space SCF (CASSCF) orbitals as the reference for the MRCI-PS. We have carried out three kinds of MRCI calculations: CIPSI,[27] where the multireferencial (MR) space is selected iteratively; MRCI-PS, where the MR space is the CASSCF formed by the valence π orbital space; and MRCCCI-PS (MR consistent correlation CI-PS), with the same MR space but with a systematic criterion for *a priori*

selection of the kind of correlation excitation, to account for the differential correlation contributions among the considered situations, following the CCCI scheme of Goddard *et al.*[31]

II. CALCULATION DETAILS

The basis set for valence shells was of double-zeta quality[32] augmented with a diffuse p (0.08) set and polarization d (0.7) set for the carbon atoms, where the carbon $1s$ shell is treated with the pseudopotentials of Durand and Barthelat.[32] Therefore, no excitations from $1s$ shell were allowed, as appears in other works.[22] No lack of accuracy is produced by using pseudopotentials for the inner shell, as it is shown by comparing with all electron calculations. Diffuse orbitals on the carbon atom seem necessary in order to stabilize the negative centers (Rydbergyzation) and the polarization orbitals are necessary to correlate angularly the instantaneous electron pairs on the same atom, because of the ionic character of the $1\ ^1B_u$ state.[33] The geometry used for the ground-state $X\ ^1A_g$ and for the other states in vertical transitions was that optimized from CI calculations by Malrieu *et al.*[34] for the C_{2h} planar structure.

A very important step in molecular calculations is the adequate treatment of the electron correlation internal to the valence shell. Four electron and six orbital CASSCF calculations were made with an all-electron DZ basis set with a p diffuse and polarization d function[32] on the car-

TABLE II. Main *ab initio* vertical energies (eV) to low-lying valence states of *trans*-1,3-butadiene.

State	Val. CI	GVB-CI	EVSH[a]		MRCI							SAC[b]
					Reference							
	23	44	45	46	24	33	47	48	22	25	50	51
$1\ ^3B_u$	3.31	3.35	3.04	3.23	3.47	3.60	3.66					3.48
$1\ ^3A_g$	4.92	5.08	5.29	4.90	5.20	5.33						5.15
$2\ ^1A_g$	7.02	7.06	7.24	6.19	9.97	8.67		6.81[c]	6.2–6.8[d]	6.78	6.67[d]	7.00
$1\ ^1B_u$	7.67	6.90		6.14	7.68	7.07	6.39	6.42[c]	6.2[d]	6.70	6.23[d]	6.39

[a] Heisenberg Effective Hamiltonians.
[b] Symmetry adapted cluster CI.
[c] Corrected QDVPT.
[d] Includes Davidson correction.

TABLE III. CI contributions for the low-lying valence states of trans-1,3-butadiene. Calculations SIRIUS/CASSCF ($4e^-$-6 orb) with ground-state geometry.

Configuration	$X\,^1A_g$	$1\,^3B_u$	$1\,^3A_g$	$2\,^1A_g$	$1\,^1B_u$
$(1a_u)^2 (1b_g)^2$	0.951	a		0.455	
$(1a_u)^2 (2a_u)^2$	0.179			0.528	
$(1a_u)^1 (1b_g)^1 (2a_u)^1 (2b_g)^1$	0.272			0.655	
$(1a_u)^1 (1b_g)^2 (2a_u)^1$			0.691	0.320	
$(1a_u)^2 (1b_g)^1 (2b_g)^1$			0.688	0.371	
$(1a_u)^2 (1b_g)^1 (2a_u)^1$		0.935			0.975
$(1a_u)^1 (1b_g)^1 (2a_u)^1 (3a_u)^1$					0.190
$(1b_g)^2 (2b_g)^2$	0.081			0.127	
$(1a_u)^1 (2a_u)^2 (2b_g)^1$		0.114			
$(1b_g)^1 (2a_u)^1 (2b_g)^2$		0.124			
$(1a_u)^2 (1b_g)^1 (2a_u)^1$		0.284			
$(1a_u)^1 (2a_u)^1 (2b_g)^2$			0.137		
$(1b_g)^2 (2a_u)^2 (2b_g)^1$			0.149		

aContribution less than 0.05.

bons, using the SIRIUS algorithm.[35] The results appear in Table III and show that the most important CI contributions were obtained within the π space ($1a_u$, $1b_g$, $2a_u$, $2b_g$ orbitals in C_{2h} symmetry); then, the initial reference for the CASSCF orbital and the CI multireference is the CAS-π space in butadiene (described as MR1). The reference function includes 20 configurations for ^1A_g states and 16 for B_u ones because they represent complementary spaces. The importance of the $3a_u$ orbital in the $1\,^1B_u$ state has led us to include it in the reference space in some calculations (hereafter named MR2). We have done several sets of calculations using several molecular-orbital (MO) basis sets, because of the strong dependence on a such reference of the CI calculations. The SCF results were obtained using the PSHF program[36] included in the CIPSI chain of programs, and the CASSCF orbitals were generated with the GMCP program.[37] Some calculations involve a redefinition of the unoccupied space using the projected atomic orbital (PAO) projection proposed by Levy et al.[38] The process is based on unitary transformations, and the orbitals keep the same energy of the SCF procedure. This technique localizes the orbitals and avoids the diffuse character of the virtual HF space, being an inexpensive way to improve the SCF orbitals. Notwithstanding, we consider the best calculations those obtained using the CASSCF orbitals. The three kinds of CI treatments we carried out are listed in the following.

