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SAC-CI CALCULATIONS OF THE EXCITED AND IONIZED STATES OF CONJUGATED MOLECULES

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Abstract: Using SAC (symmetry adapted cluster) and SAC-CI theories, accurate *ab initio* calculations have been performed on the excited and ionized states of several conjugated molecules such as ethylene, butadiene, benzene, pyridine, and naphthalene. On the basis of these studies, we try to solve the famous serious problem in the theory of excited states: the difficulty in the reliable description of the so called V-type excited states of conjugated molecules. Systematic assignments are also given to other valence and Rydberg excited states and ionized states.

1. INTRODUCTION

Chemistry and physics of excited molecules and species now constitute one of the most rapidly expanding frontiers of science and technology. Accordingly, the needs for accurate and useful theories of molecular excited states are more and more increasing. Because of the short-lived nature of the excited states, it is generally very difficult to obtain total pictures of the excited states only by experimental methods. Quantitatively reliable theories and calculations are indeed very useful for elucidating total pictures of the excited states, and thereby for the understandings and designs of the dynamic processes involving molecular excited states.

However, in this respect, there is (was, more strictly) a serious problem in the reliability of the quantum chemistry of molecular excited states. Namely, when it is applied to the so called V states ('*ionic*' valence excited states) [1,2] of conjugated molecules, the result of the excitation energy can differ as large as 1.5 eV from the experimental value, though it can give fairly reliable results for the other valence and Rydberg excitations. For ethylene, modern quantum chemistry is able to reproduce the $\pi \rightarrow \pi^*$ excited state to within 0.5 eV of the experimental value [3-6]. However, for butadiene, the most reliable (at least up to 1986) *ab initio* CI calculations due to Buenker et al. [7] gave the valence $^1B_{1u}$ state at 7.67 eV above the ground state in comparison with the experimental value of 5.92 eV [8]: the discrepancy is as large as 1.75 eV, though their results for the 'covalent' valence and Rydberg states were satisfactory. Similarly for benzene, the most reliable π-CI results of Hay and Shavitt [9] for the excitation energies of the V states were 7.00, 7.64, and 8.34 eV

for the 1^3B_{2u}, 1^1B_{1u}, and 1^1E_{1u} states, respectively, in comparison with the experimental values of 5.60, 6.20, and 6.95 eV. The discrepancy is about 1.4 eV, again very large, though, again, their results for the covalent valence and Rydberg states agreed well with the experimental values. Thus, we have to conceive that something is wrong or missing in the existing descriptions of the valence V excited states of conjugated molecules. This problem has caused a serious suspicion on the reliability of the quantum chemistry of excited states, and thereby has hindered a fruitful interplay between theory and experiment.

About a decade ago, we have proposed SAC (symmetry adapted cluster) [10] and SAC-CI [11] theory as an accurate and yet useful theory for studying ground, excited, ionized, and electron attached states of molecules. The SAC/SAC-CI program [12] has been published more recently. Using this theory, we have recently performed systematic calculations on the valence and Rydberg excitations and ionizations of some conjugated molecules such as ethylene [6], formaldehyde [13], trans- and cis-butadiene [14], five-membered ring compounds (pyrrole, furan, and cyclopentadiene) [15], benzene [16,17], pyridine [18], and naphthalene [19]. We have also investigated the excited and ionized states of H_2O [11,20], CH_2 [21], CO_2, N_2O [22], NO radical [23], glyoxal [24], NH_4^+ [25], and the shake-up ionization spectra of H_2O [26], CO_2, N_2O [22], CS_2, COS [27], and NO radical [23]. The hyperfine splitting constants of some organic radicals and the importance of electron correlation for this property have also reported [28,29].

In this review, we would like to overview some of our recent studies on the excited and ionized states of π-conjugated molecules, and show how the serious problem mentioned above is resolved by our theoretical efforts.

2. SAC and SAC-CI theory

The SAC expansion theory [10] is the theory for ground state and the SAC-CI theory [11] is the theory for excited, ionized, and electron attached states.

The cluster expansion ansatz was first introduced by Coester and Kümmel [30] for a closed-shell ground state and extended in the field of quantum chemistry by Sinanoglu [31], Primas [32], Cizek and Paldus [33], Mukherjee et al. [34] and others [35]. The SAC expansion [10] belongs to this approach and is a generalization to open-shell systems. In the SAC expansion, we operate the exponential of the (spin) symmetry adapted excitation operator $S_I^\dagger$ to the Hartree-Fock (HF) function $|0\rangle$.

$$\psi^{SAC} = 0 \exp(\sum_I C_I S_I^\dagger)|0\rangle \tag{1}$$

Here, the symmetry adaptation of the operator $S_I^\dagger$ is necessary because of a non-linear nature of the expansion. Otherwise, the wave function is not necessarily symmetry adapted as the conventional coupled cluster (CC) wave function. The operator 0 is a symmetry projector, but it is unnecessary for closed-shell systems. This expansion

is suitable for both closed- and open-shell molecules, and describes self-consistency [36] and dynamic correlations [31] very well.

The SAC theory is different from the conventional CC theory. When we consider only single excitations, the CC wave function reduces to the unrestricted HF (non-variational) wave function, as the Thouless theorem [36] implies, but the SAC theory reduces to the pseudo-orbital theory [28] which is a generalization of the orbital theory, and well describes spin-correlation.

Two roles of the SAC theory are important. One is to give an accurate wave function for the ground state. The other is to give, at the same time, a subspace of the functions which is orthogonal and hamiltonian-orthogonal to the SAC wave function, namely [11]

$$\langle \Phi_K | \Psi^{SAC} \rangle = 0,$$

$$\langle \Phi_K | H | \Psi^{SAC} \rangle = 0, \tag{2}$$

with the functions $\{\Phi_K\}$ being defined by

$$\Phi_K = \mathcal{P} R_K^{\dagger} \Psi^{SAC}, \tag{3}$$

where $R_K^{\dagger}$ is a symmetry-adapted excitation operator and $\mathcal{P}$ projects out the SAC function. The relation given by Eq.(2) constitutes a necessary condition which the excited state should satisfy: viz., the functions $\{\Phi_K\}$ span the space for the excited state. Therefore, we describe the excited state by a linear combination of these functions

$$\Psi^{SAC\text{-}CI} = \sum_K d_K \Phi_K \tag{4}$$

which is the SAC-CI theory [11].

We use the SAC-CI theory to describe excited states, ionized states, and electron attached states. For the latter two cases, the operator $R_K^{\dagger}$ in Eq.(3) is an ionization or electron attachment operator, respectively. The condition expressed by Eq.(2) is satisfied automatically in these cases. The SAC-CI theory is more rapidly convergent than an ordinary CI because it satisfies the necessary conditions for the excited states (Eq.(2)), and because it starts from the ground state correlation as seen from Eq.(3). The primary processes of excitations and ionizations involve only one or two electrons and the other electrons lie in the situation similar to that in the ground state. It is, therefore, a better approximation of the excited or ionized states to describe them based on the ground state correlated wave function, as in Eq.(3), rather than to describe the excited-state correlations from the first beginning as in the CI theory.

The program system for the SAC and SAC-CI calculations has been published [12]. It can deal with singlet closed shell ground state by the SAC theory and singlet and triplet excited states, doublet ionized and electron attached states by the SAC-CI

theory. In the present version [12], we truncate the expansion in Eq.(3) at the second order for both operators $S_I^\dagger$ and $R_K^\dagger$, which are single and double excitation operators. The number of these linked operators is the dimension of the matrices involved in the SAC and SAC-CI theory. In practice, such operators are selected, to diminish the size of the calculations, by the method of perturbation selection [22]. In the present calculations, the thresholds λ_g and λ_e are 1×10^{-5} a.u. for the π space. For the configurations arising additionally in the $\pi+\sigma$ calculations, we adopted $3\times10^{-5}\sim 8\times10^{-5}$ a.u. for λ_g and λ_e.

