

Cluster expansion of the wave function. Valence and Rydberg excitations and ionizations of benzene

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The SAC (symmetry-adapted cluster) expansion and the SAC-CI theory are applied to the calculations of the valence and Rydberg excitations and the ionizations of benzene. The active space consists of 80 MO's including both π and σ spaces; viz., $35\pi + 45\sigma$ for the valence excitations and ionizations and $29\pi + 51\sigma$ for the Rydberg excitations. For the lower six valence excited states, ${}^3B_{1u}(T_1)$, ${}^3E_{1u}(T_2)$, ${}^1B_{2u}(S_1)$, ${}^3B_{2u}(T_3)$, ${}^1B_{1u}(S_2)$, and ${}^1E_{1u}(S_3)$, generated from the $\pi(e_{1g}) \rightarrow \pi^*(e_{2u})$ transitions, the excitation energies are reproduced to within 0.5 eV of the experimental values with the average discrepancy being 0.34 eV. The first three states are explainable within the π electron space. For the other three states, the σ -reorganization effect is very important; viz., 0.6, 0.7, and 0.8 eV for the T_3 , S_2 , and S_3 states, respectively. The polarization d_π function also works to lower the T_3 and S_2 states by 0.3 and 0.4 eV, respectively. The total lowerings from the SDT π -CI of Hay and Shavitt to the $35\pi + 45\sigma$ SAC-CI are about 1 eV for these three states. With including the σ -reorganization effect, the diffuse nature of the S_3 state, a typical V state, decrease from $\langle x^2 \rangle = 62$ (π SAC-CI) to 41 ($\pi + \sigma$ SAC-CI) a.u., in comparison with the ground state value of 30 a.u. Accordingly, the oscillator strength changes from 0.61 (π SAC-CI) to 1.03 ($\pi + \sigma$ SAC-CI). The first systematic theoretical study is given for the Rydberg excitations including both π and σ states. With the aid of the recent experimental studies due to the MPI (multiphoton ionization) spectroscopy, the lower Rydberg excited states are almost completely identified. The SAC-CI results agree with the experimental values to within 0.3 eV for all the Rydberg states studied here. The σ -reorganization effect on the Rydberg transitions is about 0.3 eV. The SAC-CI calculation further gives satisfactory results for the outer and inner valence ionizations and their satellite peaks. The theoretical ionization spectrum well reproduces the general trends of the observed ESCA spectrum.

I. INTRODUCTION

Benzene is a key aromatic molecule in chemistry. It is probably one of the best studied molecules in the history of structural chemistry. It was also a central molecule in the π -electron theory of Hückel,¹ and in the resonance theory after Pauling.² These ideas were further developed by Goeppert-Mayer and Sklar,³ Pariser and Parr,^{4(a)} and Pople^{4(b)} as the π -electron theory of conjugated hydrocarbons. These semiempirical methods have later been developed as HAM by Lindholm and Asbrink⁵ from the density functional view point. However, *ab initio* study of the excited states of benzene has still been very limited.^{6,11-18} On the other hand, owing to a recent development in molecular spectroscopy, much information has been accumulated⁵ on the excited states of this molecule. Theoretical information is nevertheless indispensable because of the complicated nature of the excited and ionized states. A reliable theoretical study on these states is thus increasingly more important than before.

In this series of articles, we have developed a cluster-expansion-based formalism for the studies of ground and excited states of molecules. The SAC (symmetry-adapted-cluster) expansion¹⁹ is applied to a closed- or open-shell ground state, and the SAC-CI theory²⁰ to its excited states, ionized states, and electron-attached states. The details of

the SAC and SAC-CI theory and the algorithm of calculations have already been reported.¹⁹⁻²⁴ The SAC theory describes the electron correlation of the molecular ground state in an efficient way by considering simultaneous collisions of electrons in the unlinked term. It is size extensive,²⁵ a property probably necessary to describe a large system such as benzene. The SAC-CI theory effectively describes the electron correlation of the excited and ionized states, based on an approximate transferability of the dynamic correlation between ground and excited states. The orthogonality and Hamiltonian orthogonality are satisfied between the SAC and the SAC-CI solutions. This property is required for the wave functions of the ground and excited states.

Previously, we studied ethylene,^{22(a)} formaldehyde,^{22(b)} and five-membered ring compounds, pyrrole, furan, and cyclopentadiene²³ on their excited and ionized states. Here, we study the valence and Rydberg excited states and the ionized states of benzene. The valence $\pi \rightarrow \pi^*$ excitations from e_{1g} to e_{2u} MO give six different states; three singlets ${}^1B_{2u}$, ${}^1B_{1u}$, ${}^1E_{1u}$ and three triplets ${}^3B_{1u}$, ${}^3E_{1u}$, ${}^3B_{2u}$, which are referred to in the present paper as S_1 , S_2 , S_3 and T_1 , T_2 , T_3 , respectively. The $\pi \rightarrow \pi^*$ transitions from a_{2u} to e_{2u} MO and from e_{1g} to b_{2g} MO give ${}^1E_{2g}$ and ${}^3E_{2g}$ states, which are called S_4 and T_4 states, respectively.

Now what is the present stage of theoretical studies on the valence excited states of benzene? Figure 1 is taken from the recent review article on benzene by Ohno and Noro.⁶ *Ab*

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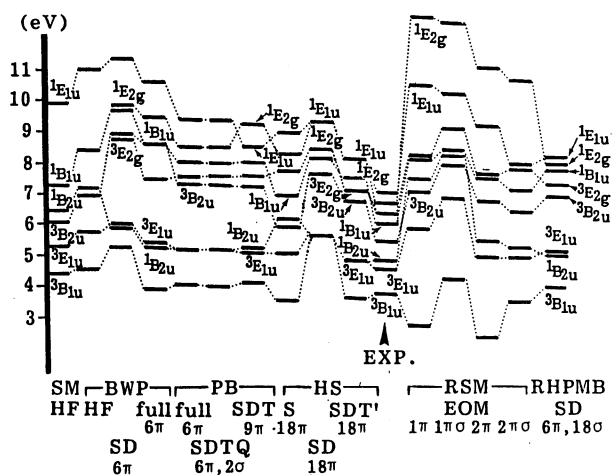


FIG. 1. *Ab initio* valence excited states of benzene reported so far. SM: Ref. 11, BWP: Ref. 12, PB: Ref. 13, HS: Ref. 14, RSM: Ref. 15, RHPMB: Ref. 16. This figure is taken from Ref. 6 with a small modification.

initio theoretical results so far reported for the valence excited states are compared with the experimental values.⁷⁻¹⁰ The results shown on the left-hand side of the experimental level are calculated by the *ab initio* Hartree-Fock and CI methods mostly within π MO's.¹¹⁻¹⁴ The first four results on the right-hand side are due to EOM (equation of motion) method,¹⁵ and the RHPMB result is due to the perturbation theory.¹⁶ Ohno and Noro concluded that the SDT π -CI by Hay and Shavitt¹⁴ is the best among them. This result is referred to in the present paper as HS. Other than that cited in Fig. 1, Tantardini *et al.*¹⁷ reported the π -space *ab initio* valence-bond calculation, but the results were poorer than that of HS. Osamura¹⁸ studied theoretically the geometry of the ground and excited S_1 states by MC-SCF method. One finds from Fig. 1 that only the lower three states, T_1 , T_2 , and S_1 , are described reasonably by the *ab initio* π theory if it includes more than triple excitations relative to the Hartree-Fock configuration. For the remaining five states, large discrepancies from the experimental results are seen. Even HS gave the S_2 , S_3 , and T_3 states higher by ~ 1.4 eV than the experimental values. The S_4 and T_4 states were calculated to be higher than the experimental values by 1.1 and 0.7 eV, respectively. An average discrepancy of HS from the experimental results was 0.8 eV. Since HS considered the CI only within π space, they attributed these errors mainly to the frozen σ space and partially to the basis set limitation. HS further showed that the S_4 and T_4 states had a multiple excitation nature.

About the S_4 and T_4 states, some different assignments have been reported.^{10,26,27} Recently Nakashima *et al.*²⁸ measured S_4 at 7.8 eV and T_4 at 7.2–7.7 eV by the nanosecond laser flash photolysis. Whetten *et al.*³¹ reported this S_4 state at 7.54 eV using the MPI (multiphoton ionization) spectroscopy. These values are higher in energy than the experimental values cited in Fig. 1 (7.20 eV for S_4 and 6.53 eV for T_4).¹⁰ These experimental data may suggest that the treatment of HS¹⁴ for the S_4 and T_4 states turns out to be relatively better than previously supposed.

No systematic calculation seems to have been performed so far for the Rydberg excitations of benzene.^{29,30} Only HS reported a reliable result for the first few peaks of π

nature. Since almost all the Rydberg states due to the excitations from the HO (highest occupied) π MO have been observed recently by MPI spectroscopy,³¹⁻³⁶ a systematic theoretical assignment including both π and σ states is certainly very important.