The CIPSI procedure,[26,27] where the reference function for the MRCI calculations is different for each state, were selected iteratively including those configurations with greater contributions to the first-order wave function according to the Epstein–Nesbet definition of the unperturbed Hamiltonian, and using the Rayleigh–Schrödinger perturbative expansion. The resulting configurations are divided in two spaces: S the reference space, where we iteratively included the configurations with contributions in the Epstein–Nesbet partition greater than a given threshold t. Then, all the single and double excitations from the reference are built, and form the space P, perturbatively estimated. Thus, the total space is composed of more than 20 million configurations. A problem arises when comparing two states or two different points of a potential-energy hypersurface, however. The two calculations might be of the same quality in order to avoid a bias in favor of the state better calculated which should make the energy differences larger or smaller than the exact ones. In other words, the criterion to include the reference determinants in the S space is not definitive nowadays. A similar value of the norm of the correction to the first-order wave function in all the states that we compare is a criterion often used. This uncertainty can be solved by the more extensive MOYEN procedure, where a third class of determinants M is defined. This third class includes those determinants not belonging to S, whose contributions to wave function are lesser than t but greater than the other threshold τ, such as $\tau \leqslant t$. $S+M$ is then resolved variationally, and the rest of determinants generated by mono or diexcitation from S are calculated perturbatively. The treatment that only involves S and P spaces has been called CIPSI-2, while the more extensive one is described as CIPSI-3.[28]

The MRCI-PS, where the reference space includes the CAS we select (CAS-π or CAS-π plus $3a_u$ orbital along this work). All single and double excitations from the reference space integrate the active MRCI-PS space formed by more than 3 million configurations. The most important contributions are perturbatively selected: All the MRCI configurations with a coefficient in the first-order Epstein–Nesbet wave function larger than 0.01 were included in the S space, but only the CAS configurations act as a reference; the configurations having a contribution to a CI wave function larger than a certain threshold (lesser than 0.01) are treated variationally. Finally, the remaining configurations are taken into account through their second-order perturbation energy on the S space. Our perturbational approach compares results between the states where the perturbational contributions by the Møller–Plesset or Epstein–Nesbet partitions of the P space on the S space are of the same order, since we cannot diagonalize the complete matrix.

The last treatment is the multireferencial correlation consistent CI-perturbatively selected (MRCCCI-PS). The references are the same as used in the MRCI-PS approach, but the treatment involves an a priori selection of the configuration set. In these CI's, following the scheme of Goddard et al.,[31] attention was focused on the differential correlation contributions among the considered situations, rather than attempting to correlate all σ and π electrons.

This theoretical method, applied to dissociation of single-bonded systems in previous works,[28] distinguishes between occupied and unoccupied MO's. The occupied MO's can be further classified in core MO's where it is assumed that the correlation effects due to the core electrons remain constant in the transition process (carbon $1s$ shell for our system), adjacent valence MO's ($a,b,c...$), and the bonding (π_1 and π_2) and antibonding (π_1^* and π_2^*) valence MO's. The unoccupied MO's will be hereafter labeled by $r,s,t,u...$. Considering as active MO's the π_1, π_2 ($1a_u$,$1b_g$) and π_1^*, π_2^* ($2a_u$,$2b_g$) ones obtained from SCF or

MCSCF calculations (sometimes we will include the $3a_u$ orbital), we build a CAS CI wave function of twenty (A_g) or sixteen (B_u) determinants, those involved in a CASSCF calculation. In our approach of the CCCI partition we consider those types of CCCI contributions that have non-vanishing coupling with the CAS determinants. That is, we make all the single and double excitations of the four electrons implied in the transitions