3. EXCITED AND IONIZED STATES OF CONJUGATED MOLECULES

3.1. Ethylene

Ethylene, a starting molecule in conjugated systems, has been investigated by many theories [1-6,37-40], including the SAC/SAC-CI theory [6]. The history has been described previously [6]. We here focus our attention mainly to the singlet $\pi\rightarrow\pi^*$ excited states, $V(^1B_{1u})$. Detailed discussions including other valence excited states and Rydberg states were given previously [6].

We here have performed new calculations using the basis set slightly better than before [6]. It consists of Huzinaga-Dunning [41] [5s2p/2s] set plus diffuse p functions (0.07469, 0.03477, 0.01075) and polarization d functions (1.322, 0.3916) on each carbon. The numbers of the AO's and the active space MO's are 72 and 64 ($18\pi+46\sigma$), respectively. Throughout this article, the HF SCF MO's of the ground state are calculated by the HONDOG program [42]. The total energies of the HF, π SAC, and $\pi+\sigma$ SAC wave functions for the ground state are -78.04448, -78.07638 and -78.29722 a.u.,

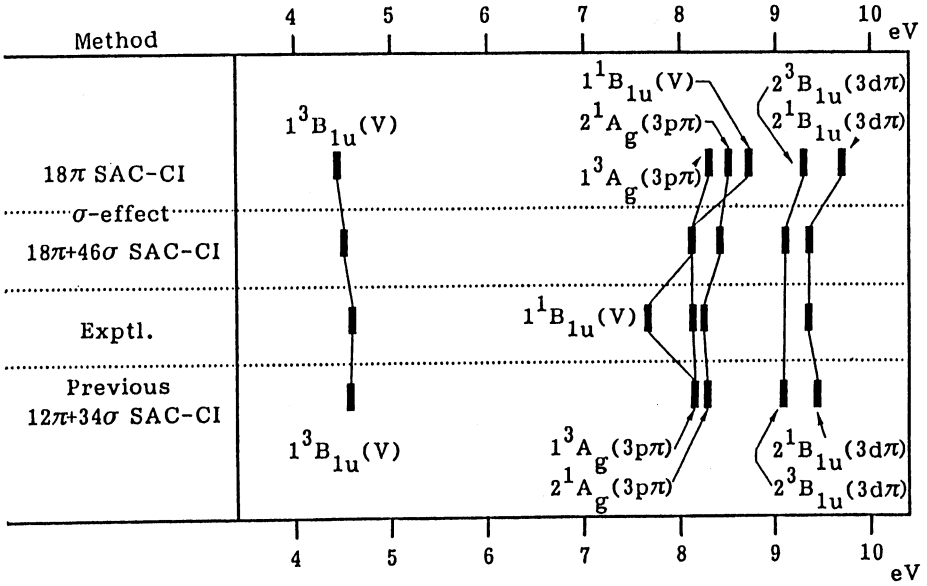

Fig. 1 Comparison of the theoretical and experimental excitation energies of ethylene. The experimental data are taken from [43-45].

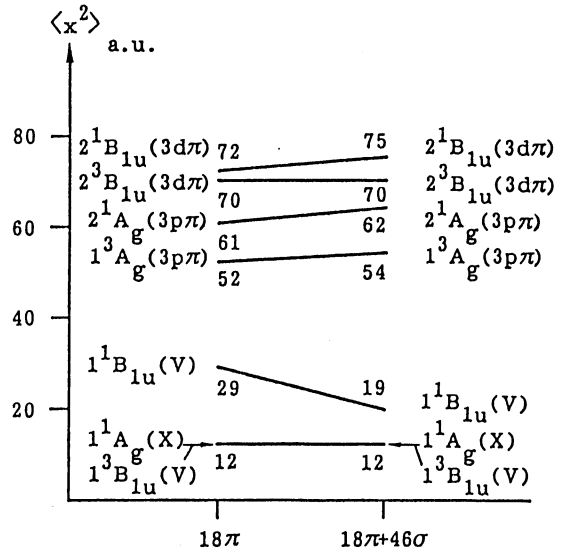

Fig. 2 Schematic summary of the 18π and 18π+46σ SAC-CI results for the electronic part of the second moment of ethylene. The x axis is perpendicular to the molecular plane.

respectively.

The present results are summarized in Fig. 1 and compared with the experimental [43-45] and the previous theoretical results [6]. The σ electron correlation lowers the excitation energy of the 1^1B_{1u} state by 0.59 eV and reproduces the experimental value to within 0.49 eV. This change is considerably large in comparison with those for the 1^3B_{1u} state and the Rydberg states. The electronic part of the second moment is shown in Fig. 2. Throughout this article, the x axis is in the out-of-plane direction. The electron cloud of the 1^1B_{1u} state considerably shrinks owing to the inclusion of the σ electron space. These behaviors are similar to those pointed out previously by many investigators [38,39].

A large σπ interaction in this 1^1B_{1u} state of ethylene is interpreted with the concept of *left-right correlation* [3,38,39]: viz., a large bias of the π electron cloud on the *left*-side along its molecular axis is compensated by the net polarization of the σ electron cloud on the *right*-side, and vice versa.

3.2. Trans- and Cis-Butadiene

There have been many investigations for butadiene, especially for the trans-form, though the result for the $V(^1B_u)$ state is pessimistic. Through these studies, roughly two possibilities have been proposed as a solution of this situation.

(i) Inclusion of a large amount of σ electron correlation will improve the description of the ^1B_u state and the excitation energy from the ground state.

(ii) The peak maximum may not correspond to the vertical transition, so that the considerations of the geometry deformation after the electronic excitation will be

important.
The UV-IR double resonance experiment [46] suggested the V state to be planer and questioned on the second possibility.

The geometries are the same as those used by Buenker and Whitten [47]; for the trans form, it is due to the experimental data [48]. Two basis sets are used: Basis set I consists of the [5s2p/2s] set of Huzinaga-Dunning [41] plus diffuse p_π functions (0.07469, 0.03477, 0.01075) and polarization d functions (1.322, 0.3916) on each carbon. 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 functions (0.3916) on each carbon. The numbers of the AO's are 116 (I) and 100 (II). The active space consists of the $36\pi+64\sigma$ (I) and $28\pi+60\sigma$ (II) MO's calculated for the ground state. The HF ground state energies with basis set I are -154.94245 (trans) and -154.92780 (cis) a.u. The values with basis set II are -154.91920 (trans) and -154.90449 (cis) a.u. The ground state energies of the π SAC wave function with basis set I are -155.00428 (trans) and -154.99051 (cis) a.u. The values with basis set II are -154.98108 (trans) and -154.96723 (cis) a.u. The ground state energies of the $\pi+\sigma$ SAC wave function with basis set I are -155.18483 (trans) and -155.17588 (cis) a.u. The values with basis set II are -155.14598 (trans) and -155.13639 (cis) a.u.

The theoretical and experimental results are summarized in Tables 1 and 2. The electronic part of the second moment is depicted in Fig. 3. The study of Buenker et al. for the trans [7] and cis [49] forms have been the most reliable theoretical results for a long time. The experimental data for the trans form are taken from the electron energy loss spectroscopy (EELS) data [8] and the values correspond to the peak maxima. For the cis form, the EELS data for cyclopentadiene [50] and for the trans form are compared. The data for the np_π Rydberg transitions of cyclopentadiene are taken from the analysis of the ultraviolet spectrum [51].

The σ electron correlation plays a crucial role in the ionic valence excited states. 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 1 and 2, in comparison with those for the other valence and Rydberg excited states studied here. In the present SAC-CI calculation, the valence excited 1^1B_u 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.

An interesting effect of the σ electron correlation is also seen for the $3^1A_1(V)$ state of the cis form. The calculated excitation energy for the $\pi+\sigma$ wave function is *higher* by 0.77 eV than that for the π one. The final value differs by 0.35 eV from the experimental value for the corresponding state of cyclopentadiene. This behaviour is similar to the one of the $T(^3B_{1u})$ state of ethylene [38,39]. This is because the state

under consideration is *less* ionic than the ground state. The effect for the $1^1A_g(V)$ state of the trans form is 0.07 eV in the same direction.

