CLUSTER EXPANSION OF THE WAVEFUNCTION:
VALENCE AND RYDBERG EXCITATIONS OF TRANS- AND CIS-BUTADIENE

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The singlet and triplet valence and Rydberg excitations of trans- and cis-butadiene are studied using SAC/SAC CI theory with a large number of active MOs. The $1 \,^1B_u$ state of the trans form is calculated to lie 6.39 eV above the ground state, which compares with the experimental peak maximum at 5.92 eV. The $1 \,^1B_2$ state of the cis form is calculated to be 5.55 eV higher, which differs by 0.29 eV from the experimental value for the corresponding state of cyclopentadiene. The calculated second moments in the out-of-plane direction are 44 (trans) and 27 au (cis) in comparison with the experimental value of 22 au for the ground states of both forms. The calculated oscillator strength for the $1 \,^1B_u$ state of the trans form, 0.466, also agrees well with the experimental value of ≈ 0.4.

Using SAC (symmetry adapted cluster) and SAC CI theories [1–5], we have been able to study electron correlation in the excited and ionized states of conjugated π-electron systems incorporating a large amount of σ-electron correlation [4]. Theoretical results are reported here on the valence $\pi \rightarrow \pi^*$ and Rydberg excitations of trans- and cis-butadiene.

We used the same geometries as Buenker and Whitten [6] (the trans geometry is derived from experimental data [7]). Two basis sets were used: Basis set I consists of the [5s2p/2s] set of Huzinaga–Dunning [8] plus diffuse p_π functions (0.07469, 0.03477, 0.01075) and polarization d functions (1.322, 0.3916) on each carbon [8]. Basis set II consists of the [5s2p/2s] set of Huzinaga–Dunning plus diffuse p (0.07469) and p_π functions (0.03477, 0.01075) and polarization d function (0.3916) on each carbon. The numbers of AOs are 116 (I) and 100 (II). The active space consisted of the 36 π + 64 σ (I) and 28 π + 60 σ (II) SCF MOs calculated for the ground state. The dimensions after configuration selection [3] are shown in table 1. For the π space, the thresholds λ_g and λ_e were both 1×10^{-5} au in all of the present calculations. For the configu-

rations arising additionally in the $\pi + \sigma$ calculations, we adopted 3×10^{-5} au for λ_g and λ_e.

The theoretical and experimental results are summarized in tables 2 and 3, and depicted in figs. 1 and 2. The electronic part of the second moment is shown in figs. 3 and 4. The x axis is in the out-of-plane direction. The ground state energies of the π SAC wavefunction with basis set I are -155.00428 (trans) and -154.99051 au (cis). The values with basis set II are -154.98108 (trans) and -154.96723 au (cis). The ground state energies of the $\pi + \sigma$ SAC wavefunction with basis set I are -155.18483 (trans) and -155.17588 au (cis). The values with basis set II are -155.14598 (trans) and -155.13639 au (cis). These values are used as the reference ground state energies. The study of Buenker, Shih and Peyerimhoff [11] for the trans form and that of Shih, Buenker and Peyerimhoff [10] for the cis are probably the most reliable theoretical results so far reported. The experimental data for the trans form are taken from the electron energy-loss spectroscopy (EELS) data of Flicker et al. [9] and the values correspond to the peak maxima. For the cis form, the EELS data for cyclopentadiene of Fruehdz et al. [13] and those for the trans form are compared. Data for the np_π transitions of cyclopentadiene are taken from

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Table 1
Dimensions of the SAC and SAC CI calculations on butadiene

State		Basis set I		Basis set II	
		$36\,\pi$	$36\,\pi + 64\,\sigma$	$28\,\pi$	$28\,\pi + 60\,\sigma$
trans					
ground	^1A_g	354	4367	314	4101
excited	^1A_g	692	5326	589	5764
	^1B_u	604	5202	569	5664
	^3A_g	710	11777		
	^3B_u	718	10896		
cis					
ground	$^1A_1$	340	4187	293	4041
excited	$^1A_1$	574	5142	546	5507
	$^1B_2$	578	5067	538	5490
	$^3A_1$	662	10845		
	$^3B_2$	708	10793		

the summary of the ultraviolet spectrum by Derrick et al. [14].

