Cluster expansion of the wave function. Valence and Rydberg excitations and ionizations of pyrrole, furan, and cyclopentadiene

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The symmetry-adapted cluster (SAC) expansion and the SAC-CI theory have been applied to the calculations of the valence and Rydberg excitations and ionizations of the five-membered ring compounds, pyrrole, furan, and cyclopentadiene. For almost all cases, the experimental values were reproduced to within 0.3 eV for the excitation energy, and to within 0.5–0.7 eV for the ionization potential. We have given several new assignments for the excitation spectra of pyrrole and furan, and the first *ab initio* assignments for cyclopentadiene. However, there were remarkable disagreements of about 1.2 eV for the singlet $\pi \rightarrow \pi^*$ excitations of $2\,^1A_1$ state for furan, and of $1\,^1B_2$ state for cyclopentadiene. This is the same tendency as those due to the MRSD-CI method. For ionization potential, our assignments of the peaks are essentially the same as those due to the Green's function method by von Niessen *et al.*, but the present SAC-CI method reproduces the experimental data better than this method.

I. INTRODUCTION

Recent development in molecular spectroscopy, especially in laser chemistry and SOR (synchrotron orbital radiation) chemistry, has given much information of molecular excited states and, at the same time, increased the demands for the reliable theoretical information of these states. For some properties of the excited and ionized states, only theory can give reliable informations.

For this purpose, we have developed a cluster-expansion formalism for studies of electron correlations in ground and various kinds of excited states. The symmetry-adapted-cluster (SAC) expansion[1] was formulated for the closed- and open-shell systems, and the SAC-CI theory[2] for the excited states, ionized states, and electron-attached states.[3,4] We have also studied the spin and electron correlations in several organic radicals.[5]

The theoretical details and the algorithms of calculations for the SAC and SAC-CI theory have been already reported.[1–4] The SAC theory describes the electron correlations of molecules in an efficient way by considering the simultaneous collisions of electrons in an unlinked term. It is size extensive.[6] The SAC-CI theory describes the electron correlations of the excited and ionized states very effectively owing to an approximate transferability of the (dynamic) electron correlations between ground and excited states. These theories are more rapidly convergent than ordinary CI as have been shown already through the applications to the molecules, H_2O, BH_3, CO_2, N_2O, CS_2, COS, ethylene and some doublet radicals, BH, methyl, methylene, ethyl, vinyl, formyl, and NO.[1–5]

In this paper, we report calculations of the valence and Rydberg excited and ionized states of pyrrole, furan, and cyclopentadiene. These three molecules are key molecules in organic chemistry and biochemistry. Accurate descriptions and assignments of the ground and excited states of these molecules are important in understanding the roles and behaviors of these molecules in chemistry. These molecules are larger than those to which the present theory has successfully been applied. We want to examine a continuous applicability of the theory to larger systems. We compare the present results especially with the previous results of ethylene.[4] We will give a systematic assignment of the singlet and triplet valence and Rydberg excited states, and the ionization potentials of these five-membered ring compounds. We note that pyrrole and furan is the so-called 6π electron aromatic compounds but cyclopentadiene has only 4π electrons and similar to *cis*-butadiene.

II. CALCULATIONAL DETAILS

We calculated the ground state of pyrrole, furan, and cyclopentadiene by the SAC theory and the singlet and triplet excited states and the ionized states by the SAC-CI theory. The Hartree-Fock MO's of the closed-shell ground states were used as a reference MO's for all of these states. They were calculated by the HONDOG program.[7]

The geometries of pyrrole,[8] furan,[9] and cyclopentadiene[10] used in the present calculations are those reported by the microwave spectroscopy for the ground state. We have adopted this geometry for all the excited and ionized states and did not consider the geometrical relaxation effect. The molecule was in the yz plane with the main axis collinear to the z axis.

The basis set used in the present calculations is of double zeta quality for both valence and Rydberg orbitals. The valence part was described by the [4*s*2*p*/2*s*] set of Hazinaga–Dunning.[11] For the Rydberg part of pyrrole, a set of diffuse *s*, *p*, and *d* functions with exponent 0.048 45, 0.0204(*s*), 0.0437, 0.0184(*p*), and 0.015(*d*), respectively, was placed at the center of gravity of the molecule. For furan a set of Rydberg basis with the exponents 0.0523, 0.0220(*s*), 0.0456, 0.0196(*p*), and 0.015(*d*) was employed, and for cyclopentadiene a set of Rydberg basis with exponents 0.0437, 0.0184(*s*), 0.0399, 0.0168(*p*), and 0.015(*d*) was employed. These *s* and *p* exponents of Rydberg functions were formed

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as follows. First the exponents of the heteroatom and carbon atom estimated by Dunning and Hay[11] were averaged. Then, this exponent was split into two by multiplying the factors 0.8 and 1.9 as recommended by these authors. For the Rydberg d function we considered only the a_2 component which mixes into π orbitals. The number of basis set is 69 for pyrrole, 67 for furan, and 71 for cyclopentadiene. For furan, we have further performed additional calculations using the basis set which includes, in addition to the above basis set, the d-polarization function on oxygen. The exponent is 0.85.