For the ionization spectra of benzene, von Niessen, Cederbaum *et al.* reported theoretical spectra for the outer and inner valence ionizations.³⁷ Their Green function method seems to be useful to investigate these properties.³⁸ About the outer valence ionization potential, Hirao and Kato³⁹ reported SAC-CI calculations with a relative small basis set.

In this paper, we systematically study the valence and Rydberg excitations and ionizations of benzene by the SAC and SAC-CI method, considering both π and σ spaces. In the next section, we summarize calculational details. In Sec. III, we give the results and discussions for the ground state, valence and Rydberg excited states, and ionized states. The conclusion of the present study is given in the last section. A preliminary result has been presented elsewhere.⁴⁰

II. CALCULATIONAL DETAILS

The ground state of benzene is calculated by the SAC theory.¹⁹ The SAC-CI theory²⁰ is used for the calculations of the singlet and triplet excited states and ionized states. We use the slightly modified version of the SAC85 program.²⁴ As reference orbitals, we use Hartree-Fock SCF MO's of the ground state for all the states studied here. They are calculated by the HONDOG program.⁴¹

The geometry of the ground state of benzene was determined by Raman spectroscopy.⁴² This geometry is used not only for the ground state, but also for all the excited and ionized states, so that the present results are strictly vertical in nature. The molecule is laid in the yz plane with the principal axis collinear to the x axis.

We use the following basis sets:

Basis set 0: $[4s2p/2s]$ set of Huzinaga-Dunning⁴³ plus Rydberg p_π functions (0.03477, 0.01075) on each carbon atom.
Basis set 1: basis set 0 plus polarization d_π function (0.75) each carbon atom.

Basis set 2: basis set 1 plus polarization p_π function (1.0) on each hydrogen atom.

Basis set 3: basis set 0 plus Rydberg s (0.0437, 0.0184), p (0.0399, 0.0168), and d (0.0285, 0.0120) functions on the center of the molecule.

Basis set 0 is the one used by Hay and Shavitt.¹⁴ Basis set 1 and 2 are designed for the valence state calculation and basis set 3 for the Rydberg state calculation. The exponents of the polarization function and the Rydberg orbitals are taken from Dunning and Hay.⁴⁴ In basis set 3, the exponent is split into two by multiplying the factors 0.8 and 1.9 as recommended by these authors. In Table I, we show the number of the π and σ MO's obtained with these basis sets.

In the SAC and SAC-CI calculations, all π -MO's are included in the active space. The calculations including both π and σ spaces are done for basis sets 1 and 3. We included as the σ space almost all valence and Rydberg MO's. The number of active MO's in the $\pi + \sigma$ calculations is 80. Within the $\pi + \sigma$ space, the valence $\pi \rightarrow \pi^*$ excited states are computed with basis set 1, and the Rydberg states and the valence $\sigma \rightarrow \pi^*$ excited states are calculated with basis set 3.

TABLE I. Number of π and σ MO's for basis set 0~3.

Basis set	Number of MO's		
	Total	π space	σ space
0	83	23	60
1	95	35	60
2	101	41	60
3	102	29	73

To diminish the size of calculations, we select the linked operators by a perturbation selection technique.^{21(a)} Main reference configurations are those which have large coefficients (> 0.1) in the SE-CI. For the excitations for which doubly excited configurations are expected to make an important contribution, some such configurations are included in the main reference space. We use different thresholds for the configurations within the π space and for the others arising in the $\pi + \sigma$ calculations. For the π space the thresholds λ_g and λ_e are both 1×10^{-5} a.u. in all of the present calculations. For the configurations arising additionally in the $\pi + \sigma$ calculations, we adopt the thresholds $8 \times 10^{-5} - 3 \times 10^{-4}$ a.u. Table II shows the dimensions of the SAC and SAC-CI calculations for the valence excitations, Rydberg excitations, and ionizations, respectively. By virtue of the SAC and SAC-CI formalism, the dimension of the calculation is small in comparison with that of the CI theory of a comparable accuracy. In our case, the dimension is of the order of the singles plus selected doubles configurations. In these tables, the dimension of the π -CI by HS is also cited. Their calculations include single and double excitations within 23π MO's and triple excitations within 18π MO's, and have almost the same quality as our π SAC-CI with the same basis set. The dimensions of the SDT-CI of HS within 23π MO's are two or three times as large as those of the SAC and SAC-CI within the 35π MO's. This difference should become much larger in the $\pi + \sigma$ calculations. For this merit, we have been able to perform the present calculations including $80\pi + \sigma$ active MO's.

In the SAC theory the effect of simultaneous binary collisions (four-body collisions) of electrons is dealt with in the form of the unlinked term. We included there all the doubly excitation operators whose coefficients in the SD-CI are larger than 1×10^{-2} . In the SAC-CI theory, the transferable part of the electron correlation between ground and excited states is expressed by the unlinked term. This term is expressed as the sum of double excitations from main reference configurations of the state. These double excitations are those whose coefficients in the ground state SD-CI are larger than 1×10^{-3} , and the main reference configurations are selected as those whose coefficients in the SD-CI are larger than 1×10^{-1} .

A remark may be necessary for a transformation of electron repulsion integrals. Since the size of the basis set is relatively large, the transformation code involved in LINK901 due to Lathan⁴⁵ is inappropriate. We therefore adopt the algorithm of Yoshimine⁴⁶ for the integral sorting and of Bender⁴⁷ for the main transformation.

TABLE II. Dimensions of the SAC and SAC-CI calculations of benzene.

State	SDT-CI (HS ^a)		SAC and SAC-CI	
	D_{6h}	D_{2h}	$23\pi[\text{SD}], 18\pi[\text{T}]$	35π $35\pi + 45\sigma$
(a) Valence excitations				
Ground ${}^1A_{1g}$	1A_g		903	400 1089
Excited				
${}^1E_{2g}$	1A_g		1766	610 2592
${}^1B_{1u}, {}^1E_{1u}$	${}^1B_{2u}$		889,1758	645 2965
${}^1B_{2u}$	${}^1B_{3u}$		872	691 3054
${}^3E_{2g}$	3A_g		2628	828 3813
${}^3B_{1u}, {}^3E_{1u}$	${}^3B_{2u}$		1316,2636	633 2567
${}^3B_{2u}$	${}^3B_{3u}$		1323	574 2289
(b) Rydberg excitations				
Ground ${}^1A_{1g}$	1A_g		903	279 1251
Excited				
${}^1A_{1g}, {}^1E_{2g}$	1A_g		903,1766	426 2436
${}^1A_{1u}, {}^1E_{2u}$	1A_u			3068
${}^1A_{2g}$	${}^1B_{1g}$		863	406 1805
${}^1A_{2u}$	${}^1B_{1u}$			2620
${}^1B_{1g}, {}^1E_{1g}$	${}^1B_{2g}$			2606
${}^1B_{1u}, {}^1E_{1u}$	${}^1B_{2u}$		889,1758	572 2863
${}^1B_{2g}$	${}^1B_{3g}$			1257
${}^1B_{2u}$	${}^1B_{3u}$		872	563 1522
${}^3A_{1g}, {}^3E_{2g}$	3A_g		1295,2628	825 3446
${}^3A_{1u}, {}^3E_{2u}$	3A_u			3565
${}^3A_{2g}$	${}^3B_{1g}$		1330	761 2117
${}^3A_{2u}$	${}^3B_{1u}$			3538
${}^3B_{1g}, {}^3E_{1g}$	${}^3B_{2g}$			3006
${}^3B_{1u}, {}^3E_{1u}$	${}^3B_{2u}$		1316,2636	690 2911
${}^3B_{2g}$	${}^3B_{3g}$			1464
${}^3B_{2u}$	${}^3B_{3u}$		1323	684 1743
(c) Ionizations				
Ground ${}^1A_{1g}$	1A_g		903	1089
Ionized				
${}^2A_{1g}, {}^2E_{2g}$	2A_g			985
${}^2A_{1u}, {}^2E_{2u}$	2A_u			233
${}^2A_{2g}$	${}^2B_{1g}$			717
${}^2A_{2u}$	${}^2B_{1u}$			263
${}^2B_{1g}, {}^2E_{1g}$	${}^2B_{2g}$			245
${}^2B_{1u}, {}^2E_{1u}$	${}^2B_{2u}$			919
${}^2B_{2g}$	${}^2B_{3g}$			247
${}^2B_{2u}$	${}^2B_{3u}$			917

^a Reference 14.

III. RESULTS AND DISCUSSIONS

A. Ground state

The SCF orbital energy sequence obtained with basis set 1 is shown in Table III. This table involves only valence occupied orbitals and lower virtual orbitals up to the π_4^* MO. The total energy of the ground state of benzene is shown in Table IV, which includes Hartree-Fock, SD-CI, and SAC energies. The polarization d_π function placed on each carbon (included in basis sets 2 and 3) considerably lowers the energy. The effect of the p_π function on each hydrogen is

TABLE III. SCF result for the ground state of benzene with basis set 1.