σ electron correlation plays a crucial role in the ionic valence excited states of the π-conjugated systems [4]. This effect is as large as 1.36 eV for the $1\,^1B_u(V)$ state of the trans form and 0.70 eV for the $1\,^1B_2(V)$ state of the cis form. These figures are extraordinarily large, as seen in tables 2 and 3 in comparison with those for the other valence and Rydberg excited states studied here. It has long been known that the ionic valence excited $1\,^1B_u$ state of trans-butadiene is calculated by ab initio methods to be higher by 1–2 eV than the experimental value [6,10,11,15]. In the present SAC CI calculation, this state is calculated at 6.39–6.43 eV, which reproduces the experimental value to within 0.47–0.51 eV. The corresponding $1\,^1B_2$ state of the cis form is calculated at 5.55 eV, which differs by 0.29 eV from the experimental value for the corresponding state of cyclopentadiene. We note that the results of the two different basis sets are quite similar.

An interesting effect of the σ-electron correlation is seen for the $2\,^1A_1(V)$ state of the cis form. The calculated excitation energy for the $\pi + \sigma$ wavefunction is *higher* by 0.77 eV than that for the π alone. The final value differs by 0.35 eV from the experimental value for the corresponding state of cyclopentadiene. This behaviour is similar to that for the $T(^3B_{1u})$ state of ethylene [16]. This is because the state under consideration is less ionic than the ground state. The ef-

fect for the $1\,^1A_g(V)$ state is 0.07 eV in the same direction.

In table 2 some other low-lying valence $\pi \rightarrow \pi^*$ and Rydberg excitations of the trans form are shown for the singlet and triplet states. The agreement between theory and experiment is excellent for these states, and the final average deviation is ≈ 0.2 eV. For the cis form, the deviations from the experimental data given in table 3 are defined as the difference from the corresponding state of cyclopentadiene, if available, but if not, the data of the trans form are used. The final average deviation is ≈ 0.2 eV. The basis set dependence is also very small for both trans and cis forms.

From the experimental study on the 1,3-diene, McDiarmid and Doering found that the B_u state of the s-cis compounds was ≈ 0.5 eV lower in energy than that of the corresponding s-trans compound [17]. Our theoretical results for trans- and cis-butadiene support this observation. The total energy of the ground state of the trans form ($1\,^1A_g$) is lower by 0.26 eV than that of the cis form ($1\,^1A_1$), but the first valence excited state of the trans form ($1\,^1B_u$) is higher by 0.58 eV than that of the cis form ($1\,^1B_2$).

Within the π SAC CI treatment, the mixing of the valence and Rydberg states is large for the first and second ^1B_u states of trans-butadiene. This mixing is resolved by the inclusion of σ-electron correlation as seen in fig. 3. The second moment changes from 61 au (π SAC CI) to 44 au ($\pi + \sigma$ SAC CI). On the other

Table 2
π→π* excitation energies of trans-butadiene (eV)