In Table 1, some other low-lying valence $\pi\rightarrow\pi^*$ and Rydberg excitations of the trans form are shown. The agreement between theory and experiment is also excellent and the final average deviation is ~0.2 eV. For the cis form shown in Table 2, the deviation from the experimental data is defined as the difference from the corresponding one of cyclopentadiene, if available, but if not, the data of the trans form are used. The final average deviation is ~0.2 eV.

From the experimental study on the 1,3-diene, McDiarmid and Doering [52] found that

TABLE 1. $\pi\rightarrow\pi^*$, np_x, and nd_x excitation energies of trans-butadiene (eV).

State	Exptl.	SAC-CI				SBP[d]	BSP[e]	CD[f]	
		Basis set I		Basis set II				PTCI	CI4
		36π(Δ[c])	36π+64σ(Δ)	28π(Δ)	28π+60σ(Δ)	12π(Δ)	12π+34σ(Δ)	(Δ)	(Δ)
$2^1A_g(V)$	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)
$3^1A_g(3d_x)$	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)
$2^1B_u(3p_x)$	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)
$3^1B_u(4p_x)$	8.00	8.24(0.24)	7.91(-0.09)	8.29(0.29)	7.87(-0.13)	7.98(-0.02)	7.98(-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						
$3^3A_g(3d_x)$		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)		
$2^3B_u(3p_x)$		6.99	6.65			7.55			
$3^3B_u(4p_x)$		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][8]. [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][49]. [e][7]. [f][54]. PTCI and CI4 stand for perturbation theory selected CI and a priori selected CI, respectively.

TABLE 2. $\pi\rightarrow\pi^*$, np_x, and nd_x excitation energies of cis-butadiene (eV).

State	Exptl.		SAC-CI				SBP[f]	CD[g]	
			Basis set I		Basis set II			PTCI	CI4
	TB[a]	CP	36π(Δ[e])	36π+64σ(Δ)	28π(Δ)	28π+60σ(Δ)	12π(Δ)	(Δ)	(Δ)
$2^1A_1(3d_x)$	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)
$2^1B_2(3p_x)$	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)
$3^1B_2(4p_x)$	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)		
$2^3A_1(3d_x)$			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)		
$2^3B_2(3p_x)$			6.89	6.52			7.42		
$3^3B_2(4p_x)$			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 [8]. [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]Experimental data for the corresponding states of cyclopentadiene. These values are taken from [50]. [d]Experimental data for the corresponding states of cyclopentadiene. These values are taken from [51]. [e]Δ shows the difference from the experimental value. The reference is the corresponding state of cyclopentadiene, if available, but if not, the reference is the corresponding state of trans-butadiene. [f][49]. [g][54]. PTCI and CI4 stand for perturbation theory selected CI and a priori selected CI, respectively.

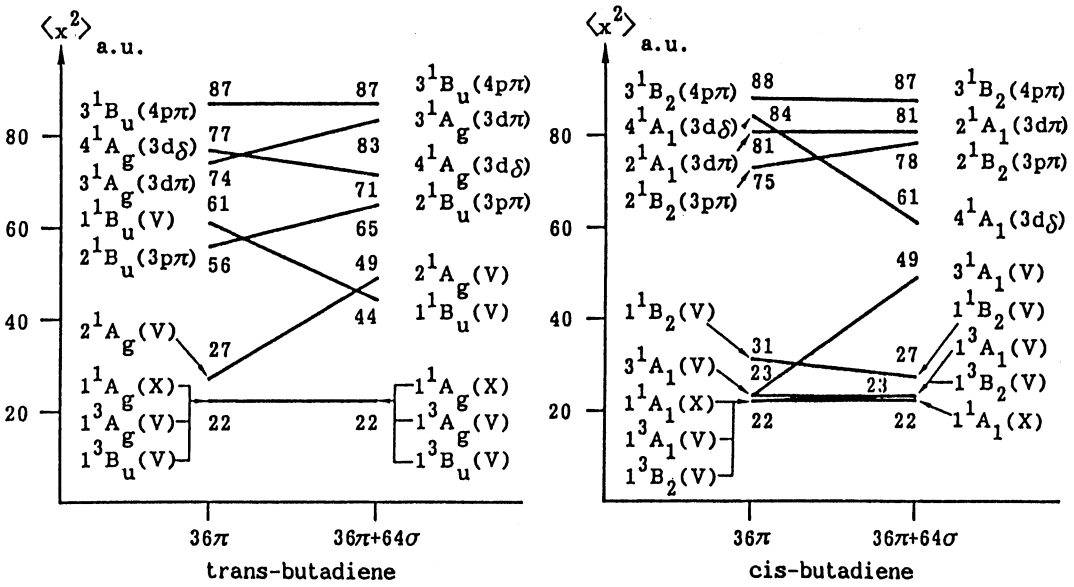

Fig. 3 Schematic summary of the 36π and 36π+64σ SAC-CI results for the electronic part of the second moment of trans (left) and cis (right)-butadienes. The x axis is perpendicular to the molecular plane.

the B_u states of the s-cis compounds were ~0.5 eV lower than those of the s-trans compounds. Our theoretical results for trans- and cis-butadiene support this observation. 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), though, in the ground state, the trans form (1^1A_g) is lower by 0.26 eV than that of the cis form (1^1A_1). For the Rydberg states, the differences between the trans and the cis forms are smaller than for the valence states, as expected.

To within the π SAC-CI treatment, the mixing of the valence and Rydberg natures is large for the first and second ^1B_u states of trans-butadiene. This mixing is resolved by the inclusion of the σ electron correlation as seen in Fig. 3. The second moment changes from 61 a.u. (π SAC-CI) to 44 a.u. (π+σ SAC-CI). This behaviour is similar to the characteristic one of the $V(1^1B_{1u})$ state of ethylene. The oscillator strength calculated with the SAC and the SAC-CI wave functions is 0.466, which shows a good agreement with the experimental value, ~0.4 [53]. The calculated value for the 2^1B_u state is 0.377.

Other 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 for the $3^1A_1(V)$ and $4^1A_1(3d_\delta)$ states of the cis from. A large mixing of the π^* and $3d_\delta$ natures is observed *after* including the σ electron correlations. This is reflected on the electronic part of the second moment.

Cave and Davidson [54] have recently performed a large scale CI on butadiene. The transition energy to the 1^1B_u state of trans-butadiene was 6.08 eV, which is excellent.

This result and our result have thus resolved the famous theoretical difficulty in reproducing the $1^1B_u(\pi\rightarrow\pi^*)$ state of trans-butadiene as being due to the insufficiency in including the σ-electron correlation.

3.3. Benzene

Benzene is a key aromatic molecule. Although there are many semiempirical studies [55], *ab initio* studies of the excited states of this important molecule are still very limited [9,56-60]. Hay and Shavitt [9] calculated several excited states by the π MR-CI method with the relatively large basis set. Their results have been considered to be best for a long time [56]. Recently, a substantial improvement has been performed by Matos et al. [61] and by us [16,17] with including a large amount of σ electron correlation.

The geometry of the ground state of benzene was determined by Raman spectroscopy [62]. Two basis sets are used by expanding the basis set used by Hay and Shavitt [9]: [4s2p/2s] set of Huzinaga-Dunning [41] plus Rydberg p_π functions (0.03477,0.01075) on each carbon atom (basis set 0). Basis set I consists of the basis set 0 plus polarization d_π functions (0.75) on each carbon atom. Basis set II consists of the basis set 0 plus Rydberg s (0.0437,0.0184), p (0.0399,0.0168), and d (0.0285,0.0120) functions [63] on the center of the molecule. For the valence excitations and ionizations, we have used basis set I and the active space consists of 35π+45σ MO's. For the Rydberg excitations, basis set II is used and the active space is 29π+51σ MO's. The total energies for the HF, π-SAC, and π+σ-SAC wave functions are -230.660466, -230.74818, and -230.85811 a.u., respectively, for the basis set I, and those for the basis set II are -230.642480, -230.72555, and -230.83882 a.u., respectively.