MO	Orbital energy (a.u.)	
$2a_{1g}$	-1.152 119	
$2e_{1u}$	-1.016 527	
$2e_{2g}$	-0.824 849	
$3a_{1g}$	-0.712 707	
$2b_{1u}$	-0.643 721	
$1b_{2u}$	-0.618 625	
$3e_{1u}$	-0.588 175	
$1a_{2u}$	-0.504 711	π_1
$3e_{2g}$	-0.490 896	
$1e_{1g}$	-0.340 454	π_2
$2a_{2u}$	0.027 766	R_π
$2e_{1g}$	0.035 767	R_π
$1e_{2u}$	0.045 544	R_π
$2e_{2u}$	0.109 240	π_3^*
$3a_{2u}$	0.135 140	R_π
$3e_{1g}$	0.147 029	R_π
$1b_{2g}$	0.172 470	R_π
$3e_{2u}$	0.191 495	R_π
$4e_{2g}$	0.277 875	
$4a_{1g}$	0.299 943	
$4e_{1u}$	0.323 316	
$3b_{1u}$	0.329 565	
$2b_{2g}$	0.342 481	π_4^*

small. The Rydberg orbitals have almost nothing to do with the ground state electronic structure, as expected. The $\pi + \sigma$ SAC and SAC-CI calculations are done for basis sets 1 and 3. The correlation energy is only $-0.087 71$ a.u. by the 35π SAC calculation, but $-0.197 64$ a.u., more than twice, by the $35\pi + 45\sigma$ SAC calculation. The same tendency is seen for basis set 3. The second moment calculated with the SAC wave function is 31 a.u. for $\langle x^2 \rangle$ and 215 a.u. for $\langle y^2 \rangle$ and $\langle z^2 \rangle$. The experimental values are 28 ± 6 and 218 ± 5 a.u., respectively.⁴⁸ The agreement between theory and experiment is excellent.

B. Valence $\pi \rightarrow \pi^*$ excited states

Table V shows the energy and the oscillator strength for the $\pi \rightarrow \pi^*$ valence excitations of benzene. The single excitations from the highest occupied π_2 MO (e_{1g}) to the unoccupied π_3^* MO (e_{2u}) give six excited states, $S_1 \sim S_3$ and $T_1 \sim T_3$. For the next higher states, S_4 and T_4 , a considerable mixing of multiexcitations is reported by Hay and Shavitt.¹⁴ We therefore restrict ourselves to study only the lower six states,

$S_1 \sim S_3$ and $T_1 \sim T_3$, since the SAC-CI theory is more easily applied to these states than to the S_4 and T_4 states. In Table V, we refer the SDT π -CI results of HS obtained with basis set 0. In the SAC-CI calculation, we use basis set 1 and the calculations are performed in both π and $\pi + \sigma$ spaces. The active space consists of 35π MO's and $35\pi + 45\sigma$ MO's, respectively. Experimental results are taken from EELS (electron energy loss spectroscopy) by Lassette *et al.*⁸ and Doering,⁹ and the band maxima are compared with the theoretical results. A schematic description of the present result is given in Fig. 2. The SAC-CI theoretical excitation spectrum is compared with the experimental spectrum of Doering in Fig. 3. It includes not only the valence excitations but also some Rydberg excitations.

First we discuss the lowest three states S_1 , T_1 , and T_2 . The excitation energies of these states calculated by the present theory are larger than the experimental value by 0.35, 0.11, and 0.27 eV, respectively. As seen from Fig. 2 and Table V, these states are reasonably well describable within the π -electron model. The *ab initio* π -CI calculations of Buenker, Whitten, and Petke (BWP),¹² Peyerimhoff and Buenker (PB),¹³ and HS¹⁴ have also reproduced these states reasonably well, as seen in Fig. 1, when more than triple excitations are included in the calculations. As discussed by Iwata and Freed,⁴⁹ these three states have covalent structure in the minimum basis set VB (valence bond) description. Therefore, the correlation energy owing to the σ core readjustment is considered to be approximately the same between the ground and these excited states. Since our $\pi + \sigma$ calculation includes all the terms involved in the π space calculation, the differences between our π space and $\pi + \sigma$ space calculations shown in Table V are directly attributed to the effect of the σ electron participation. The small differences in these states support the above explanation based on the VB theory. In Fig. 4, we display the contour maps of the density differences due to the singlet excitations. These maps exhibit the contours on the π plane including two opposite C-H bonds of benzene, and perpendicular to the molecular σ plane. We show as (a), (b), (c), and (d) the differences in

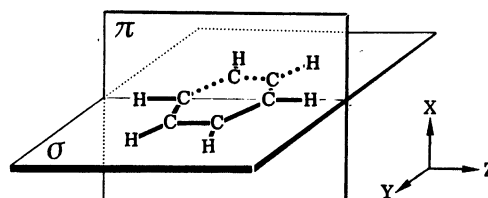


TABLE IV. Total energy of the ground state of benzene (a.u.).

Basis set	Total energy						
	Hartree-Fock energy	π space			$\pi + \sigma$ space		
		Active space	SD-CI	SAC	Active space	SD-CI	SAC
0	-230.641 304	23π	-230.720 40	-230.724 97			
1	-230.660 466	35π	-230.744 34	-230.748 18	$35\pi + 45\sigma$	-230.852 15	-230.858 11
2	-230.663 113	41π	-230.746 06	-230.749 89			
3	-230.642 480	29π	-230.721 00	-230.725 55	$29\pi + 51\sigma$	-230.834 01	-230.838 82

TABLE V. The valence $\pi_2 \rightarrow \pi_3^*$ excitation energy of benzene.

State	Excitation energy (eV)						Oscillator strength		
	SDT-CI (HS ^a)		SAC-CI		Exptl.	Oscillator strength		Expt.	
	23 π [SD],18 π [T](Δ^b)	35 π (Δ)	35 π + 45 σ (Δ)	35 π		35 π + 45 σ			
1 ¹ B _{2u} (S ₁)	5.00 (0.10)	5.25 (0.35)	5.25 (0.35)	4.90 ^c	0.0	0.0			
1 ¹ B _{1u} (S ₂)	7.64 (1.44)	7.31 (1.11)	6.60 (0.40)	6.20 ^c	0.0	0.0			
1 ¹ E _{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 ^d (y,z)		
1 ³ B _{1u} (T ₁)	3.83 (–0.12)	3.80 (–0.15)	4.06 (0.11)	3.95 ^e					
1 ³ E _{1u} (T ₂)	4.98 (0.23)	5.05 (0.30)	5.02 (0.27)	4.75 ^e					
1 ³ B _{2u} (T ₃)	7.00 (1.40)	6.65 (1.05)	6.02 (0.42)	5.60 ^e					

^a Reference 14.^b Δ shows the difference from the experimental value.^c Reference 8.^d References 58 and 59.^e Reference 9.

the π SAC-CI, in the π component of the $\pi + \sigma$ SAC-CI, in the σ component of the $\pi + \sigma$ SAC-CI, and in the $\pi + \sigma$ SAC-CI, respectively. For the transition S₁ under consideration, the map (a) owing to the π SAC-CI and (d) owing to the $\pi + \sigma$ SAC-CI are similar except for the region just along the C–H bonds, since of course the density in this region is described only by the σ electrons. The same is true for the T₁ and T₂ transitions. Table VI shows the electronic part of the second moment calculated by the present theory. Benzene is laid on the yz plane, and the z axis includes the two C–H bonds. $\langle x^2 \rangle$ represents an out-of-plane extension. We see that the sizes of the electron clouds of the S₁, T₁, and T₂ states are almost the same as that of the ground state. Namely, these states are certainly valence in nature.

Second we discuss the T₃ and S₂ states. For these states, the π -CI results of HS differ from the experimental values by 1.40 and 1.44 eV, respectively. Within the π space, our results are improved by 0.35 and 0.33 eV, respectively, from

the results of HS. The main difference between these two π calculations is an inclusion of the d_π polarization function on each carbon atom in the present calculation. The polarization function thus seems to be important for the T₃ and S₂ states. To further confirm this point, we carried out the π SAC-CI calculations using several basis sets. Table VII shows the result. Basis set 0 is common to that of HS. The results cited in this table are due to the configuration selection in which low energy doubly excited configurations are included in a reference group. Then, for basis set 1, the calcu-

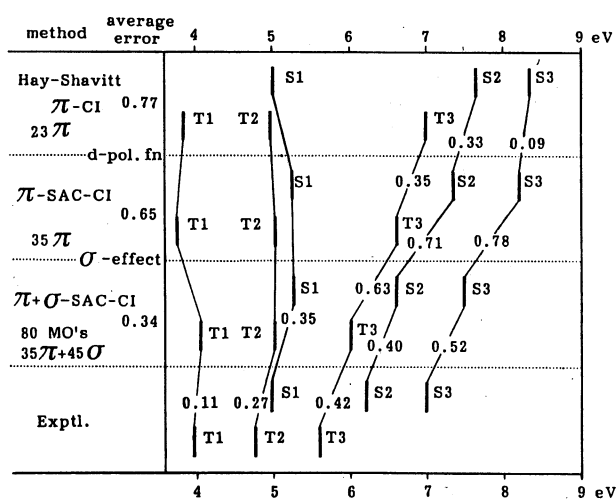


FIG. 2. Schematic summary of the SAC-CI results for the valence $\pi \rightarrow \pi^*$ excitations of benzene. The results of Hay–Shavitt are from Ref. 14. The experimental results are taken from Ref. 8 for singlet excitations and from Ref. 9 for triplet ones. The values shows the differences.