$$\pi_i \rightarrow r,$$

$$\pi_i \pi_j \rightarrow \pi_i^* r,$$

$$\pi_i \pi_j \rightarrow rs,$$

$$\pi_i \pi_i \pi_j \rightarrow \pi_i^* \pi_i^* r,$$

$$\pi_i \pi_i \pi_j \rightarrow \pi_i^* \pi_j^* r,$$

$$\pi_i \pi_i \pi_j \rightarrow \pi_i^* rs,$$

$$\pi_i \pi_i \pi_j \rightarrow \pi_j^* rs,$$

$$\pi_i \pi_i \pi_j \pi_j \rightarrow \pi_i^* \pi_i^* rs,$$

$$\pi_i \pi_i \pi_j \pi_j \rightarrow \pi_i^* \pi_j^* rs,$$

where i and j are 1 or 2. Coupled polarization contributions of the adjacent valence MO's, i.e., a monoexcitation $a \rightarrow r$, coupled to each of the above determinants are also added. This set of configurations is an approximation to the CCCI partition where all the $a\pi_i\pi_i\pi_j\pi_j \rightarrow rstuv$ types of contribution are considered. Hence, the nondynamical and dynamical correlation involved in the electronic transition, plus those contributions representing the instantaneous polarization of the adjacent valence MO's, which have nonzero coupling with the CAS wave function, is taken into account.

This approach leads to a space with approximately 500 000 configurations. CCCI-PS approach has been used on single-bonded systems like HF, F_2, H_2, BH, methylene, C_2F_4, CuH, or Cu_2 (Ref. 28) with very accurate results for the dissociation energies or energy differences between electronic states. We propose in this paper the generalization of this methodology to systems with a delocalized bond like the trans-1,3-butadiene. Partitions of the CI space similar to this are often used by other authors, including calculations on butadiene.[22] All the CI calculations were carried out with the CIPSI program[26,27] modified by us in the MRCCCI-PS calculations.

III. RESULTS AND DISCUSSION

MCSCF, CIPSI-2, CIPSI-3, MRCI-PS, and MRCCCI-PS results for the energy differences between the electronic valence excited states of the trans-1,3-butadiene are shown in Tables IV and V. The qualitative problems with the single-configuration Hartree–Fock approximation can normally be corrected by adding a few other configurations that will shape the multireferencial space for the CI treatments. The selection of the initial configurations is an open problem and it depends on the system under study. One adequate way to choose the multireferencial space is

TABLE IV. Vertical energy differences (eV) between the $X\,^1A_g$ ground state and the low-lying valence excited states of trans-1,3-butadiene.

	State			
Type of calculation	$1\,^3B_u$	$1\,^3A_g$	$2\,^1A_g$	$1\,^1B_u$
MCSCF (4e⁻-4 orb)[a]	3.12	4.76	6.32	8.37
MCSCF (4e⁻-6 orb)[a]	3.26	4.82	6.35	7.65
	CIPSI			
Orb.RHF[b]+PAO (CIPSI-2)[c]	3.04	4.69	5.95	6.23
Orb.RHF+PAO (CIPSI-3)[c]	3.25	4.91	6.53	6.57
	MRCI-PS			
Orb.RHF+PAO	3.42	5.18	6.94	7.54
Orb.RHF			6.52	7.15
Orb.CASSCF (CAS-π)[d]	3.17	4.88	6.57	6.84
	MRCCCI-PS			
Orb.RHF+PAO	3.30	5.01	6.52	6.85
Orb.RHF			6.71	6.59
Orb.CASSCF (CAS-π)	3.18	4.83	6.53	6.67
Orb.RHF+PAO (MR2)[e]				6.61
Orb.CASSCF (CAS-π+$3a_u$)+MR2[f]				6.48

[a]Complete basis set DZ+$(p+d$ on $C)$. SIRIUS algorithm (Ref. 35).
[b]RHF orbitals always from the $X\,^1A_g$ state.
[c]CIPSI-2 and CIPSI-3 as described in Ref. 27.
[d]CASSCF (4e⁻-4 orb.) from $1a_u 1b_g 2a_u 2b_g$ orbitals in C_{2h} symmetry.
[e]MR2 (see text). The reference space includes $1a_u 1b_g 2a_u 2b_g 3a_u$ orbitals.
[f]Both CASCF orbitals and the multireference space also includes the $3a_u$ orbital.
[g]All the CI-PS calculations at the Epstein–Nesbet second-order level and CIPSI-2 at the Møller–Plesset level (see text).

to use the complete active space (CAS) from a MCSCF calculation. Table III shows the most important CI contributions for the states we are interested, through a MC-SCF study with four active electrons and six active orbitals, i.e., the four π electrons (in the traditional Hückel π

TABLE V. Variational and second-order corrected vertical energy differences (eV) for selected valence excited states of trans-1,3-butadiene.