The theoretical and experimental [64,65] results for the valence excited states are summarized in Table 3. For the valence $\pi\rightarrow\pi^*$ excitations, the SAC-CI theory has reproduced the experimental excitation energies of the $S_1(^1B_{2u})$, $S_2(^1B_{1u})$, $S_3(^1E_{1u})$, $T_1(^3B_{1u})$, $T_2(^3E_{1u})$, and $T_3(^3B_{2u})$ states to within 0.52 eV, the average discrepancy being 0.34 eV. Among these states, the S_1, T_1, and T_2 states are explainable within the π-electron space. For the S_2 and T_3 states, the σ-reorganization effect is 0.6~0.7 eV and the contribution of the polarization d_π functions is 0.3~0.4 eV. With these two effects, the π-CI results of Hay and Shavitt [9] are improved by 1.04 eV for the S_2 state and 0.98 eV for the T_3 state. For the S_3 state, a typical V state, the σ-reorganization plays a significant role with the contribution as large as 0.8 eV, while the d_π polarization function contributes only about 0.1 eV. The overall improvement over the previous π-CI result [9] is 0.9 eV. The final results are compared with the electron energy loss spectra [65] in Fig. 4, in which some Rydberg excitations are also included.

Some interesting behaviors are seen on the π and σ electron clouds of the S_3 state.

TABLE 3. The valence $\pi_2-\pi_3^*$ excitation energies of benzene.

State	Excitation Energy(eV)			Exptl.	Oscillator Strength		
	SDT-CI(HS[a])	SAC-CI					
	23π[SD],18π[T](Δ[b])	35π(Δ)	35π+45σ(Δ)		35π	35π+45σ	Exptl.
$1^1B_{2u}(S_1)$	5.00(0.10)	5.25(0.35)	5.25(0.35)	4.90[c]	0.0	0.0	0.0013[e]
$1^1B_{1u}(S_2)$	7.64(1.44)	7.31(1.11)	6.60(0.40)	6.20[c]	0.0	0.0	0.09[f]
$1^1E_{1u}(S_3)$	8.34(1.39)	8.25(1.30)	7.47(0.52)	6.95[c]	0.61	1.03	0.60~1.25[g] (y,z)
$1^3B_{1u}(T_1)$	3.83(-0.12)	3.80(-0.15)	4.06(0.11)	3.95[d]			
$1^3E_{1u}(T_2)$	4.98(0.23)	5.05(0.30)	5.02(0.27)	4.75[d]			
$1^3B_{2u}(T_3)$	7.00(1.40)	6.65(1.05)	6.02(0.42)	5.60[d]			

[a][9]. [b]Δ shows the difference from the experimental value. [c][64]. [d][65]. [e][66]. [f][67]. [g][68].

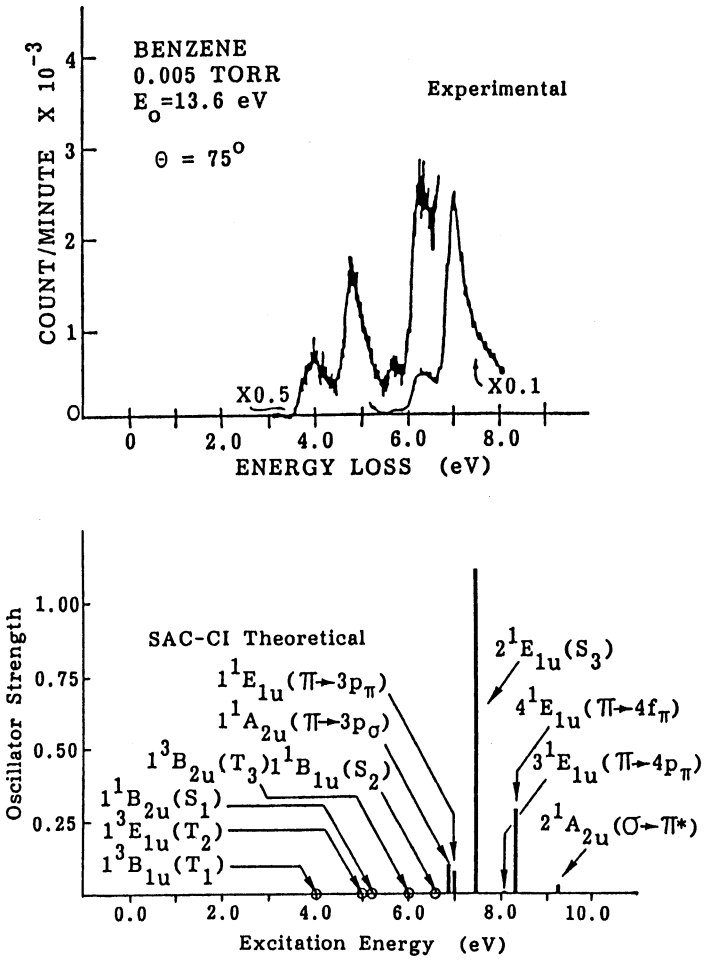

Fig. 4 Experimental (above) and theoretical (below) excitation spectra of benzene. The experimental results are taken from [65].

The electronic part of the second moment is depicted in Fig. 5. Before the σ-reorganization effect is included, this state looks almost like Rydberg from the $\langle x^2 \rangle$ value. However, when it is included, the electron cloud considerably shrinks and the state becomes essentially valence in nature. Accordingly, the oscillator strength increases from 0.61 (35π) to 1.03 (35π+45σ). This behaviour is in common to

the valence excited V states of conjugated polyenes as the similar behaviors have also been seen for ethylene, butadiene, and pyridine as shown below. A large bias of the π electron cloud on the *outer*-side is compensated by the net polarization of the σ electron cloud on the *inner*-side. We call this $\sigma\pi$ interaction as *molecular in-out correlation*, which is clearly a generalization of the left-right correlation previously considered [3,38,39].

We have also reported the first systematic calculations of the Rydberg excited states involving both π and σ states [17]. Recently almost all the Rydberg transitions from the HO π MO have been assigned experimentally by the MPI spectroscopy [70-72]. The theoretical and experimental results are summarized in Table 4 for the singlet Rydberg excited states. The SAC-CI calculations have reproduced the experimental values to within 0.3 eV (mostly within 0.2 eV). The $\pi\rightarrow ns$ transitions (n=3,4) are first dealt with theoretically, and the agreement with experiment is excellent. The transitions $\pi\rightarrow 3p_\sigma$ and $\pi\rightarrow 3p_\pi$ are also computed. The agreement between theory and experiment is better for the $\pi\rightarrow 3p_\sigma$ transition rather than for the $\pi\rightarrow 3p_\pi$ transition. This is due to the interaction between the Rydberg $\pi\rightarrow 3p_\pi$ state and the valence $\pi\rightarrow\pi^*$ S_3 state, both lying closely at about 7 eV. The $\pi\rightarrow 4p_\pi$ transition is calculated at about 0.24 eV lower than the experimental value. The $\pi\rightarrow nd$ and $\pi\rightarrow nf$ transitions are also computed. The

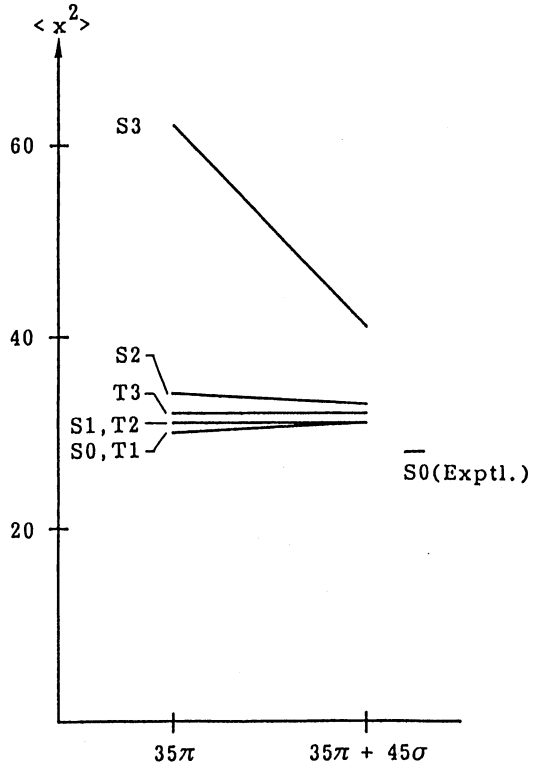

Fig. 5 Schematic summary of the 35π and $35\pi+45\sigma$ SAC-CI results for the electronic part of the second moment of benzene. The x axis is perpendicular to the molecular plane. The experimental data for S0 is taken from [69].