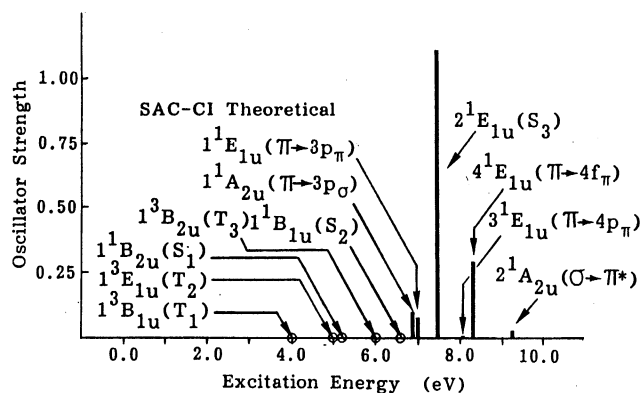
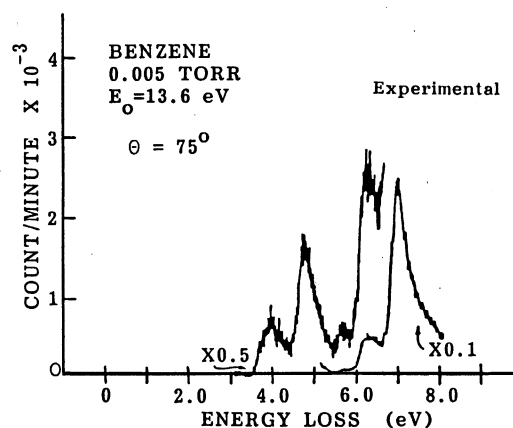


FIG. 3. Experimental (above) and theoretical (below) excitation spectra of benzene. The experimental results are taken from Ref. 9.

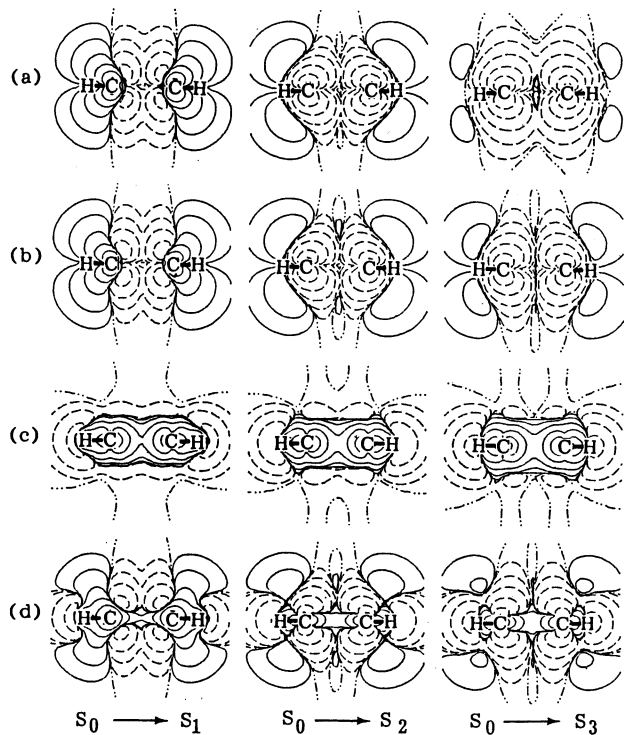


FIG. 4. Contour maps of the density differences due to the singlet excitations. These maps exhibit the contours on the plane including two opposite C-H bonds of benzene and perpendicular to the molecular plane. Maps for (a) π SAC-CI, (b) π space in $\pi + \sigma$ SAC-CI, (c) σ space in $\pi + \sigma$ SAC-CI, (d) $\pi + \sigma$ SAC-CI are shown. The real and broken lines correspond to an increase and decrease, respectively, in the electron density with the contour values of 0.0, $\pm 1 \times 10^{-7}$, $\pm 1 \times 10^{-6}$, $\pm 1 \times 10^{-5}$, $\pm 1 \times 10^{-4}$, $\pm 1 \times 10^{-3}$, $\pm 1 \times 10^{-2}$, $\pm 1 \times 10^{-1}$ a.u.

lational quality is slightly better than that given in Table V. Comparing the SAC-CI results with basis sets 0 and 1, we see that the effect of the d_π polarization function is 0.48 and 0.39 eV for the T_3 and S_2 states, respectively. For the other states, the effects are small. From the calculation using basis set 2, we see that the effect of the polarization p_π function on each hydrogen atom is negligibly small. This is the reason why we

TABLE VI. The electronic part of the second moment of the valence excited states of benzene (a.u.).

State	SAC and SAC-CI					
	35 π			35 π + 45 σ		
	$\langle x^2 \rangle^a$	$\langle y^2 \rangle$	$\langle z^2 \rangle$	$\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle z^2 \rangle$
S_0^b	30 ^b	215 ^b	215 ^b	31 ^b	215 ^b	215 ^b
S_1	31	216	216	31	216	216
S_2	34	219	219	33	217	217
S_3	62	234	248	41	220	225
T_1	30	216	216	31	216	216
T_2	31	216	216	31	216	216
T_3	32	217	217	32	217	217

^a X axis is perpendicular to the molecular plane.

^b Exptl. $\langle x^2 \rangle = 28 \pm 6$, $\langle y^2 \rangle = \langle z^2 \rangle = 218 \pm 5$ (Ref. 48).

TABLE VII. Basis set dependence of the valence excitation energy of benzene within π space (eV).

State	SDT-CI (HS ^a) Basis set 0 23 π [SD], 18 π [T]	SAC-CI			Expt.
		Basis set 0 23 π	Basis set 1 35 π	Basis set 2 41 π	
S_1	5.00	5.19	5.16	5.14	4.90 ^b
S_2	7.64	7.66	7.27	7.26	6.20 ^b
S_3	8.34	8.30	8.21	8.20	6.95 ^b
T_1	3.83	3.66	3.75	3.72	3.95 ^c
T_2	4.98	5.08	4.95	4.93	4.75 ^c
T_3	7.00	7.09	6.61	6.60	5.60 ^c

^a Reference 14.

^b Reference 8.

^c Reference 9.

adopt basis set 1 as the basis for the calculation of the valence excited states. Table VII further shows that the SAC-CI results for basis set 0 is very similar to the SDT-CI results of HS using the same basis.

The effect of the σ -electron reorganization to the T_3 and S_2 states is very large. It is estimated from Table V to be as large as 0.63 and 0.71 eV, respectively. Adding this effect to the effect of the polarization function, we obtain an improvement from the result of HS as large as 0.98 eV for the T_3 state and 1.04 eV for the S_2 state. As a result the SAC-CI theory reproduces the experimental values to within 0.4 eV for these two states. This situation is clearly seen in Fig. 2.

We examine the reorganization of the σ -electron space following to the $\pi \rightarrow \pi^*$, S_2 excitation. Contrary to the lowest three excited states previously discussed, these two states belong to the so-called V state, which is described only with ionic structures in the simple VB theory.^{49,50} The π -CI treatment is not adequate for the description of the V state, because the ionic structure makes the interaction between the π and σ space large in comparison with that in the ground-state covalent structure. This interaction is adequately described by considering the interaction of the electron correlations between the π and σ spaces. Physically, the σ electron dynamic shielding effect improves the description of the V state,^{51,52} and there the $\sigma \rightarrow \sigma^*$ excitation makes an important contribution.⁴⁹⁻⁵³ Referring to the density difference maps shown in Fig. 4, we notice to some characteristics. One is in the maps (a) and (b), the electron density of the π space decreases just on the carbon atom. Second is a large increase in the (c) map, the σ -reorganization map, just within the benzene ring. This corresponds to the ionic structure of the V state. Generally speaking, the σ -reorganization effect can be divided into two kinds. One is the reorganization of σ space itself. Another is the back effect into the π space owing to the σ space readjustment. For the $S_0 \rightarrow S_2$ transition, the changes in the maps (a) and (b), both in the π space in π SAC-CI and $\pi + \sigma$ SAC-CI, are almost the same, showing that the σ -reorganization effects in these states are mainly due to the reorganization of the σ space itself, with the back effect to the π space being small. Similar feature has also been observed for the T_3 transition.

Next we discuss the S_3 state. This state is optically allowed and considered to be a typical V state.⁵⁰ For the V state, especially for that of ethylene, many theoretical investigations have been reported.^{49–57} Through such studies, two common aspects have been pointed out. One is a large dynamic screening effect due to the σ electrons and the other is a shrink of the electron density distribution with including the σ -electron correlation effect. Since benzene is a larger molecule, the σ -electron dynamic effect is expected to occur more easily than ethylene. Actually, as seen from Table V, the σ -reorganization effect for the S_3 state is as large as 0.78 eV, though the effect of the d_π polarization function is very small (0.09 eV). The present SAC-CI calculation improves the energy of this state by 0.87 eV from the π -CI calculation of HS, and the remaining discrepancy from the experimental value is 0.52 eV.