	State				
Type of calculation	$X\,^1A_g$	$1\,^3B_u$	$1\,^3A_g$	$2\,^1A_g$	$1\,^1B_u$
Orb. RHF+PAO	CIPSI				
N det.[a]	6999	21 750	31 850	47 960	42 072
ΔE_{var}	0.00	2.65	4.67	6.22	6.47
ΔE_{MP}	0.00	3.17	4.78	6.19	6.59
ΔE_{EN}	0.00	3.25	4.91	6.53	6.57
ΔE_{BEN}	0.00	3.23	4.83	6.28	6.63
Orb.CASSCF (CAS-π)	MRCI-PS				
N det.	12 500	35 992	38 904	40 920	44 954
ΔE_{var}	0.00	2.97	4.66	6.99	7.03
ΔE_{MP}	0.00	3.04	4.75	6.54	6.92
ΔE_{EN}	0.00	3.17	4.88	6.57	6.84
ΔE_{BEN}	0.00	3.02	4.66	6.47	6.98
Orb.CASSCF (CAS-π)	MRCCCI-PS				
N det.	19 360	36 888	37 030	42 476	38 630
ΔE_{var}	0.00	3.57	5.55	7.35	6.95
ΔE_{MP}	0.00	3.19	4.85	6.52	6.68
ΔE_{EN}	0.00	3.18	4.83	6.52	6.68
ΔE_{BEN}	0.00	3.13	4.75	6.39	6.67

[a]Number of determinants included in the variational treatment (M space).

model) and the $1a_u1b_g2a_u2b_g3a_u3b_g$ orbitals. The single-configurational character of the $X\ ^1A_g$, $1\ ^3B_u$ and $1\ ^1B_u$ states, the multiconfigurational character of $1\ ^3A_g$ and $2\ ^1A_g$, and the slight importance of the $3a_u$ orbital in the description of the $1\ ^1B_u$ state can be noted. Many previous results are explained by this description of the wave functions, especially the worse treatment of the $1\ ^3A_g$ and $2\ ^1A_g$ states at the SCF level.[1]

We select the CAS formed by the four $1a_u1b_g2a_u2b_g$ orbitals as the most adequate to properly describe this set of valence states, although some calculations on $1\ ^1B_u$ will include the influence of $3a_u$ orbital. Therefore, all the possible dispositions of four electrons in four orbitals, under spin and spatial symmetry restrictions, form the reference space (MR1). It is obvious that the criteria to choose the active space are still undetermined and they can lead to incorrect results in systems with near-degeneracy problems[52] if the selection is not careful. Following the criterion of defining the nondynamical correlation by the study of the occupation numbers of the natural orbitals,[53] our CASSCF 4 electrons-4 orbital calculation would then treat all the nondynamical correlation. In fact, we compare this calculation with the CASSCF 4 electron-6 orbital calculation in Table IV, and it can be concluded that the inclusion of the $3a_u$ orbital ($3b_g$ was revealed of lesser importance in CI calculations) is only decisive at this level of treatment for the $1\ ^1B_u$ state. The other ones seem unaffected. The inclusion of the a_g and b_u orbitals and electrons in the CAS to consider the $\sigma\pi$ or $\sigma\sigma^*$ correlation showed no influence in the results, while the occupation numbers for those a_g and b_u higher orbitals (σ^*) were very small. Moreover, the $3b_g$ orbital shows to be less decisive for the $1\ ^1B_u$ treatment. Then, most of the calculations were carried out with the first reference CAS (MR1), 4 electrons in 4 orbitals, and only two of the studies included the $3a_u$ in the CAS (MR2) to properly treat the $1\ ^1B_u$ state.

CIPSI calculations included as reference spaces 173, 136, 123, 141, and 146 determinants for $X\ ^1A_g$, $1\ ^3B_u$, $1\ ^3A_g$, $2\ ^1A_g$, and $1\ ^1B_u$ states, respectively. We described the selection method in Sec. II. The number of generated configurations is larger than 20 million in all the cases. Such a large number of determinants, not included in the variational treatment, involves a large value of the perturbation energy, approximately 0.22 hartree, in the Epstein–Nesbet partition. When a certain number of determinants having larger weight is included in the M space, the perturbation energy is reduced to a half. In order to guarantee as much as possible a similar quality in all the calculated states, we search a similar perturbation on all of them (at least a maximum difference of 10^{-3} hartree, i.e., an uncertainty of 0.01 eV in ΔE). Moreover, the better calculations will be those showing a perturbation as small as possible. The criterion used has been the following. We have included determinants in the reference space until the norm of the first-order correction to the wave function reaches a similar value for all the studied states. Table IV shows the differences between $X\ ^1A_g$ and the excited states obtained with the CIPSI-2 and CIPSI-3 calculations. As it can be seen, the order of the states is the same in both calculations, but

the value of the excitation changes. It is an open question whether the norm criterion is the most adequate. Thus, the fact that the more extensive treatment, CIPSI-3, offers differences of ~0.3 eV for the excited singlets, brings some uncertainty in the results.