TABLE 4. The singlet Rydberg excited states of benzene.

Orbital picture	State	Excitation Energy(eV)					Electronic part of second moment(au)			Oscillator strength	
		Exptl.	SAC-CI			SDT-CI(HS[a])					
			29π+51σ	(Δ[b])	σ-effect	29π	23π[SD],18π[T]	$\langle x^2\rangle$	$\langle y^2\rangle$	$\langle z^2\rangle$	SAC-CI	
Ground	1^1A_{1g}	0.0	0.0			0.0	0.0	31	216	216		
Excited												
π→3s	1^1E_{1g}	6.33[c]	6.31	(0.02)				52	236	235	0.0	
π→3p$_o$	1^1A_{1u}		7.10					47	246	245	0.0	
	1^1A_{2u}	6.93[d]	6.88	(0.05)				46	245	244	0.071	x
	1^1E_{2u}	6.95[d]	6.99	(0.04)				46	245	245	0.0	
π→3p$_x$	1^1E_{1u}	7.19[e],7.41[f]	6.91		0.32	7.23	7.26	85	231	230	0.049	(y,z)
			7.02[g]	(0.28)								
π→3d$_o$	1^1B_{1g}	7.46[h]	7.42	(0.04)				47	263	269	0.0	
	1^1B_{2g}	7.46[h]	7.42	(0.04)				47	264	268	0.0	
	2^1E_{1g}		7.44					50	250	278	0.0	
π→3d$_δ$	3^1E_{1g}	7.54[e]	7.35	(0.19)				69	254	231	0.0	
π→3d$_z$	2^1A_{1g}	7.80[e]	7.64	(0.16)	0.25	7.89	7.92	98	277	239	0.0	
	1^1A_{2g}		7.57		0.36	7.93	7.94	99	261	256	0.0	
	1^1E_{2g}	7.81[e]	7.64	(0.17)	0.26	7.90	7.90	98	238	277	0.0	
π→4s	4^1E_{1g}	7.95[e]	7.90	(0.05)				113	250	248	0.0	
π→4p$_x$	2^1E_{1u}	8.37[f]	8.13	(0.24)	0.35	8.48	9.25	124	239	279	0.004	(y,z)
π→4d$_z$	3^1A_{1g}	8.44[e]	8.53	(0.09)	0.23	8.76	9.71	126	280	306	0.0	
	2^1A_{2g}		8.44		0.36	8.80	9.62	125	297	287	0.0	
	2^1E_{2g}	8.44[e]	8.52	(0.08)	0.26	8.78	9.56	126	306	280	0.0	
π→4f$_x$	1^1B_{1u}		8.17		0.40	8.57	8.58	96	278	280	0.0	
	1^1B_{2u}		8.16		0.34	8.50	8.52	86	268	268	0.0	
	3^1E_{1u}	8.38[i]	8.33	(0.05)	0.59	8.92	8.74	87	273	241	0.293	(y,z)

[a][9]. [b]Δ shovs the difference from the experimental value. [c][70]. [d][71]. [e][72].
[f][73]. [g]Only this value is calculated with basis set I. [h]These values were estimated from π→4d$_o$. [i][74].

recent experiments [72,74] have clarified that the Wilkinson's R'' and R''' series [73], which were once considered as π→nd [73], should be assigned to π→nf. The SAC-CI calculations have excellently reproduced the lower components of these transitions. The effects of the σ reorganization on the Rydberg transitions are about 0.3 eV, smaller than those for the higher valence transitions, $S_0 \rightarrow S_2$, S_3, and T_3.

For the ionization potential, the SAC-CI results are compared in Table 5 with the experimental [75,76] and other theoretical values. The outer valence ionizations are reproduced to within ~ 0.6 eV of the experimental values. Our results support the assignment due to the Green function method [77]. Fig. 6 is a display of the experimental and theoretical ionization spectra which involve outer and inner valence ionizations and their satellite peaks. The experimental data is the ESCA spectrum [79], and the theoretical data is due to the SAC-CI calculation including S_2*I_2 integrals as well as the S_2*I_1 integrals in the unlinked term [22]. The intensity of the peak is calculated with the mono pole approximation [80]. The

TABLE 5. The outer valence ionization potentials of benzene (eV).

State	Exptl.[a]	SAC-CI		Green fn'[b]	Koopmans'
		Energy(Δ[c])	Intensity	Energy(Δ)	
1^2E_{1g} (π)	9.25(9.3)	8.88(0.40)	0.95	9.1 (0.18)	9.26
3^2E_{2g}	11.53(11.4)	11.27(0.20)	0.93	11.95(0.49)	13.36
1^2A_{2u} (π)	12.38(12.1)	12.41(0.17)	0.90	12.26(0.02)	13.73
3^2E_{1u}	13.98(13.8)	13.78(0.17)	0.92	14.46(0.57)	16.00
1^2B_{2u}	14.86(14.7)	14.22(0.56)	0.91	14.38(0.05)	16.83
2^2B_{1u}	15.46(15.4)	15.96(0.53)	0.92	15.75(0.32)	17.52
3^2A_{1g}	16.84(16.9)	16.91(0.04)	0.90	17.48(0.61)	19.39
				17.15[d](0.28)	
2^2E_{2g}	(19.2)	19.45(0.25)	0.88	20.01(0.81)	22.44
				19.60[d](0.40)	

[a][75] and [76] (in parentheses). [b][77]. [c]Δ shows the difference from the experimental value. [d][78].

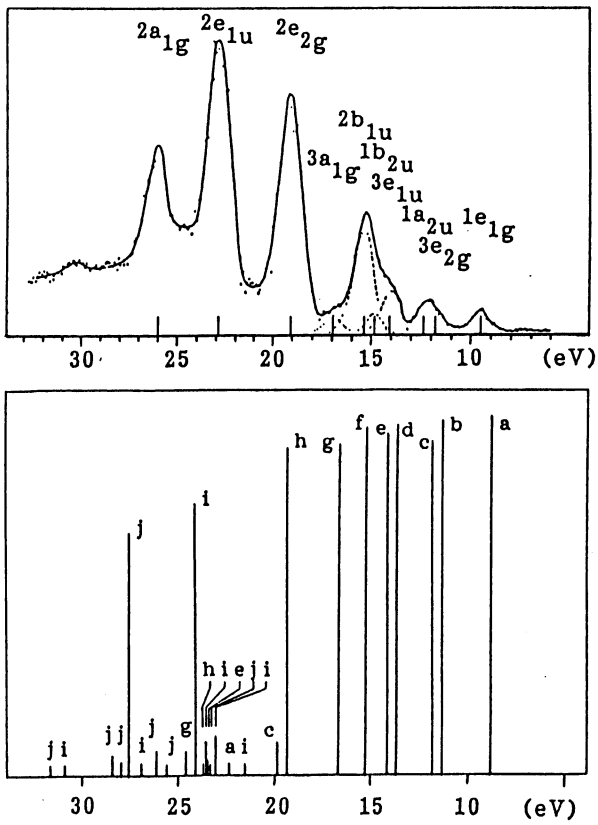

Fig. 6 Experimental (above) and theoretical (below) valence ionization spectra of benzene. The experimental results are taken from [79]. a:$1e_{1g}$, b:$3e_{2g}$, c:$1a_{2u}$, d:$3e_{1u}$, e:$1b_{2u}$, f:$2b_{1u}$, g:$3a_{1g}$, h:$2e_{2g}$, i:$2e_{1u}$, j:$2a_{1g}$.

alphabet on each peak shows the MO from which one electron is annihilated. We have obtained many satellite peaks in the inner valence region and explained some features of the observed ESCA spectrum.