The description of the wave function of the S_3 state is considerably modified by the σ -reorganization effect. The weight of the mixing of the Rydberg $\pi \rightarrow \pi^*$ transition is altered from $\sim 60\%$ in the π SAC-CI to $\sim 20\%$ in the $\pi + \sigma$ SAC-CI. This state is optically allowed and the oscillator strength is calculated to be 0.61 within the π -space calculation and 1.08 with the $\pi + \sigma$ space calculation. This change in the oscillator strength is consistent with the shrink of the π electron of S_3 due to the inclusion of the σ -reorganization effect. The experimental oscillator strength is reported in the range of 0.60–1.25.^{58,59}

Let us consider the second moment property of the S_3 state in more detail. From Table VI we see that the second moment in $\pi(x)$ direction is calculated to be 62 a.u. at the π SAC-CI level of calculation, but reduces to 41 a.u. at the $\pi + \sigma$ SAC-CI calculation. The values in the σ plane ($\langle y^2 \rangle$ and $\langle z^2 \rangle$) also show a similar tendency. In the π SAC-CI calculation, the extension of the electron cloud of the S_3 state is almost that of the Rydberg state (compare with the values given in Tables IX and X for the Rydberg states), but in the $\pi + \sigma$ calculation, the extension is essentially that of the valence state. This behavior seems to be general for the V states of the conjugated hydrocarbons. From the π -electron calculation of ethylene, Huzinaga⁵⁴ reported that the optimum π^* orbital of the V state was very diffuse. Tanaka⁵¹ found the shrink of the π^* orbital when the σ readjustment was considered. Due to the more complete calculations of the excited states of ethylene,^{53,55–57} including the previous SAC-CI calculation,^{22(a)} the V state of ethylene is essentially valence in nature, though the extension of the electron cloud is larger than that of the typical valence state. For benzene, HS¹⁴ reported within π -CI an interesting observation that the expectation value $\langle \pi^* | x^2 | \pi^* \rangle$ of the π^* natural orbital increased with increasing inclusion of the electron correlation: it was 31 bohr² in SD-CI and 38 bohr² in SDT-CI. In the present π SAC-CI, this value is 32 bohr². However, when the σ -reorganization effect is included, this value changes to 14 bohr², showing that the electron cloud of the π^* natural orbital shrinks considerably. We conclude that the S_3 state, the typical V state, of benzene is essentially valence in nature.

We next investigate the contour maps of the electron density difference of the S_3 state given in Fig. 4. A large decrease in the π region of the carbon in the (a) map and a

significant increase of the σ electron density in the (c) map are similar to the behaviors in the previous V states, S_2 and T_3 . A very diffuse increase in the outer region of the molecule seen in the (a) map is consistent with the very large value of the second moment $\langle x^2 \rangle$ in the π SAC-CI. The σ -electron reorganization in the (c) map is very interesting. The electron cloud around the hydrogen atoms is brought into the inside of the hexagon; viz., the hydrogen nuclei become somewhat bare after reorganization. This σ reorganization considerably affects the π space, so that the π -electron density maps given in (a) and (b) are considerably different. Because of the bare protons seen by the π electrons after the shrink of the σ electron density [map(c)], the increase of the π density becomes more significant and the density itself certainly shrinks in map (b). We note that only in this S_3 state, the (a) and (b) maps differ significantly. A similar behavior in ethylene is called left–right correlation. We may call this behavior in benzene as molecular in–out correlation.

C. Valence $\sigma \rightarrow \pi^*$ excited states

In benzene, the HO σ -MO lies relatively in a higher energy region. It is the next HOMO and is the degenerate e_{2g} MO which lies about 3 eV below the HO π (e_{1g}) MO. This MO lies between the two occupied π (e_{1g} and a_{2u}) MO's. (For more details, see Tables III and XI.) Many excited states originating from the excitations from this σ MO are expected in the relatively lower energy region. In Table VIII, the SAC-CI results are shown for the $\sigma(e_{2g}) \rightarrow \pi^*(e_{2u})$ transitions about the excitation energy, electronic part of the second moment, and oscillator strength. We used basis set 3 for the calculation. Three points are remarkable for these states.

- (i) The second moment is almost the same as that of the ground state. This clearly shows that these states are valence in nature.
- (ii) The singlet–triplet separation is about 0.2eV for all the states.
- (iii) The $^1A_{2u}$ state is optically allowed and the calculated oscillator strength is 0.018, which is relatively weak as a valence excitation. This peak is down in Fig. 3.

Peyerimhoff and Buenker¹³ have theoretically studied these excitations. Their treatment was SDTQ-CI within 6 π plus 2 σ MO's. Their results are higher by ~ 1.0 eV than ours. Experimentally, the Rydberg excitation $\sigma \rightarrow 3p_\sigma$, which is not calculated in this study, is reported in this region.^{36(a),60} Many valence and Rydberg excitations appear to exist and overlap about the 9 eV region.

D. Rydberg excited states

The calculated Rydberg excitation energies are collected in Tables IX and X for singlet and triplet excitations, respectively. We consider the Rydberg excitations in which an electron is removed from the HO π MO. The experimental values are taken mainly from the adiabatic values obtained by the MPI spectroscopy.^{31–36} The calculations are done with basis set 3, which give many Rydberg MO's in the virtual region of the active space. We give the SAC-CI results within $\pi + \sigma$ space and within π space alone. The value

TABLE VIII. The valence $\sigma \rightarrow \pi^*$ excited states of benzene.

Orbital picture	State	SAC-CI $29\pi + 51\sigma$ ΔE (eV)	Electronic part of second moment (a.u.)			Oscillator strength
			$\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle z^2 \rangle$	
Ground	1^1A_{1g}	0.0	31	216	216	
Excited						
$\sigma \rightarrow \pi^*$	2^1A_{1u}	9.02	34	215	215	0.0
	2^1A_{2u}	9.27	34	215	215	0.018 x
	2^1E_{2u}	9.11	34	215	215	0.0
$\sigma \rightarrow \pi^*$	2^3A_{1u}	8.83	34	217	214	
	2^3A_{2u}	9.05	34	215	214	
	2^3E_{2u}	8.92	34	213	217	

in parentheses indicates the effect of the σ space. Hay and Shavitt¹⁴ reported some Rydberg states within π -CI with basis set 0. Their results are cited to compare with the SAC-CI results. The electronic part of the second moment and the oscillator strength are also given in the same tables. Some optically allowed transitions are displayed in Fig. 3 to compare with the experimental spectra by Doering.⁹ Figure 5 gives a schematic comparison between the experimental and

theoretical singlet Rydberg excitation energies. For triplet, no experimental data have been reported, as far as we know, so that in Table X we cited the singlet excitation energies as experimental values because of the expected smallness of the singlet triplet separation. In this section, we discuss the Rydberg excitations, in the order of $\pi \rightarrow ns$, $\pi \rightarrow np$, $\pi \rightarrow nd$, and $\pi \rightarrow nf$. This is probably the first systematic calculation of the Rydberg states of benzene including both π and σ spaces.

TABLE IX. The singlet Rydberg excited states of benzene.

Orbital picture	State	Excitation energy (eV)					Electronic part of second moment (a.u.)			Oscillator strength SAC-CI
		Expt.	SAC-CI		SDT-CI (HS ^a)		$\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle z^2 \rangle$	
			$29\pi + 51\sigma$	(Δ^b)	29π	$23\pi[\text{SD}], 18\pi[\text{T}]$				
Ground	1^1A_{1g}	0.0	0.0		0.0	0.0	31	216	216	
Excited										
$\pi \rightarrow 3s$	1^1E_{1g}	6.33 ^c	6.31				52	236	235	0.0
$\pi \rightarrow 3p_\sigma$	1^1A_{1u}		7.10				47	246	245	0.0
	1^1A_{2u}	6.93 ^d	6.88				46	245	244	0.071 x
	1^1E_{2u}	6.95 ^d	6.99				46	245	245	0.0
$\pi \rightarrow 3p_\pi$	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							
$\pi \rightarrow 3d_\sigma$	1^1B_{1g}	7.46 ^h	7.42				47	263	269	0.0
	1^1B_{2g}	7.46 ^h	7.42				47	264	268	0.0
	2^1E_{1g}		7.44				50	250	278	0.0
$\pi \rightarrow 3d_\delta$	3^1E_{1g}	7.54 ^c	7.35				69	254	231	0.0
$\pi \rightarrow 3d_\pi$	2^1A_{1g}	7.80 ^e	7.64	(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	(0.26)	7.90	7.90	98	238	277	0.0
$\pi \rightarrow 4s$	4^1E_{1g}	7.95 ^c	7.90				113	250	248	0.0
$\pi \rightarrow 4p_\pi$	2^1E_{1u}	8.37 ^f	8.13	(0.35)	8.48	9.25	124	239	279	0.004 (y,z)
$\pi \rightarrow 4d_\pi$	3^1A_{1g}	8.44 ^c	8.53	(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 ^c	8.52	(0.26)	8.78	9.56	126	306	280	0.0
$\pi 4f_\pi$	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	(0.59)	8.92	8.74	87	273	241	0.293 (y,z)

^a Reference 14.