CIPSI calculations, like the other CI-PS results that appear in Table IV, correspond to the second-order Epstein–Nesbet perturbation. CIPSI algorithm uses three kinds of perturbative partitions:[26] Møller–Plesset (MP), Epstein–Nesbet (EN), and Barycentric Epstein–Nesbet (BEN). Although the three partitions show similar results in those calculations where the perturbation values are small, this is not true for all the systems, situations, and treatments. Table V shows the differences for the most important calculations. It is well known that the Møller–Plesset partition shows a satisfactory N-dependence behavior, while Epstein–Nesbet does not allow the demonstration of the linked cluster theorem and then it presents only a qualitatively good N dependence. Notwithstanding, this is less important for symmetric problems as ours, when one uses delocalized symmetry adapted MO's. On the other hand, the two partitions have different behavior in front of the convergence. MP converges slowly when the perturbation decreases, and we think it is actually the relevant problem for this system. Then, we propose the Epstein–Nesbet partition as that showing the most accurate results in these calculations. A detailed account of the possibilities of the partitions can be found in Ref. 54.

The conclusions of the CIPSI-3 calculations are the following. The agreement of the results with the experimental values for the triplet states is complete; $2\ ^1A_g$ and $1\ ^1B_u$ states appear very near as it has been frequently suggested,[2,22] although we cannot forget that these are vertical calculations. As in the rest of our studies and in other CI calculations (Table II), the $1\ ^1B_u$ state appears higher than the experimental value of 5.92 eV, while the $2\ ^1A_g$ lies below the $1\ ^1B_u$ by less than 0.1 eV. Our calculations were made with the RHF orbitals from the $X\ ^1A_g$ ground state improved with the use of the PAO projection for the virtual orbitals. Moreover, the calculations were made at the $X\ ^1A_g$ optimized geometry[34] and therefore are referred to vertical transitions. The poor convergence of Møller–Plesset and Epstein–Nesbet results, specially for $2\ ^1A_g$, since the difference between them is ~0.3 eV, brings to suspect that the results are not completely converged.

The MRCI-PS treatment, using the CAS-π as the multireference space, reduces the dimension of the CI to ~3 million of configurations. As Table IV illustrates, the triplet states and $2\ ^1A_g$ results change in 0.2 to 0.4 eV when we use the RHF $X\ ^1A_g$ orbitals plus projection as the MO set of reference, but the $1\ ^1B_u$ result goes up by 0.97 eV. As we noted in MCSCF calculations, the excitations to the $3a_u$ orbital could be decisive in the treatment of the $1\ ^1B_u$ state and then while CIPSI calculations include that and other possible configurations with a high weight in the description of the state, MRCI-PS does not. Use of PAO projection has led to a localization of the virtual orbitals, diffuse, in general. If we calculate the singlet states without this projection both transition energies decrease. We probably

have converged into states with a strong mixing of Rydberg character.

MRCI-PS calculations with CASSCF (CAS-π) orbitals as MO basis set and using the CAS-π as CI reference space produce a general decreasing of the energy differences, in a logical way, because the $X\,^1A_g$ does not highly improve its results with respect to RHF plus PAO calculations (it is almost a single-configuration state), while the other states now have their own optimized orbitals. The results are similar to the more extensive CIPSI study although the $1\,^1B_u$ is ~0.3 eV higher. The dispersion of the three perturbative expansions (Table V) is less than 0.2 eV in the worst situation, due to the smaller number of configurations included in the CI space.

MRCCCI-PS treats to include only the differential correlation contributions between the considered states. Thus, a less expensive method that handles with half a million of determinants must be able to reach as good results as the more expensive one. The calculations with $X\,^1A_g$ RHF plus PAO orbitals offer us results near the CASSCF/MRCI-PS ones, with a ΔE for $1\,^1B_u$ higher (~0.2 eV) than the CIPSI results. The lack of some important CI references could be again the responsible of that value. The exclusion of the projection method to improve the orbitals leads to smaller energy differences for the $1\,^1B_u$ state; the presence of possible Rydberg mixing as in the MRCI calculation may get small the difference. Notwithstanding, the behavior of $2\,^1A_g$ state within these calculations is just the opposite to that of the MRCI case: the ΔE increases. The Rydberg states $3\,^1A_g$ ($3d_{xy}$) and $4\,^1A_g$($3d_{xz}$) appear at 7.68 and 7.79 eV (Ref. 44), therefore, some Rydberg contributions to the $2\,^1A_g$ description would lead to higher energies. This reasoning could not be used in the MRCI-PS calculations for this state, where the energy of $2\,^1A_g$ without employing the projection technique led to smaller energies. It is possible to think that the MRCCCI-PS approach has a better behavior to treat the system. At last, using CASSCF (CAS-π) orbitals, the MRCCCI-PS calculations show a decreasing of the results for the triplets and the $1\,^1B_u$ state, while the $2\,^1A_g$ state does not change. The analysis of these values is the same that the MRCI-PS calculations. The most relevant result is 6.67 eV for the $1\,^1B_u$ state, while the MRCI-PS one is 6.84 eV and CIPSI reports 6.57 eV. The MRCCCI-PS method has decreased this value because its treatment of the correlation, but it seems that the references within the CAS-π are not strictly the best.