3.4. Pyridine

Pyridine is a key molecule in hetero aromatics. There was, however, no reliable *ab initio* theoretical treatment [81]. Our paper is probably the first report [18] which deals with the excited states of pyridine from the strict *ab initio* viewpoint.

The geometry we used is due to the microwave study [82] for the ground state. The basis set is [4*s*2*p*/2*s*] set of Huzinaga-Dunning [41] plus diffuse p_π functions (0.03477,0.01075) on each carbon and nitrogen atom. This set is augmented by the polarization d_π functions (0.75) on each carbon atom and d functions (0.80) on a nitrogen atom [63]. Three active spaces, 3π, 3π+1N and 3π+5σ, are used. Here, 1N stands for the occupied lone pair MO of the nitrogen. The total energies owing to the HF, π+N-SAC, and π+σ-SAC wave functions are -246.66403, -246.75596, and -246.86943

a.u., respectively.

The SAC-CI theoretical results for the valence excited states are summarized in Table 6 and compared with the experimental values [66,83-85]. About the valence $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ excited states, $S_1(1^1B_2)$, $S_2(1^1A_1)$, $S_3(2^1B_2)$, $S_n(1^1B_1)$, $T_1(1^3A_1)$, and $T_n(1^3B_1)$, the experimental results are reproduced to within 0.66 eV. The $S_4(2^1A_1)$ state is experimentally considered not to be split from the S_3 state [66], but is calculated, by our theory, to be higher by 0.31 eV than the S_3 state. The average discrepancy from the experimental data is 0.55 eV without including the S_4 state. There are no experimental data for the valence $\pi\rightarrow\pi^*$ excited states, $T_2(1^3B_2)$, $T_3(2^3A_1)$, $T_4(2^3B_2)$ and the $n\rightarrow\pi^*$ excited states, $S_n'(1^1A_2)$ and $T_n'(1^3A_2)$. We predict the excitation energies of these states to be about 0.3 - 0.6 eV lower than the present theoretical values.

TABLE 6. Valence excitation energies of pyridine (eV).

State	SAC-CI			Exptl.
	$35\pi(\Delta^a)$	$35\pi+1N(\Delta)$	$35\pi+50\sigma(\Delta)$	
$S_1(1^1B_2)$	5.37(0.38)	5.37(0.38)	5.44(0.45)	4.99[b]
$S_2(1^1A_1)$	7.64(1.28)	7.63(1.25)	7.04(0.66)	6.38[b]
$S_3(2^1B_2)$	8.66(1.44)	8.66(1.44)	7.85(0.63)	7.22[b]
$S_4(2^1A_1)$	8.85	8.85	8.16	----[c]
$S_n(1^1B_1)$		5.89(1.30)	5.24(0.65)	4.59[d]
$S_n'(1^1A_2)$		6.58	5.69	
$T_1(1^3A_1)$	3.94(0.14)	3.95(0.15)	4.34(0.54)	3.69[e],3.8[f]
$T_2(1^3B_2)$	5.07	5.08	5.09	
$T_3(2^3A_1)$	5.17	5.17	5.32	
$T_4(2^3B_2)$	7.03	7.03	6.60	
$T_n(1^3B_1)$		5.21(1.11)	4.49(0.39)	4.1[f]
$T_n'(1^3A_2)$		6.47	5.69	

[a]Δ shows the difference from the experimental value. [b][66]. [c]See text. [d][83]. [e][84]. [f][85].

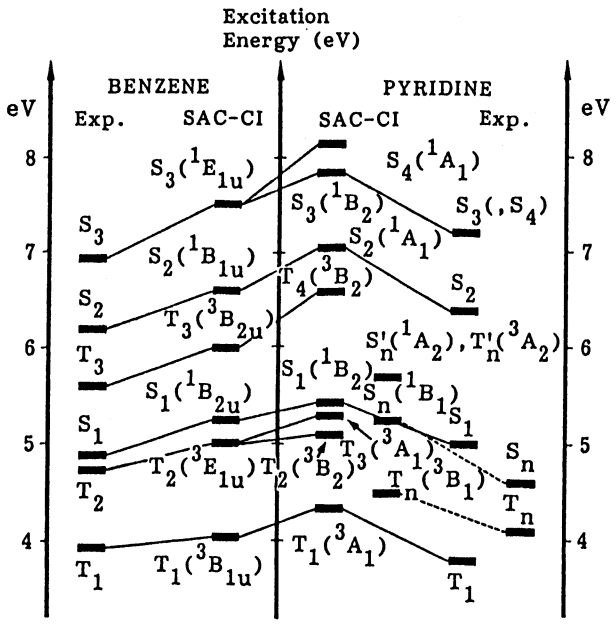

Fig. 7 Comparison of the experimental and theoretical excitation energies between benzene and pyridine.

The $\pi \rightarrow \pi^*$ transitions of pyridine are understood from those of benzene as a result of the perturbation which is a replacement of one CH group with a nitrogen atom. The $n \rightarrow \pi^*$ states lie closely to these $\pi \rightarrow \pi^*$ states and the relative ordering is often a cause of some controversial assignment. Fig. 7 shows the correspondence between the $\pi \rightarrow \pi^*$ states of benzene and pyridine. The degenerate E_{1u} state splits into the B_2 and the A_1 states, the former being closer to the original benzene state because it has a node at the position of nitrogen.

The lowest electronic state T_1 is calculated relatively higher than the experimental value in comparison with the corresponding T_1 state of benzene. This is probably due to the interaction with the nearly degenerate T_n state. Experimentally, the existence of the T_n state is considered to make the T_1 surface double minimum [86], so that the adiabatic excitation to the T_1 state is lower than the vertical excitation. The lower electronic states, S_1, T_2, and T_3 are quite similar to the corresponding S_1 and T_2 states of benzene. These states show the characteristics of the so-called covalent state. The higher electronic states, S_2 and T_4, on the other hand, are ionic and the σ correlation effect is important for the transition energy as shown in Table 6, but affects little to the second moment and the dipole moment as shown in Fig. 8. This