^b Δ shows the contribution of the σ reorganization.

^c Reference 32.

^d Reference 34.

^e Reference 36.

^f Reference 29.

^g Only this value is calculated with basis set 1. See the text.

^h These values were estimated from $\pi \rightarrow 4d_\sigma$. See the text.

ⁱ Reference 70.

TABLE X. The triplet Rydberg excited states of benzene.

Orbital picture	State	Expt. (singlet)	Excitation energy (eV)			Electronic part of second moment (a.u.)			
			SAC-CI			SDT-CI (HS ^a) 23 π [SD],18 π [T]	$\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle z^2 \rangle$
			29 $\pi + 51\sigma$	(Δ^b)	29 π				
Ground	1 $^1A_{1g}$	0.0	0.0		0.0	31	216	216	
Excited									
$\pi \rightarrow 3s$	1 $^3E_{1g}$	6.33 ^c	6.28			52	236	235	
$\pi \rightarrow 3p_\sigma$	1 $^3A_{1u}$		7.15			47	247	245	
	1 $^3A_{2u}$	6.93 ^d	6.82			46	243	244	
	1 $^3E_{2u}$	6.95 ^d	7.02			46	244	246	
$\pi \rightarrow 3p_\pi$	1 $^3E_{1u}$	7.19 ^e ,7.41 ^f	6.89	(0.33)	7.22	84	231	229	
$\pi \rightarrow 3d_\sigma$	1 $^3B_{1g}$	7.46 ^g	7.43			48	252	277	
	1 $^3B_{2g}$	7.46 ^g	7.42			47	265	266	
	2 $^3E_{1g}$		7.42			47	261	271	
$\pi \rightarrow 3d_\delta$	3 $^3E_{1g}$	7.54 ^e	7.33			67	252	231	
$\pi \rightarrow 3d_\pi$	1 $^3A_{1g}$	7.80 ^e	7.66	(0.15)	7.81	90	253	253	
	1 $^3A_{2g}$		7.57	(0.36)	7.93	100	261	257	
	1 $^3E_{2g}$	7.81 ^e	7.71	(0.18)	7.89	92	254	255	
$\pi \rightarrow 4s$	4 $^3E_{1g}$	7.95 ^e	7.88			116	251	246	
$\pi \rightarrow 4p_\pi$	2 $^3E_{1u}$	8.37 ^f	8.11	(0.34)	8.45	125	278	240	
$\pi \rightarrow 4d_\pi$	2 $^3A_{1g}$	8.44 ^e	8.52	(0.16)	8.68	125	296	291	
	2 $^3A_{2g}$		8.44	(0.35)	8.79	125	296	288	
	2 $^3E_{2g}$	8.44 ^e	8.58	(0.16)	8.74	121	287	293	
$\pi \rightarrow 4f_\pi$	1 $^3B_{1u}$		8.12	(0.37)	8.49	95	281	274	
	1 $^3B_{2u}$		8.09	(0.41)	8.50	98	280	281	
	3 $^3E_{1u}$	8.38 ^h	8.16	(0.37)	8.53	97	246	281	

^a Reference 14.^b Δ shows the contribution of the σ reorganization.^c Reference 32.^d Reference 34.^e Reference 36.^f Reference 29.^g These values were estimated from $\pi \rightarrow 4d_\sigma$. See the text.^h Reference 70.

First we discuss the $\pi \rightarrow ns$ excitations. Although this series has already been definitely assigned experimentally, there is an interesting history in the identification. Lassette *et al.*⁸ reported that two electronic states existed around 6 eV. They measured EELS with different scattering angles and found a pronounced change in the relative intensity of the peaks in the 6–6.5 eV region. One of these peaks is due to the valence S_2 ($^1B_{1u}$) state and the other is considered, from the term value, as being due to the Rydberg 3s state.⁶¹ Doering⁹ however did a similar experiment and shown that the ratio of the unresolved 6.2 eV peak to the 6.95 eV (S_3) peak was constant. His data questioned the conclusion of Lassette *et al.* and made the identification of this state difficult. A clue to this problem was given later by the MPI spectroscopy. From the two photon resonance spectra, Johnson³² concluded that the peak observed at 6.33 eV would be to either the $^1E_{1g}$ Rydberg state or $^1E_{2g}$ valence state. Twarowski and Klinger³³ performed the same experiment in liquid benzene and found that the peak observed by Johnson in vapor phase was absent. This observation means that the state at 6.33 eV is Rydberg. Doering⁶² repeated the experiments and confirmed this conclusion. Whetten *et al.*³⁶ recently investigated the $\pi \rightarrow 4s$ and higher components of this

series by MPI spectroscopy. The 4s state was measured at 7.95 eV above the ground state.

The singlet and triplet $\pi \rightarrow 3s$ excitation energies calculated by the SAC-CI theory are 6.31 ($^1E_{1g}$) and 6.28 eV ($^3E_{1g}$), respectively. For the $\pi \rightarrow 4s$ transition, the energies are calculated at 7.90 ($^1E_{1g}$) and 7.88 eV ($^3E_{1g}$). The experimental values for the singlet excitations are 6.33 ($\pi \rightarrow 3s$) and 7.95 eV ($\pi \rightarrow 4s$); an excellent agreement between theory and experiment. The out-of-plane extension of the electron cloud measured by the second moment $\langle x^2 \rangle$ is 52, 113 a.u. (singlet) and 52, 116 a.u. (triplet) for Rydberg 3s and 4s states, respectively, in comparison with 31 a.u. for the ground state.

Second we discuss the $\pi \rightarrow np_\sigma, np_\pi$ series, which Wilkinson²⁹ called R and R' series. Many studies have been done on the assignment of these series. Wilkinson assigned $\pi \rightarrow np_\sigma$ to the R series based on the polarized light study on hexamethylbenzene⁶³ and the theoretical study by Mulliken and Roothaan.⁶⁴ Liehr and Moffitt,⁶⁵ on the other hand, assigned $\pi \rightarrow np_\sigma$ to the R' series, based on a simple calculation and the spacing expected from the fourfold quasidegenerate configurations. Jonsson and Lindholm⁶⁰ assigned $\pi \rightarrow np_\sigma$ and $\pi \rightarrow np_\pi$ to the R and R' series, respectively, from

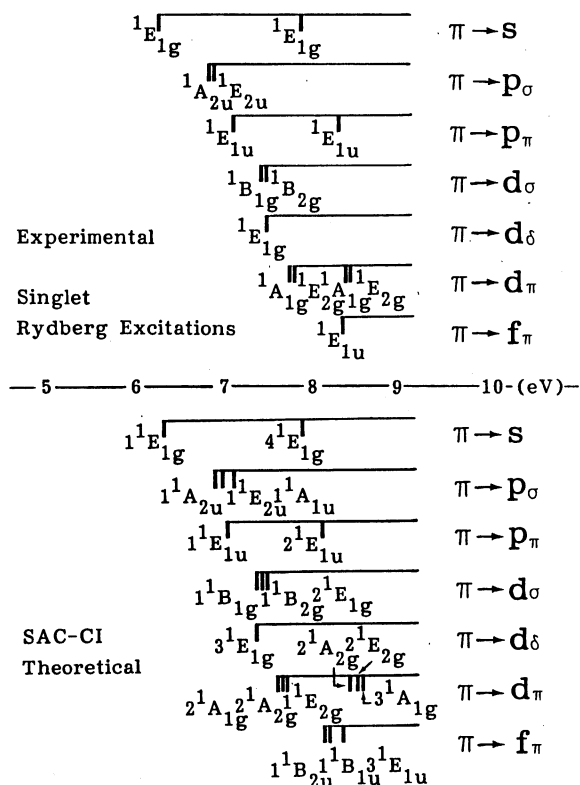


FIG. 5. Experimental (above) and theoretical (below) single Rydberg excitation energies of benzene.

the consideration on the quantum defect value. This assignment has been supported later by several experiments. Scheps *et al.*⁶⁶ investigated this problem from the antiresonance interaction.^{67,68} They found that the first component of the Wilkinson's *R* series showed no antiresonance interaction. They therefore concluded that there are two peaks near 7 eV, the valence S_3 peak which has the oscillator strength in plane and the Rydberg peak whose transition moment polarizes out of the plane. Vitenberg *et al.*⁶⁹ investigated in a detail the hot bands in the VUV spectra. They explained the abnormal splitting in the *R'* series based on the quadratic Jahn-Teller effect due to the vibronic coupling of ${}^1E_{1u} \otimes e_{2u} (\nu_{20})$ and confirmed this series as $\pi \rightarrow np_\pi$. Snyder *et al.*⁷⁰ got the same conclusion from the MCD (magnetic circular dichroism) studies. Finally, Johnson and Korenowski³⁴ found the ${}^1A_{2u}$ and ${}^1E_{2u}$ states, namely $\pi \rightarrow 3p_\sigma$, in the *R* series, at 6.93 and 6.95 eV, respectively. Whetten *et al.*^{36(a)} assigned $\pi \rightarrow 3p_\pi$ (${}^1E_{1u}$) to 7.19 eV.