Results in Table III and as discussed earlier show us the $3a_u$ orbital could have a relative importance in the treatment of $1\,^1B_u$ state. We carried out calculations including this orbital in the CAS and CI reference spaces. First, we present a MRCCCI-PS result using $X\,^1A_g$ RHF plus PAO orbitals and with $1a_u1b_g2a_u2b_g3a_u$ orbitals in the CI multireference. A decreasing of 0.24 eV is obtained from the results excluding this upper orbital. Finally, we studied the $1\,^1B_u$ state using CASSCF orbitals with four electrons in five orbitals, and the same CI reference (MR2). The value obtained for the $X\,^1A_g\rightarrow1\,^1B_u$ vertical transition is 6.48 eV. We think, as other authors,[22] that the

$3a_u$ orbital is necessary to describe properly the $1\,^1B_u$ state.

The conclusions for the vertical states are diverse. We have reproduced with great accuracy the experimental results for the triplet states in our best calculations: CIPSI-3, CASSCF/MRCI-PS, and CASSCF/MRCCCI-PS. No definitive experimental data are known on $2\,^1A_g$ because the state is probably reached by a nonvertical transition and, therefore, our value is in the range of the expected vertical transition.[22] The results on the $1\,^1B_u$ state are less accurate. We consider the best one the value of 6.48 eV for the vertical transition, including the $3a_u$ orbital in the reference spaces (Table V). Although there are vertical results of 6.2 and 6.23 eV using the Davidson correction,[22,50] we agree with the two last MRCI results.[47,48] Recent papers from Graham et al.[46] and McDiarmid[55] places the pure valence ^1B_u state at 6.19 and 6.25 eV, respectively. Thus, the agreement with the experimental result of 5.92 eV will not be achieved until the nonvertical transitions be calculated or the valence-Rydberg mixing extensively included.

Another conclusion is that the MRCCCI-PS calculations are useful to improve results in systems with delocalized bonding like trans-1,3-butadiene, and they have equivalent results to that more expensive, unavoidable, or uncertain methods like CIPSI. The fact that the results obtained for triplets were so accurate is an indication of the improvement that a MRCCCI-PS methodology can introduce in the treatment of the correlation in the study of excited states.[31] At last, we can say that CIPSI calculations seem accurate and, therefore, the normal criterion to include configurations in the reference space should be adequate for this system.

The question of the relative $2\,^1A_g/1\,^1B_u$ ordering is in the edge of the problem of polyene spectroscopy. Indirect evidence[2] suggests the B_u state does not decay to the ground electronic state but to another electronic state or potential surface. Results collected from the literature suggest that the $1\,^1B_u$ state is twisted around its double bond[2-4] and the same distortion is proposed for $2\,^1A_g$.[2,4] The results greatly differ on changing the optimization or calculation methodology. The decreasing of ΔE from vertical results is clear as we could expect but no more accurate conclusions can be derived from them. The geometry relaxation effect that has been proposed as the responsible of the extreme diffuseness of the subbands of absorption transitions is not explained by any results. Recent studies[56] also suggest that core-excited anion states could be the reason for the narrow feature in butadiene spectra.

We think that an extensive study including CI methodologies on the potential surfaces of the excited states is necessary to take into account the possibility of geometry relaxation on the butadiene absorption data. The proper behavior shown by our methods to describe the vertical transitions promise good results in nonvertical ones. The differential correlation treatment allows the study of systems like that, where the inclusion of highly correlated functions seems to be inevitable.

IV. CONCLUSIONS

Results from *ab initio* calculations on the low-lying valencelike states for *trans*-1,3-butadiene have been presented. We employed a variety of CI methods to show the most important features of the system. We have obtained excellent agreement with experimental data for the transitions to the low-lying triplet states $1\,^3B_u$ and $1\,^3A_g$. The results 3.18 and 4.88 eV, respectively, obtained for both states from MRCCCI-PS calculations seem the most accurate, near the experimental ranges 3.2–3.3 eV for $1\,^3B_u$ and 4.8–4.93 eV for $1\,^3A_g$. The best results obtained for the vertical transitions to $2\,^1A_g$ and $1\,^1B_u$ states within MRCCCI-PS methodology are 6.53 and 6.48 eV, respectively, the lowest achieved in CI methods without employing the Davidson correction. The $2\,^1A_g$ lies below $1\,^1B_u$ for almost all our vertical studies, although these states are near degenerated. Notwithstanding, the last result suggests that the $1\,^1B_u$ state would be the lowest excited singlet state at the vertical transition.