State	Expt.[a]	SAC CI				SBP[d] $12\pi(\Delta)$	BSP[e] $12\pi+34\sigma(\Delta)$	CD[f]	
		basis set I		basis set II				PTCI(Δ)	CI4(Δ)
		$36\pi(\Delta^{c})$	$36\pi+64\sigma(\Delta)$	$28\pi(\Delta)$	$28\pi+60\sigma(\Delta)$				
$2^1A_g(V)$	7.08	6.93(−0.15)	7.05(−0.03)	6.94(−0.14)	7.00(−0.08)	6.67(−0.41)	7.02(−0.06)	6.24(−0.84)	6.77(−0.31)
$3^1A_g(3d_\pi)$	7.48	7.73(0.25)	7.38(−0.10)	7.77(0.29)	7.33(−0.15)	7.79(0.31)	7.53(0.05)		
$4^1A_g(3d_\delta)$	7.80	7.69(−0.11)	7.86(0.06)	7.73(−0.07)	7.80(0.00)		7.78(−0.02)		
$1^1B_u(V)$	5.92[b]	7.71(1.79)	6.43(0.51)	7.75(1.83)	6.39(0.47)	8.88(2.96)	7.67(1.75)	6.08(0.16)	6.23(0.31)
$2^1B_u(3p_\pi)$	6.64	6.84(0.20)	7.08(0.44)	6.88(0.24)	7.05(0.41)	6.60(0.04)	6.67(0.03)	6.76(0.12)	7.16(0.52)
$3^1B_u(4p_\pi)$	8.00	8.24(0.24)	7.91(−0.09)	8.29(0.29)	7.87(−0.13)	7.98(−0.02)	7.96(−0.04)	7.64(−0.36)	
$1^3A_g(V)$	4.91	5.14(0.23)	5.15(0.24)			4.95(0.04)	4.92(0.01)		
$2^3A_g(3d_\delta)$		7.61	7.22						
$3^3A_g(3d_\pi)$		7.64	7.26						
$1^3B_u(V)$	3.22	3.44(0.22)	3.48(0.26)			3.24(0.02)	3.31(0.09)		
$2^3B_u(3p_\pi)$		6.99	6.65			7.55			
$3^3B_u(4p_\pi)$		8.17	7.83			7.42			
average deviation		0.40	0.22	0.60	0.21	0.54	0.26	0.37	0.38

[a] Ref. [9].
[b] This is a broad intense band from 5.7 to 6.3 eV with three peaks at 5.76, 5.92, and 6.05 eV (maximum occurring at 5.92 eV)[a].
[c] Δ shows the difference from the experimental value.
[d] Ref. [10]. [e] Ref. [11].
[f] Ref. [12]. PTCI and CI4 refer to perturbation theory selected CI and a priori selected CI, respectively.

Table 3
$\pi \to \pi^*$ excitation energies of cis-butadiene (eV)

State	Expt. TB[a]	Expt. CP	SAC CI basis set I 36π(Δᶜ)	SAC CI basis set I 36π+64σ(Δ)	SAC CI basis set II 28π(Δ)	SAC CI basis set II 28π+60σ(Δ)	SBP[f] 12π(Δ)	CD[g] PTCI(Δ)	CD[g] CI4(Δ)
$2\,^1A_1(3d_\pi)$	7.48		7.63(0.15)	7.27(−0.21)	7.68(0.20)	7.23(−0.25)	7.89(0.41)		
$3\,^1A_1(V)$	7.08	8.03 [c]	6.90(−1.13)	7.73(−0.30)	6.91(−1.12)	7.68(−0.35)	6.66(−1.37)	5.74(−2.29)	6.13(−1.90)
$4\,^1A_1(3d_\delta)$	7.80		8.23(0.43)	7.95(0.15)	8.28(0.48)	7.90(0.10)			
$1\,^1B_2(V)$	5.92 [b]	5.26 [c]	6.21(0.95)	5.55(0.29)	6.25(0.99)	5.55(0.29)	8.53(3.27)	5.55(0.29)	5.49(0.20)
$2\,^1B_2(3p_\pi)$	6.64	6.31 [d]	7.10(0.79)	6.72(0.41)	7.14(0.83)	6.67(0.36)	6.35(0.04)	7.02(0.71)	7.02(0.71)
$3\,^1B_2(4p_\pi)$	8.00	7.44 [d]	7.80(0.36)	7.41(−0.03)	7.85(0.41)	7.37(−0.07)	7.11(−0.33)		
$1\,^3A_1(V)$	4.91		5.01(0.10)	5.06(0.15)			4.90(−0.01)		
$2\,^3A_1(3d_\pi)$			7.56	7.15					
$3\,^3A_1(3d_\delta)$			8.22	7.76					
$1\,^3B_2(V)$	3.22	3.10 [c]	3.05(−0.05)	3.01(−0.09)			2.95(−0.15)		
$2\,^3B_2(3p_\pi)$			6.89	6.52			7.42		
$3\,^3B_2(4p_\pi)$			7.67	7.26			7.97		
average deviation			0.50	0.20	0.67	0.24	0.80	1.10	0.94