In the theoretical study, HS¹⁴ obtained the $\pi \rightarrow 3p_\pi$ transition at 7.26 eV for singlet and 7.24 eV for triplet. They were supported by the open-shell SCF results of Ermler *et al.*⁷¹ and the quantum-defect arguments of Jonsson and Lindholm.⁶⁰ The present SAC-CI calculation gives these two peaks at almost the same region. For the $\pi \rightarrow 3p_\sigma$ (*R* series) transitions, the SAC-CI results are 7.10, 6.88, and 6.99 eV for singlet, and 7.51, 6.82, and 7.02 eV for triplet with the spatial symmetry of A_{1u} , A_{2u} , and E_{2u} , respectively. For the $\pi \rightarrow 3p_\pi$ (*R'* series) transitions, our results are 7.02 eV for singlet and 6.89 eV for triplet. For the singlet $\pi \rightarrow 3p_\pi$ transi-

tion, we cite the value due to basis set 1, the basis set used for the calculations of the valence transitions.

Since this Rydberg state interacts with the nearby S_3 state, as discussed in the previous section, we have to use the basis set which can properly describe both of these states. With basis set 3 the singlet $\pi \rightarrow 3p_\pi$ state is calculated at 6.91 eV, about 0.1 eV lower than that with basis set 1. The effect of the σ reorganization on the $\pi \rightarrow 3p_\pi$ transition is about 0.3 eV for both singlet and triplet. This value is estimated as the difference of $29\pi + 51\sigma$ and 29π calculations. The second moment of the $3p_\sigma$ and $3p_\pi$ states show an expected behavior; viz., the $3p_\sigma$ state has the electron cloud somewhat extended in plane, while in the $3p_\pi$ state, $\langle x^2 \rangle$ is almost three times as large as that of the ground state. These trends are same in both singlet and triplet states. The $\pi \rightarrow 3p_\sigma$ and $\pi \rightarrow 3p_\pi$ transitions are both optically allowed. The calculated oscillator strengths are 0.071 and 0.049, respectively. The theoretical peaks are shown in Fig. 3. They are almost in the same region as the large broad optically allowed peak of the S_3 state.

HS¹⁴ calculated $4p_\pi$ states at 9.25 (singlet) and 8.95 eV (triplet). These values are too high, for Wilkinson²⁹ measured this state at 8.37 eV. Since our π space is sufficiently flexible, the $\pi \rightarrow 4p_\pi$ transitions are calculated at 8.13 eV for singlet and at 8.11 eV for triplet. The second moment $\langle x^2 \rangle$ are 124 for $4p_\pi$, 85 for $3p_\pi$, and 31 for the ground state. The corresponding ratio is 4 : 2.7 : 1. The oscillator strength for the $\pi \rightarrow 4p_\pi$ transition is calculated to be 0.004; one tenth of that of the $\pi \rightarrow 3p_\pi$ transition, 0.049. These changes are reasonable from the electron cloud extension. For the $\pi \rightarrow 4p_\sigma$ transition, our basis set is insufficient, so that we do not deal with this state in the present paper.

Next we discuss the $\pi \rightarrow nd_\sigma$, nd_π , and nd_δ transitions. Whetten *et al.*^{36(a)} recently identified these three series from the MPI spectroscopy. The $\pi \rightarrow nd_\pi$ (${}^1E_{2g}$, ${}^1A_{1g}$) and $\pi \rightarrow nd_\delta$ transitions have been measured as the two-photon allowed peaks, and the $\pi \rightarrow nd_\sigma$ (${}^1B_{1g}$, ${}^1B_{2g}$) transition is dealt as the four-photon allowed peak. They obtained the transitions to the $3d_\pi$ states at 7.80 (${}^1A_{1g}$) and 7.81 (${}^1E_{2g}$) eV, and the transitions to the $4d_\pi$ states at 8.44 (${}^1A_{1g}$) and 8.44 (${}^1E_{2g}$) eV. The $\pi \rightarrow 3d_\delta$ excitation is measured at 7.54 eV (${}^1E_{1g}$). Since $\pi \rightarrow 4d_\sigma$ is reported at 8.28 eV, $\pi \rightarrow 3d_\sigma$ is estimated at 7.46 eV using the Rydberg series formula.

HS¹⁴ studied theoretically the $3d_\pi$ and $4d_\pi$ states. Their results for the $3d_\pi$ states were 7.92, 7.94, and 7.90 eV for singlet and 7.83, 7.95, and 7.90 eV for triplet. (For details, see Tables IX and X.) They reproduced well the experimental result, 7.80 and 7.81 eV. For the $4d_\pi$ states, their results were 9.71, 9.62, and 9.56 eV for singlet and 9.35, 9.65, and 9.51 eV for triplet, which are much higher than the experimental value, 8.44 eV. These theoretical values are inappropriate since the ionization potential to which these nd_π series converge is 9.3 eV. On the other hand, the present SAC-CI result reproduces the experimental nd series to within 0.2 eV. For the $3d_\pi$ states, the singlet states are calculated at 7.64 (7.80), 7.57, and 7.64 (7.81) eV and the triplet states are calculated at 7.66, 7.57, and 7.71 eV. Values in parentheses are the experimental ones. For the $4d_\pi$ states, the singlet states are calculated at 8.53 (8.44), 8.44, and 8.52 (8.44) eV

and the triplet states are calculated at 8.44, 8.58, and 8.12 eV. The $3d_\sigma$ states are calculated at 7.42 (7.46), 7.42 (7.46), and 7.44 eV for singlet, and 7.43, 7.42, and 7.43 eV for triplet. The $3d_\delta$ states are calculated at 7.35 (7.54) eV for singlet and 7.33 eV for triplet. The effects of the σ reorganization on the $\pi \rightarrow nd_\pi$ transitions are shown in Tables IX and X in the parentheses. They are 0.20–0.36 eV for singlets and 0.15–0.36 eV for triplets. The effects are always twice larger for the A_{2g} states than for the A_{1g} and E_{2g} states. Among these $\pi \rightarrow 3d$ series, the calculated second moment $\langle x^2 \rangle$ shows a reasonable trend. As expected from the shape of the Rydberg orbitals, they are ~ 50 , 69, ~ 99 for the $3d_\sigma$, $3d_\delta$, and $3d_\pi$ state, respectively. This value for $4d_\pi$ is ~ 126 , which is 1.25 times larger than that of the $3d_\pi$ state.

We discuss next the $\pi \rightarrow nf_\pi$ transitions. Other than the R and R' series, Wilkinson²⁹ reported R'' and R''' series. From the consideration about the quantum defect values and the weakness of the peaks, Jonsson and Lindholm⁶⁰ assigned these series to the forbidden transitions $\pi \rightarrow nd_\sigma$ and $\pi \rightarrow nd_\pi$. This assignment, however, has not been supported by the recent experiments. Snyder *et al.*⁷⁰ analyzed these peaks by the MCD studies and assigned these series to the $\pi \rightarrow f$ transitions. Grubb *et al.*^{36(b)} has recently confirmed this conclusion by the MPI studies. The R''' series are interpreted as $\pi \rightarrow nf_\sigma$ ($^1A_{2u}$) and R'' series are considered to be $\pi \rightarrow nf_\pi$ ($^1E_{1u}$).

From the π -SDT-CI study HS¹⁴ reported these peaks at 8.58, 8.52, and 8.74 eV for singlet and 8.51, 8.55, and 8.52 eV for triplet. They did not give the final conclusion since their results were too close to the first ionization potential, the converging limit. On the other hand, the SAC-CI results are 8.17, 8.16, and 8.33 eV for singlet and 8.12, 8.09, and 8.16 eV for triplet. Our results are closer to the experimental value, 8.38 eV. In the π SAC-CI level, these states are calculated at 8.57, 8.50, and 8.92 eV for singlets and 8.49, 8.50, and 8.53 eV for triplets, very close to the results of HS. The σ -reorganization effect is 0.34–0.59 eV. There are, however, several problems. The magnitude of the second moment of this f state is smaller than those of the corresponding $4p_\pi$ and $4d_\pi$ states. The calculated oscillator strength 0.293 is large for

the Rydberg state. These problems are probably due to the fact that we did not explicitly use the Rydberg f function itself, but expressed it by a superposition of the diffuse p_π functions placed on each carbon atom. A more reliable result would be obtained from the calculation which uses real Rydberg f functions within the basis set.