We conclude that the MRCCCI-PS shows an excellent behavior in a system with delocalized bonds as butadiene. The calculations are less expensive than with other methods and give the same results in most of the states. Moreover, it is able to provide a better treatment of some situations including the differential correlation, such as in an ionic and very sensitive state like $1\,^1B_u$. Therefore, it can avoid some deficiencies of the MRCI treatment when one uses small reference spaces, as we can observe in the study of $1\,^1B_u$ state. The perturbative selection has also shown that this is a very good method to evaluate great CI expansions, and it is able to provide as good results as the traditional or modified MRCI methods, for the studied systems.

[1] B. S. Hudson, B. E. Kohler, and K. Schulten, *Excited States*, edited by E. C. Lim (Academic, New York, 1982), Vol. VI, p. 1.
[2] R. McDiarmid and A. H. Sheybani, J. Chem. Phys. **89**, 1255 (1988).
[3] M. Aoyagi, Y. Osamura, and S. Iwata, J. Chem. Phys. **83**, 1140 (1990).
[4] F. Zerbetto and M. Z. Zgierski, J. Chem. Phys. **93**, 1235 (1990).
[5] R. McDiarmid, Int. J. Quantum Chem. **29**, 875 (1986).
[6] W. J. Buma, B. E. Kohler, and K. Song, J. Chem. Phys. **92**, 4622 (1990); **94**, 6367 (1991); R. R. Chadwick, M. Z. Zgierski, and B. S. Hudson, *ibid.* **95**, 7204 (1991).
[7] R. McDiarmid, Chem. Phys. Lett. **34**, 130 (1975); J. Chem. Phys. **64**, 514 (1976).
[8] R. J. Hemley, J. I. Dawson, and V. Vaida, J. Chem. Phys. **78**, 2915 (1983).
[9] V. Vaida and G. M. McClelland, Chem. Phys. Lett. **71**, 436 (1980).
[10] K. B. Wiberg, K. S. Peters, G. B. Ellison, and J. Dehmer, J. Chem. Phys. **66**, 2224 (1977).
[11] O. A. Mosher, W. M. Flicker, and A. Kuppermann, Chem. Phys. Lett. **19**, 332 (1973); J. Chem. Phys. **59**, 6502 (1973); W. M. Flicker, O. A. Mosher, and A. Kuppermann, Chem. Phys. Lett. **45**, 492 (1977); Chem. Phys. **30**, 307 (1978).
[12] J. P. Doering, J. Chem. Phys. **70**, 3902 (1979).
[13] R. McDiarmid, J. Chem. Phys. **79**, 9 (1983).
[14] J. P. Doering and R. McDiarmid, J. Chem. Phys. **73**, 3617 (1980); **75**, 2477 (1981).
[15] R. McDiarmid and J. P. Doering, Chem. Phys. Lett. **88**, 602 (1982).
[16] T. Reddish, B. Wallbank, and J. Comes, Chem. Phys. **108**, 159 (1986).
[17] M. F. Granville, B. E. Kohler, and J. B. Snow, J. Chem. Phys. **75**, 3765 (1981).
[18] P. M. Johnson, J. Chem. Phys. **64**, 4638 (1976).
[19] L. J. Rothberg, D. P. Gerrity, and V. Vaida, J. Chem. Phys. **73**, 5508 (1980).
[20] S. W. Staley, J. H. Moore, Jr., and Y. Sato (unpublished).
[21] R. R. Chadwick, D. Gerrity, and V. Vaida, J. Chem. Phys. **73**, 5508 (1980).
[22] R. J. Cave and E. R. Davidson, J. Phys. Chem. **91**, 4481 (1987).
[23] S. Shih, R. J. Buenker, and S. D. Peyerimhoff, Chem. Phys. Lett. **16**, 244 (1972); R. J. Buenker, S. Shih, and S. D. Peyerimhoff, Chem. Phys. Lett. **44**, 385 (1976).
[24] V. Bonacic-Koutecky, M. Persico, D. Döhnat, and A. Sevin, J. Am. Chem. Soc. **104**, 6900 (1982).
[25] P. G. Szalay, A. Karplen, and H. Lischka, Chem. Phys. **130**, 219 (1989).
[26] B. Huron, J. P. Malrieu, and P. Rancurel, J. Chem. Phys. **58**, 5745 (1973).
[27] S. Evangelisti, J. P. Daudey, and J. P. Malrieu, Chem. Phys. **75**, 91 (1983).
[28] M. Merchán, J. P. Daudey, R. González-Luque, and I. Nebot-Gil, Chem. Phys. **140**, 285 (1989); **148**, 67 (1990); M. Merchán, R. González-Luque, and I. Nebot-Gil, J. Chem. Phys. **93**, 495 (1990).
[29] I. García-Cuesta, A. Sánchez de Merás, and I. Nebot-Gil, Chem. Phys. Lett. **186**, 386 (1991).
[30] F. Illas, J. Rubio, J. M. Ricart, and P. S. Bagus, J. Chem. Phys. **95**, 1877 (1991); J. J. Novoa, F. Mota, and F. Arnau, Chem. Phys. Lett. **165**, 50 (1990).
[31] E. A. Carter and W. A. Goddard III, J. Phys. Chem. **83**, 1485 (1984); **91**, 4651 (1987); J. Am. Chem. Soc. **108**, 2180 (1986); J. Chem. Phys. **86**, 862 (1986); **88**, 1752 (1988); **88**, 3132 (1988); J. B. Schilling, W. A. Goddard III, and J. L. Beauchamp, J. Phys. Chem. **91**, 4470 (1987); **91**, 5616 (1987); J. Am. Chem. Soc. **109**, 5565 (1987); **109**, 5573 (1987).
[32] Ph. Durand and J. C. Barthelat, Theor. Chim. Acta **38**, 283 (1975).
[33] J. P. Malrieu, I. Nebot-Gil, and J. Sánchez-Marín, Pure Appl. Chem. **56**, 1241 (1984).
[34] J. Langlet and J. P. Malrieu, Theor. Chim. Acta **33**, 307 (1974).
[35] H. J. Aa. Jensen and H. Ågren, Chem. Phys. **104**, 229 (1986).
[36] M. Dupuis, J. Rys, and H. F. King, J. Chem. Phys. **65**, 111 (1976); HONDO-76, program 338, QCPE, University of Indiana, Bloomington, IN47401. Pseudopotential adaptation by J. P. Daudey and M. Pelissier. General ROHF adaptation by R. Caballol and J. P. Daudey. CIPSI chain of programs by M. Pellisier, J. P. Daudey, S. Evangelisti, F. Spiegelmann, and D. Maynau.
[37] The MCSCF algorithm used here is based on the Elementary Jacobi Rotations (EJR) method implemented on the CIPSI package of programs. See, R. Carbó, Ll. Domingo, and J. Peris, Adv. Quantum Chem. **15**, 215 (1982); R. Carbó, Ll. Domingo, J. Peris, and J. Novoa, J. Mol. Struct. Theochem. **93**, 15 (1983).
[38] G. Chambaud, M. Gerard-Ain, E. Kassab, B. Levy, and P. Pernot, Chem. Phys. **90**, 271 (1984).
[39] G. Herzberg. *Electronic Spectra of Polyatomic Molecules* (Van Nostrand, Princeton, 1966), p. 656.
[40] D. F. Evans, J. Chem. Soc. (London) 1735 (1960).
[41] J. H. Moore, Jr., J. Phys. Chem. **76**, 1130 (1972).
[42] H. H. Brongersma, J. A. van der Hart, and L. J. Oosterhoff, *Fast Reactions and Primary Processes in Chemical Kinetics*, edited by S. Claesson (Interscience, New York, 1967), p. 211.
[43] K. K. Innes and R. McDiarmid, J. Chem. Phys. **68**, 2007 (1978); L. C. Jones, Jr. and L. W. Taylor, Anal. Chem. **27**, 228 (1955).