[a] Experimental data for the corresponding states of trans-butadiene. These values are taken from ref. [9].
[b] This is a broad intense band from 5.7 to 6.3 eV with three peaks at 5.76, 5.92, and 6.05 eV (maximum occurring at 5.92 eV) [9].
[c] Experimental data for the corresponding states of cyclopentadiene. These values are taken from ref. [13].
[d] Experimental data for the corresponding states of cyclopentadiene. These values are taken from ref. [14].
[e] Δ shows the difference from the experimental value. The reference is the corresponding state of cyclopentadiene, if available, but if not, the corresponding state of trans-butadiene is used.
[f] Ref. [10].
[g] Ref. [12]. PTCI and CI4 refer to perturbation theory selected CI and a priori selected CI, respectively.
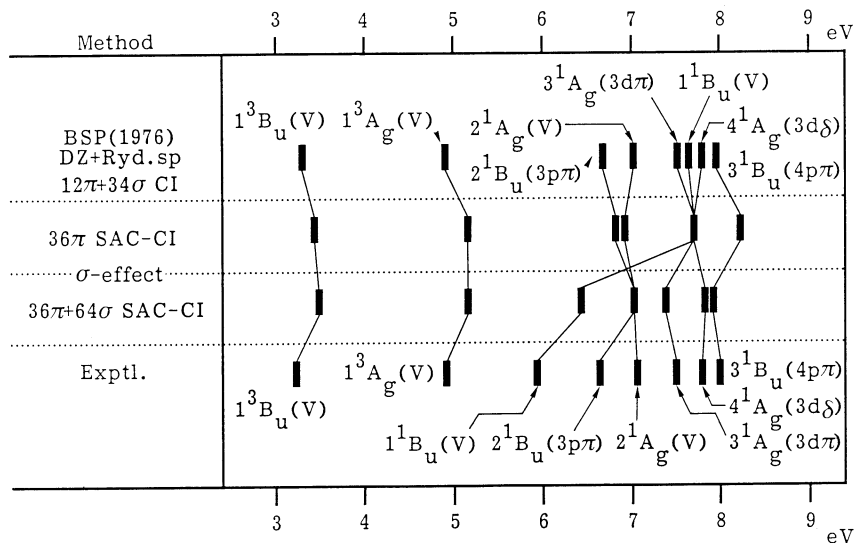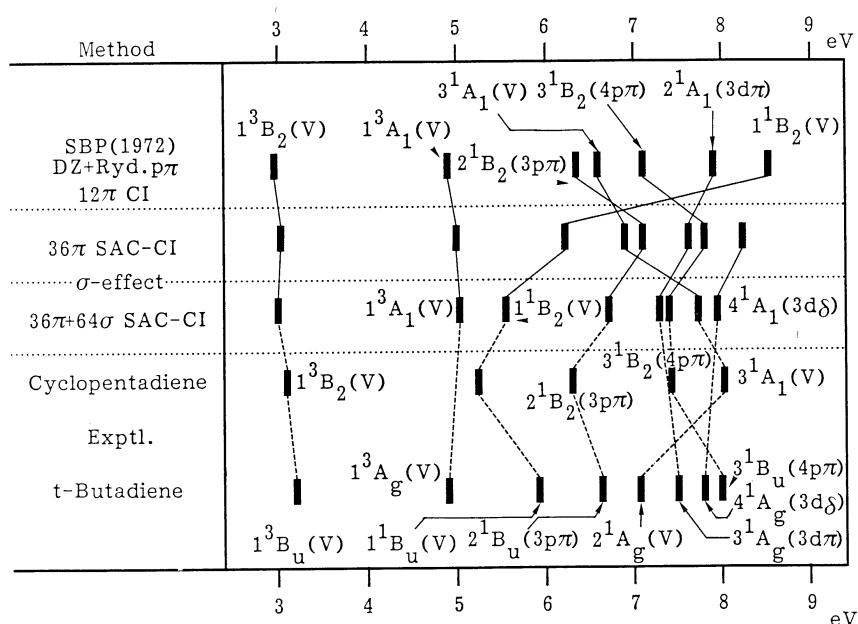
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Fig. 1. Comparison of the theoretical and experimental excitation energies of trans-butadiene. BSP refers to the results reported in ref. [11] and the experimental data are taken from ref. [9].