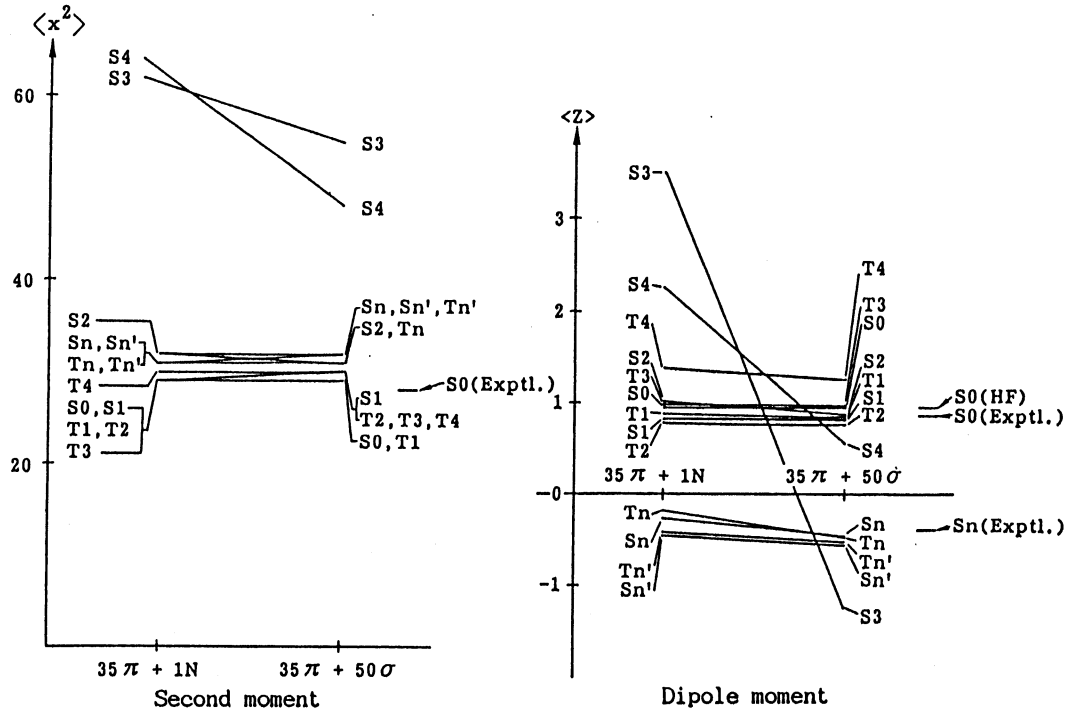

Fig. 8 Schematic summary of the 35π+1N and 35π+50σ SAC-CI results for the electronic part of the second moment (left) and dipole moment (right) of pyridine. The x axis is perpendicular to the molecular plane. The molecule is laid in the yz plane with the principal axis collinear to the z axis. The direction of the dipole moment is from nitrogen to carbon. The experimental data of second moment for S0 is taken from [87]. The experimental data of dipole moment for S0 and Sn are taken from [88] and [89], respectively.

TABLE 7. Oscillator strength for the valence excitations of pyridine.

State	SAC-CI			Exptl.	Direction
	35π	35π+1N	35π+50σ		
S_1	0.023	0.023	0.038	0.029[a],0.04[b]	y[c]
S_2	0.021	0.021	0.021	0.085[a],0.20[d]	z[c]
S_3	0.619	0.624	0.458		y
	1.132	1.140	1.062	0.90[a] ,1.36[d]	
S_4	0.513	0.516	0.604		z
S_n	-[e]	0.009	0.007	0.003[a]	x[c]
S_n'	0.0	0.0	0.0		

[a][66]. [b][90]. [c]The molecule is placed on the yz plane with the z axis being the molecular axis. [d][91]. [e]not calculated.

is expected from the corresponding S_2 and T_3 states of benzene. The S_3 and S_4 states of pyridine are the typical V states as they are split from the degenerate S_3 state of benzene. The σ-correlation effect is very important for both the transition energy and the one-electron properties such as the second moment, dipole moment (Fig. 8), and oscillator strength.

Table 7 shows the oscillator strength for the valence excitation of pyridine. The agreement between theory and experiment is good except for the S_2 state. For this state, the experimental intensity is considered to be due to the intensity borrowing from the upper S_3 and S_4 states, since even in benzene, the experimental oscillator strength of the S_2 state is 0.09 [67], despite that this transition is symmetry forbidden. The intensity of the S_1 state is, on the other hand, just due to the symmetry lowering.

The present SAC-CI study has suggested the following relative orderings between the $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ excitations. The lowest singlet excited state is calculated to be $n\rightarrow\pi^*(S_n(1^1B_2))$ and the lowest triplet state is calculated to be $\pi\rightarrow\pi^*(T_1(1^3A_1))$. The triplet $n\rightarrow\pi^*(T_n(1^3B_1))$ state exists higher by 0.15 eV than the T_1 state. Experimentally, the lowest singlet excited state is confirmed to be $n\rightarrow\pi^*$ [92], but two controversial assignments exist for the lowest triplet state: viz., $\pi\rightarrow\pi^*$ [93] or $n\rightarrow\pi^*$ [94]. The present result prefers the $\pi\rightarrow\pi^*$ state as the lowest triplet excited state.

Table 8 shows a comparison of the experimental [75,95,96] and theoretical ionization potentials of pyridine. The outer valence IP's are reproduced to within ~0.6 eV of the experimental values. There is a controversial situation about the identification of the upper three peaks. Our theoretical result shows the order, nππ, and this result is supported by the recent experiment [96]. The satellite peaks from 15 to 22 eV are summarized in Table 9. The satellite peaks exist at relatively lower region, ~17 eV, in contrast to benzene, and are caused by the existence of nitrogen atom. Our results agree, in general, with those of von Niessen et al. [99]. We have predicted several satellite peaks in the inner valence region of pyridine.

TABLE 8. Outer valence ionization potentials of pyridine (eV).

Peak	Exptl.		SAC-CI[c]	Green fn'[d]	Valence Bond[e]	Koopmans'
	KKAYI [a]	UKN [b]				
1	9.60	9.66(n)	8.96(a_1,n)	9.57(a_2,π)	9.57(a_2,π)	11.36
2	9.75	9.80(π)	9.38(a_2,π)	9.59(a_1,n)	9.82(a_1,n)	9.66
3	10.51	10.54(π)	9.95(b_1,π)	10.24(b_1,π)	10.18(b_1,π)	10.50
4	12.61	12.48(σ)	12.12(b_2,σ)	12.87(b_2,σ)	-	14.05
5	13.1	13.27(π)	13.20(b_1,π)	13.43(b_1,π)	13.01(b_1,π)	14.80
6	13.8		13.46(a_1,σ)	14.18(a_1,σ)	14.59(a_1,n)	15.75
7	14.5		14.34(b_2,σ)	15.11(b_2,σ)	-	16.36
8	15.6		15.48(b_2,σ)	16.32(a_1,σ)	-	18.00
9	15.8		15.87(a_1,σ)	16.33(b_2,σ)	-	17.84
10	17.2		17.43(a_1,σ)	18.00(a_1,σ)	-	19.78
11	(19.6)		20.33(b_2,σ)	21.17(b_2,σ)	-	23.35
12	(20.0)		20.60(a_1,σ)	21.15(a_1,σ)	-	23.47

[a][75]. Values in parentheses are from [95]. [b][98]. [c]These results are based on the calculation with the S_2+I_1 integrals. See text. [d][97]. [e][98].

TABLE 9. Satellite peaks of pyridine from 15 to 22 eV region.

Symmetry	Exptl.[a]	SAC-CI with S_2+I_2			2ph-TDA[b]	
		IP(eV)	Intensity	Main Configuration[c]	IP(eV)	Intensity
$5b_2$	15.6	15.38	0.89	$0.94(5b_2)^{-1}$	16.05	0.25
					16.31	0.57
$9a_1$	15.8	15.75	0.90	$0.95(9a_1)^{-1}$	16.26	0.84
$8a_1$	17.2	17.25	0.46	$0.68(8a_1)^{-1}$	17.94	0.71
				$+0.49(2b_1)^{-1}(11a_1)^{-1}(6b_1)$		
				$-0.48(1a_2)^{-1}(11a_1)^{-1}(4a_2)$		
		17.37	0.42	$0.65(8a_1)^{-1}$	18.40	0.12
				$+0.53(1a_2)^{-1}(11a_1)^{-1}(4a_2)$		
				$-0.49(2b_1)^{-1}(11a_1)^{-1}(6b_1)$		
$4b_2$	(19.6)	20.50	0.85	$0.92(4b_2)^{-1}$	21.16	0.25
					21.32	0.46
$7a_1$	(20.0)	20.53	0.82	$0.90(7a_1)^{-1}$	21.29	0.70
		21.32	0.06	$0.70(11a_1)^{-1}(1b_1)^{-1}(4a_2)$		
				$+0.39(11a_1)^{-1}(1b_1)^{-1}(6b_1)$		
($1b_1$)		20.77	0.05	$0.67(1a_2)^{-1}(2b_1)^{-1}(4a_2)$	19.7[d]	0.10
				$-0.58(1a_2)^{-2}(6b_1)$	20.5[d]	0.10
				$+0.58(2b_1)^{-2}(6b_1)$		

[a][75]. Values in parentheses are from [95]. [b][99]. [c]$(a)^{-1}(b)^{-1}(c)$ means $(a\rightarrow\infty, b\rightarrow c)$. [d]These values are read from figure 12 of [99].