E. Ionization potential

The ionization potentials of benzene are calculated with the basis set 1, which is used for the valence $\pi \rightarrow \pi^*$ excited states. Table XI shows the experimental and theoretical values for the outer valence ionization potentials. The experimental data are taken from Kimura *et al.*⁷² and Jonsson and Lindholm,⁶⁰ and correspond to the band maxima. As the SAC-CI results, the calculations with $S_2 * I_1$ integrals in the unlinked term^{20(a)} are cited. The intensity is calculated with the mono pole approximation.⁷³ In the fifth column, the theoretical data obtained by von Niessen *et al.*³⁷ by Green function method are given. For the deeper levels, the results of the 2ph-TDA (two-particle-hole Tamm–Dancoff approximation) method are also cited. The Koopmans' values are shown in the last column.

The SAC-CI calculation reproduces the experimental values to within 0.6 eV. The SAC-CI and Green function calculations give similar results. About the deeper levels the 2ph-TDA method gives better results than the overvalence Green function method. Even the Koopmans' approximation gives the same ordering, though the absolute magnitude itself is unreliable.

There was a controversial situation for the ordering of the $^2E_{2g}$ (Σ) and $^2A_{2u}$ (Π) states. From the combined investigation of the photoelectron spectroscopy with EELS and MS (mass spectroscopy), Jonsson and Lindholm⁶⁰ reported that the $^2E_{2g}$ (Σ) state was higher in energy than the $^2A_{2u}$ (Π) state. Potts *et al.*⁷⁴ however gave the inverse assignment based on the selective enhancement of the π MO relative to the σ MO due to the Ne I source. The former interpretation was supported later by the perfluoro effect,⁷⁵ from the angular distribution for the photoelectron spectra,⁷⁶ and from the

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

State	Exptl. ^a	SAC-CI			Green fn ^b		Koopmans'
		Energy	(Δ^c)	Intensity	Energy	(Δ)	
$1^2E_{1g}(\pi)$	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
$1^2A_{2u}(\pi)$	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	(0.11)	0.92	14.46	(0.57)	16.00
1^2B_{2u}	14.86(14.7)	14.22	(0.56)	0.91	14.83	(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)	

^aReferences 72 and 60 (in parentheses).

^bReference 37(a).

^c Δ shows the difference from the experimental value.

^dReferences 37(b) and 37(c).

Penning ionization spectroscopy.⁷⁷ The same result was theoretically obtained by von Niessen *et al.* using the Green function method, and by the present study from the SAC-CI method.

Figure 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 due to Gelius,⁷⁸ 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.^{20(a)} The intensity of the peak is calculated with the mono pole approximation.⁷³ The alphabet on each peak shows the MO from which one electron is annihilated in the state.

Three points are remarkable in this figure. One is about the spectrum around 20 eV. Figure 7 shows the electron impact data⁷⁹ of higher resolution in this region. There is at least one peak which can not be explained within the Koopmans' theorem. The SAC-CI calculation gives one satellite peak, labeled *c*, around this region, though the position is somewhat higher in energy. This peak is described as the simultaneous ionization-excitation, $(e_{1g} \rightarrow \infty, e_{1g} \rightarrow e_{2u})$, namely, $(\pi \rightarrow \infty, \pi \rightarrow \pi^*)$. This peak borrows the intensity from the third ionization $[1a_{2u}(\pi) \rightarrow \infty]$, so that the intensity of the third peak is relatively small in comparison with the other peaks in the small energy region. This result supports the argument given by Cederbaum *et al.*^{37(b)} The second point is about the background spectrum in the region from 20 to 30 eV of the experimental spectrum shown in Fig. 6. The experimental data suggests an existence of many sat-

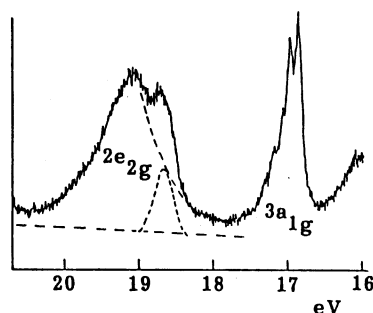


FIG. 7. Photoelectron spectra of benzene. This figure is taken from Ref. 79.

ellite peaks in this region. The SAC-CI theory certainly gives many satellite peaks in this region. These satellite peaks borrow their intensities from the peaks $i[2e_{1u}(\sigma) \rightarrow \infty]$ and $j[2a_{1g}(\sigma) \rightarrow \infty]$. The third point is about the small peak around 31 eV of the experimental spectrum. The SAC-CI calculation explains these peaks as composed of the satellite peaks which borrow intensity from $(2e_{1u} \rightarrow \infty)$ and $(2a_{1g} \rightarrow \infty)$ transitions.

VI. CONCLUSION

In this paper, we have applied the SAC and SAC-CI theory to the calculations of the valence and Rydberg excitations and the ionizations of benzene. This is probably the first paper which deals with the excited states of benzene with the use of the large π and σ active space. For the valence excitations and ionizations, we have used $35\pi + 45\sigma$ MO's as active space and for the Rydberg excitations $29\pi + 51\sigma$ MO's. Both spaces consist of 80 MO's. By virtue of the SAC and SAC-CI theory, the dimensions of the matrices handled in this calculation were less than 4000.

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 0.5 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 (HS)¹⁴ 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 π -CI result of HS is 0.9 eV. Further, some interesting behavior is seen on the extension of the electron cloud of the S_3 state. Without including the σ -reorganization effect, this state looks almost Rydberg from the $\langle x^2 \rangle$ value. When the effect of the σ reorganization is taken into account, the electron cloud considerably shrinks and the state becomes essentially valence in nature. Accordingly, the oscillator strength increases from 0.61 (π) to 1.03 ($\pi + \sigma$). This behavior might be in common to the valence excited V states of conjugated polyenes because the similar behavior was also seen for ethylene.

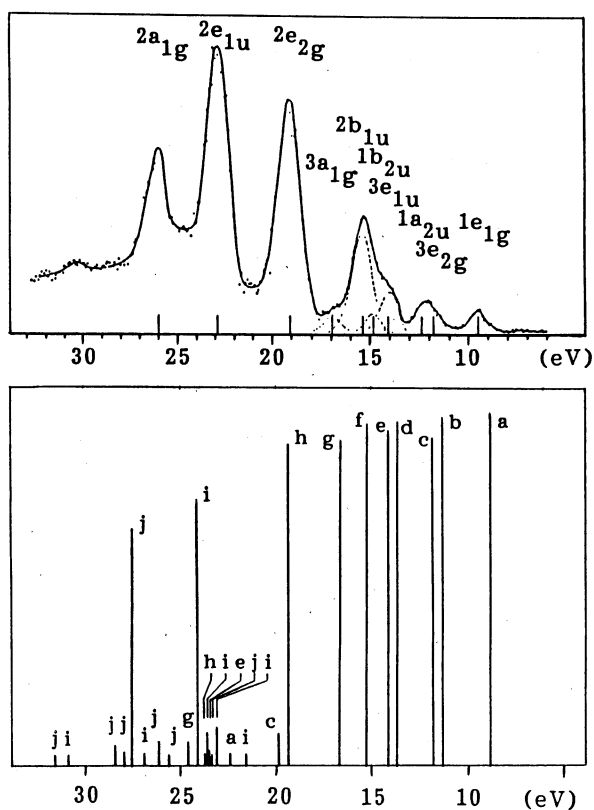


FIG. 6. Experimental (above) and theoretical (below) valence ionization spectra of benzene. The experimental results are taken from Ref. 78. a: $1e_{1g}$, b: $3e_{2g}$, c: $1a_{2u}$, d: $3e_{1u}$, e: $1b_{2u}$, f: $2b_{1u}$, g: $3a_{1g}$, h: $2e_{2g}$, i: $2e_{1u}$, j: $2a_{1g}$.

This study is probably the first systematic calculation of the Rydberg excited states involving both π and σ spaces. Recently almost all the Rydberg transitions from the HO π MO have been determined experimentally by the MPI spectroscopy.³¹⁻³⁶ The SAC-CI calculation reported here has reproduce the experimental results 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 the $\pi \rightarrow 3p_\pi$ transition. This is probably due to the interaction between the Rydberg $\pi \rightarrow 3p_\pi$ state and the valence $\pi \rightarrow \pi^* S_3$ state, both lying close at about 7 eV. The $\pi \rightarrow 4p_\pi$ transition is also calculated at about 0.24 eV lower than the experimental value. The $\pi \rightarrow nd$ and $\pi \rightarrow nf$ transitions are also computed and compared with the experimental results. The recent experiments have clarified much about the nature of these series. As a result, Wilkinson's R'' and R''' series, which were once considered as $\pi \rightarrow nd$, have been now assigned to $\pi \rightarrow nf$. The SAC-CI calculations excellently reproduce the lower components of these transitions. The effect of the σ reorganization on the Rydberg transitions are about 0.3 eV, smaller than those for the higher valence transitions, $S_0 \rightarrow S_2, S_3, T_3$.

For the ionization potential, the outer valence part is reproduced to within ~ 0.6 eV of the experimental value. Our results support the assignment of von Niessen *et al.* due to the Green function method. We obtain many satellite peaks in the inner valence region and explain some feature of the observed ESCA spectrum.

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