hand, for the cis form, there is a clear split in the density distributions of the valence and Rydberg excited states, as shown in fig. 4, so that the interaction between the first and second $^1B_2$ states of the cis form is smaller than that of the trans form. It is well known that the wavefunction of ionic valence states of π conjugated systems can be expanded like a Rydberg state when only π-electron correlation is included,

Fig. 2. Comparison of the theoretical and experimental excitation energies of cis-butadiene. SBP refers to the results reported in ref. [10] and the experimental data are taken from refs. [9,13,14].
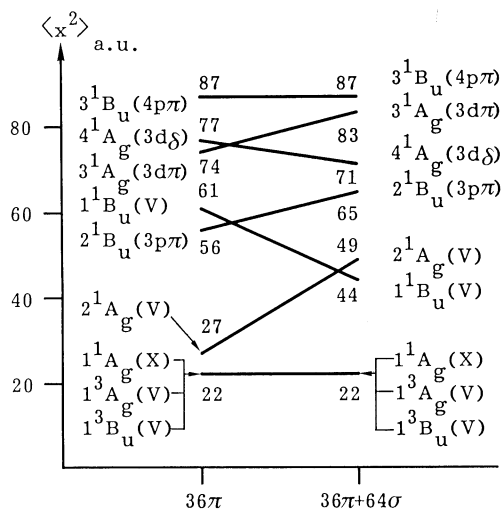
Fig. 3. Schematic summary of the 36 π and 36 π + 64 σ SAC CI results for the electronic part of the second moment of trans-butadiene. The x axis is perpendicular to the molecular plane.

but shrinks to a quasi-valence state after the inclusion of σ-electron correlation [16]. This characteristic behaviour is very clearly seen in the present SAC CI results for the $1\,^1B_u$ state of the trans form. The calculated oscillator strength for this state with the SAC and SAC CI wavefunctions is 0.466, which shows good agreement with the experimental value,

Fig. 4. Schematic summary of the 36 π and 36 π + 64 σ SAC CI results for the electronic part of the second moment of cis-butadiene. The x axis is perpendicular to the molecular plane.

≈ 0.4 [18]. The calculated value for the $2\,^1B_u$ state is 0.234.

Further remarkable changes are seen in fig. 3•for the $2\,^1A_g(V)$ and $4\,^1A_g(3d_\delta)$ states of the trans form and in fig. 4 for the $3\,^1A_1(V)$ and $4\,^1A_1(3d_\delta)$ states of the cis form. Considerable mixing of π^* and $3d_\delta$ orbitals is observed for these states after the inclusion of σ-electron correlation. This is reflected in the electronic part of the second moment.

After completion of this manuscript, we found results for the singlet states by Cave and Davidson [12] based on a large scale CI calculation. They are cited in tables 2 and 3. Their results for the transition energy and the second moment using a CI of dimension 83000 are 6.08 eV and 55.95 au for the $1\,^1B_u$ state of the trans form, and with a CI of dimension 50000 are 5.55 eV and 30.20 au for the $1\,^1B_2$ state of the cis form. These results are excellent and seem to resolve, together with our own values, the theoretical difficulty in reproducing the $1\,^1B_u(\pi\to\pi^*)$ state of trans-butadiene. We note that their second moments are somewhat larger than ours. For excited states of ^1A_g and $^1A_1$ symmetries, large differences are seen between our results and theirs. Further details of the present study will be published in the near future.