3.5. Naphthalene

Naphthalene is a relatively large molecule so that the *ab initio* treatments for the excited and ionized states have been very limited [100]. We here show from our calculations [19] the assignment of the ionization spectra.

The geometry is fixed to the experimental one for the ground state [101]. The basis set consists of the [3s2p/2s] set of Huzinaga-Dunning [41], the Rydberg p_π functions (0.03477, 0.01075) on each carbon atom, and the polarization d_π functions (0.75) on each carbon atom. The number of the atomic orbitals is 146. The active spaces consist of all 58 π MO's and 44π + 56σ MO's. Total energies owing to the HF, π-SAC, and π+σ-SAC methods are -383.27598, -383.40294, and -383.54626 a.u., respectively.

The ionization potentials calculated by the SAC-CI and Koopmans' methods are compared in Table 10 with the experimental values [102]. The average deviation from the existing experimental values (7-13 eV) is 1.31 eV for the Koopmans' method, 0.21 eV for the π SAC-CI method, and 0.28 eV for the π+σ SAC-CI method. We compare the experimental spectra [102] with the theoretical one in Fig. 9. The intensity of the peak was calculated by the mono-pole approximation [80]. Although Brundle et al.

TABLE 10. Ionization potentials of naphthalene (eV)[a]

MO	Koopmans'	5π-SAC-CI	4π+5σ-SAC-CI	Exptl.[b]	
				BRK	present assignment[c]
5π a_u	8.12	8.01(-0.12)	7.68(-0.45)	8.13	
4π b_{3u}	8.86	8.57(-0.31)	8.22(-0.66)	8.88	
3π b_{2g}	10.63	10.01(0.00)	9.75(-0.26)	10.01	
2π b_{1g}	12.38	11.22(0.32)	10.94(0.04)	10.90	
29σ a_g	13.02		10.97(-0.11)	11.08	
28σ b_{3g}	13.15		11.06(-0.31)	11.37	
27σ b_{2u}	14.32		12.22(0.33)	11.89	
1π b_{3u}	14.70	12.80(0.30)	12.59(0.09)	12.50	
26σ b_{1u}	15.54		13.38[-0.1]		13.5
25σ b_{2u}	15.89		13.47[-0.3]		13.8
24σ b_{3g}	16.09		13.98[-0.2]		14.2
23σ a_g	16.85		14.47[0.0]		14.5
22σ b_{1u}	17.12		15.10[-0.9,0.3]		16.0,14.8[d]
shake-up	-		16.00[0.0]		16.0[d]
21σ a_g	18.54		16.69[0.2]		16.5
average deviation	13.1	0.21	0.28,0.22		

[a]Values in parentheses show deviations from the experimental values. [b][102]. [c]Peak maxima of the experimental spectrum of [102] are assigned using the present SAC-CI calculation. [d]For this assignment, see text.

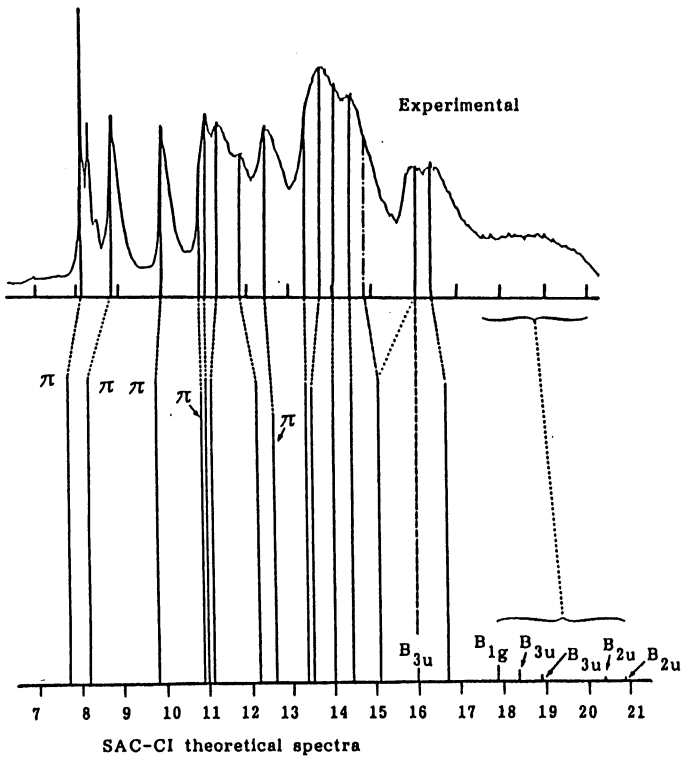

Fig. 9 Experimental (above) and theoretical (below) ionization spectra of naphthalene. The correspondence between these peaks shows the assignment. Two different assignments are given for the experimental peaks at 14.8 and 16.0 eV. See text for the details. The experimental spectrum is taken from [102].

assigned only the peaks lower than 13 eV, we have given the first assignment for the peaks in the 13-20 eV region on the basis of the SAC-CI results. The peaks from 13 eV to 15 eV in the experimental spectra consist of four or five peaks in the theoretical

one, and the peaks from 15 eV to 17 eV correspond to the two theoretical peaks. The experimental peak at 16.0 eV may be assigned either to the theoretical one at 15.1 eV or to the small shake-up peak calculated at 16.0 eV. In the latter assignment, the theoretical peak at 15.1 eV would be assigned to the peak at 14.8 eV at the shoulder of the experimental peak. In this case, the average deviation is 0.22 eV. The difficulty in the latter assignment is the smallness of the calculated intensity for the shake-up peak, though generally speaking, the intensity of the shake-up peak calculated with the mono-pole approximation for the SAC-CI results is smaller than the experimental one [22]. Further, we can explain the comparatively weak and broad experimental peak at 17.5 - 20 eV as the composite of the shake up peaks having B_{1g}, B_{3u}, and B_{2u} symmetries. These peaks borrow their intensities from the 1π, 2π and 27σ MO's, respectively.

4. CONCLUSION

The first conclusion we would like to draw from this review is that we have been able to solve essentially the famous serious problem in describing theoretically the so-called V states of conjugated molecules. Including a large amount of σ-electron correlation with the use of the relatively large basis set, we could calculate the excitation energies of these V states to within ~0.6 eV of the experimental values, in comparison with the errors of the order of 1.5 eV before this series of studies were undertaken. In the course of these studies, the SAC-CI method has been proved to be very useful for making such a large-scale calculations tractable. Otherwise, we could not have even undertaken such a calculation if we have had to use only traditional CI method. The use of the vector processors was also very helpful especially in the transformation of the AO integrals into MO ones.

We believe that the remaining errors in the vertical transition energies will be reduced in the line of this study just by using larger active space and a larger basis set. We therefore conclude that there is no intrinsic problems in the quantum chemistry of excited states. This conclusion is certainly a basis on which we are able to build up further the chemistry and physics of excited states with an interplay between theory and experiment.

The physical reason of a large σ reorganization effect in the V type excited states is well known at least conceptually[1,2,38-40]. Because these states involve ionic structures in the VB sense, the possibility of two electrons coming close is large and so the electron correlation is very important. In these states, electron correlation takes place in a relatively large space and through the polarizations of the π and σ spaces. This is why large basis set and large active space are necessary to describe it properly. (This is the reason why the previous moderate scale calculations were unable to describe these states.) The physical picture may be expressed as molecular in-out correlation as an extention of the left-right correlation

proposed for ethylene.

For the other valence excitations and Rydberg excitations, the SAC-CI results agree better (to within 0.3 eV) with the experimental values. Examples are seen in the calculations of ethylene, butadiene, and benzene. For pyridine, we have given some assignments for the excitations and ionizations, and for naphthalene, we have given the first systematic assignment of the ionization spectra. Through these and other studies carried out in this laboratory, we believe that the SAC-CI approach is a useful approach in the quantum chemistry of excited and ionized states.

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