[44] M. A. Nascimento and W. A. Goddard III, Chem. Phys. **36**, 147 (1979); **53**, 251 (1980).

[45] M. Said, D. Maynau, and J. P. Malrieu, J. Am. Chem. Soc. **106**, 580 (1984).

[46] R. L. Graham and K. F. Freed, J. Chem. Phys. **96**, 1304 (1992).

[47] R. J. Cave, J. Chem. Phys. **92**, 2450 (1990).

[48] Ping Du, S. Racine, and E. R. Davidson, J. Chem. Phys. **94**, 3944 (1990).

[49] A. C. Lasaga, R. J. Aerni, and M. Karplus, J. Chem. Phys. **73**, 5230 (1980).

[50] R. J. Cave and E. R. Davidson, Chem. Phys. Lett. **148**, 190 (1988).

[51] O. Kitao and H. Nakatsuji, Chem. Phys. Lett. **143**, 528 (1988).

[52] L. Serrano-Andrés, A. Sánchez de Merás, R. Pou-Amérigo, and I. Nebot-Gil, J. Molec. Struct. Theochem. **254**, 229 (1992); Chem. Phys. **162**, 321 (1992).

[53] B. O. Roos, "Ab initio methods in Quantum Chemistry-II" in *Advances in Chemical Physics*, edited by K. P. Lawley (Wiley–Interscience, Great Britain, 1987), Vol. XIX, p. 1.

[54] J. P. Daudey and J. P. Malrieu, in *Studies in Physical and Theoretical Chemistry*, edited by R. Carbó (Elsevier, Amsterdam, 1982), p. 35.

[55] R. McDiarmid, Chem. Phys. Lett. **188**, 423 (1992).

[56] M. F. Falcetta and K. D. Jordan, J. Am. Chem. Soc. **113**, 7455 (1991).