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References

[1] H. Nakatsuji and K. Hirao, J. Chem. Phys. 68 (1978) 2053.
[2] H. Nakatsuji, Chem. Phys. Letters 59 (1978) 362; 67 (1979) 329, 334.
[3] H. Nakatsuji, Chem. Phys. 75 (1983) 425; Intern. J. Quantum Chem. Symp. 17 (1983) 241.
[4] H. Nakatsuji, K. Ohta and K. Hirao, J. Chem. Phys. 75 (1981) 2952;
H. Nakatsuji, J. Chem. Phys. 80 (1984) 3703;
H. Nakatsuji, O. Kitao and T. Yonezawa, J. Chem. Phys. 83 (1985) 723;
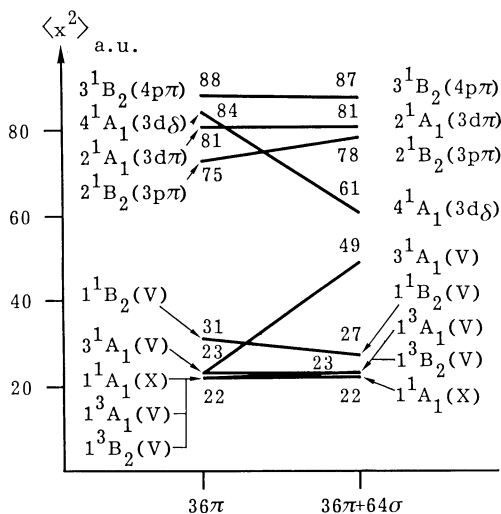O. Kitao and H. Nakatsuji, J. Chem. Phys. 87 (1987) 1169.

[5] H. Nakatsuji, Program System for SAC and SAC-CI Calculations, No. 146 (Y4/SAC), Data Processing Center of Kyoto University (1985);
Program Library SAC85 (No. 1396), the Computer Center of the Institute for Molecular Science, Okazaki, Japan (1986).

[6] R.J. Buenker and J.L. Whitten, J. Chem. Phys. 49 (1968) 5381.

[7] A. Almenningen, O. Bastiansen and M. Traetteberg, Acta Chem. Scand. 12 (1958) 1221.

[8] S. Huzinaga, J. Chem. Phys. 42 (1965) 1293;
T.H. Dunning Jr., J. Chem. Phys. 53 (1970) 2823; 55 (1971) 3958.

[9] W.M. Flicker, O.A. Mosher and A. Kuppermann, J. Chem. Phys. 59 (1973) 6502; Chem. Phys. 30 (1978) 307.

[10] S. Shih, R.J. Buenker and S.D. Peyerimhoff, Chem. Phys. Letters 16 (1972) 244.

[11] R.J. Buenker, S. Shih and S.D. Peyerimhoff, Chem. Phys. Letters 44 (1976) 385.

[12] R.J. Cave and E.R. Davidson, J. Phys. Chem. 91 (1987) 4481.

[13] R.P. Frueholz, W.M. Flicker, O.A. Mosher and A. Kuppermann, J. Chem. Phys. 70 (1979) 2003.

[14] P.J. Derrick, L. Asbrink, O. Edqvist, B.-Ö. Jonsson and E. Lindholm, Intern. J. Mass Spectrom. Ion Phys. 6 (1971) 203.

[15] R.P. Hosteny, T.H. Dunning Jr., R.R. Gilman, A. Pipano and I. Shavitt, J. Chem. Phys. 62 (1975) 4764;
M.A.C. Nascimento and W.A. Goddard III, Chem. Phys. 36 (1979) 147;
M. Aoyagi, Y. Osamura and S. Iwata, J. Chem. Phys. 83 (1985) 1140;
I. Ohmine and K. Morokuma, J. Chem. Phys. 73 (1980) 1907.

[16] S. Huzinaga, J. Chem. Phys. 36 (1962) 71;
K. Tanaka, Intern. J. Quantum Chem. 6 (1972) 1087;
J.A. Ryan and J.L. Whitten, Chem. Phys. Letters 15 (1972) 119;
S. Iwata and K.F. Freed, J. Chem. Phys. 61 (1974) 1500;
R.S. Mulliken, Chem. Phys. Letters 25 (1974) 305;
T. Shibuya, Y.J. I'Haya and V. Mckoy, Intern. J. Quantum Chem. 9 (1975) 505;
L.E. McMurchie and E.R. Davidson, J. Chem. Phys. 66 (1977) 2959.

[17] R. McDiarmid and J.P. Doering, Chem. Phys. Letters 88 (1982) 602.

[18] C.R. Brundle and M.B. Robin, J. Am. Chem. Soc. 92 (1970) 5550.