The space of active MO's consists of all the valence occupied orbitals and almost all the Rydberg and valence virtual orbitals. The number of active MO's is 53 for pyrrole, 51 for furan, and 54 for cyclopentadiene, and 13 MO's of them are occupied MO's. To diminish the size of calculations, we selected the linked operators in the way reported in Ref. 3(a). The threshold λ_g and λ_e were 4×10^{-5} and 5×10^{-5} a.u. (8×10^{-5} a.u. for cyclopentadiene), respectively. Table I shows the dimension of the SAC and SAC-CI calculations.

In the SAC theory the effect of the simultaneous binary collisions of electrons is dealt with in the form of the unlinked term. There, we have considered all the double excitation operators whose coefficients in the SDCI are larger than 1×10^{-2}. In the SAC-CI theory, the transferable part of the electron correlations between ground and excited states are expressed by the unlinked term. This term is expressed as the sum of double excitations from the main reference configurations of the states. The double excitations involved are those whose coefficients in the ground state SDCI calculation are larger than 1×10^{-3}, and the main reference configurations are those whose coefficients in the SDCI of the states under consideration are larger than 0.1.

The computer times used for the SAC and SAC-CI calculations are summarized in the Appendix.

III. RYDBERG AND VALENCE EXCITATED STATES

A. Pyrrole

The energy of the ground state of pyrrole was calculated to be $-208.754\,72$ a.u. at the Hartree-Fock level and $-208.993\,36$ a.u. at the SAC level. The calculated correlation energy is $-0.238\,64$ a.u. In Tables II and III, we have

TABLE I. Dimension of the SAC and SAC-CI calculations.

State	Pyrrole	Furan	Cyclopentadiene
Ground $^1A_1$	2457	2456	2312
Excited			
$^1A_1$	1841	1896	1285
$^1A_2$	1883	2260	3203
$^1B_1$	1913	2352	1678
$^1B_2$	1758	1805	984
$^3A_1$	2515	2496	1793
$^3A_2$	2199	2425	912
$^3B_1$	2487	2017	1200
$^3B_2$	2701	2379	1734
Ionized			
$^2A_1$	1380	1366	1130
$^2A_2$	268	263	195
$^2B_1$	514	510	357
$^2B_2$	1116	1060	888

TABLE II. Rydberg and valence singlet excitations of pyrrole (eV).

Expt.		SAC-CI		π-CI Tanaka[a]		MRSD-CI Butsher[b]		RS-B_k Davidson[c]	
ΔE	assign.	ΔE	assign.	ΔE	assign.	ΔE	assign.	ΔE	assign.
5.22[d,e]	$^1A_2(1a_2\rightarrow3s)$[f]	5.20	$1\,^1A_2(\pi_3\rightarrow3s)$			5.22	$^1A_2(1a_2\rightarrow3s)$	5.25	$^1A_2(3s)$
5.88[d,e]	$^1B_1(1a_2\rightarrow3pb_2)$[g]	5.85	$1\,^1B_1(\pi_3\rightarrow3p_y)$			6.05	$^1B_1(1a_2\rightarrow3pb_2)$	5.63	$^1B_1(3p_y)$
		5.95	$2\,^1A_2(\pi_2\rightarrow3p_z)$					6.03	$^1A_2(3p_z)$
5.98[e]	$^1B_2$	5.97	$1\,^1B_2(\pi_3\rightarrow3p_x)$	6.02	$^1B_2(1a_2\rightarrow3b_1)$	6.33	$^1B_2(1a_2\rightarrow3pb_1)$	5.80	$^1B_2(3p_x)$
6.23[d,g]	$^1B_1(2b_1\rightarrow3sa_1)$	6.13	$2\,^1B_1(\pi_2\rightarrow3s)$			6.13	$^1B_1(2b_1\rightarrow3s)$	5.96	$^1B_1(3s)$
6.78[g]	$^1A_1(1a_2\rightarrow3da_2)$	6.68	$2\,^1A_1(\pi_3\rightarrow3d_{xy})$	6.51	$^1A_1(1a_2\rightarrow2a_2,$ $2b_1\rightarrow3b_1)$	6.73	$^1A_1(2a_1\rightarrow\pi_4^*,$ $1a_2\rightarrow\pi_5^*)$	6.53	$^1A_1(\pi\rightarrow\pi^*)$
6.93[e]		6.70	$3\,^1B_1(\pi_2\rightarrow3p_z)$					6.70	$^1B_1(3p_z)$
		6.85	$3\,^1A_2(\pi_2\rightarrow3p_y)$					7.07	$^1A_2(3p_y)$
		6.88	$3\,^1A_1(\pi_2\rightarrow3p_x)$	7.07	$^1B_2(1a_2\rightarrow4b_1)$			6.91	$^1A_1(3p_x)$
7.12[g],7.22[e,g]	$^1B_1(1a_2\rightarrow4pb_2)$	7.20	$4\,^1A_1(\pi_2\rightarrow\pi_4^*,\pi_3\rightarrow\pi_5^*)$	7.30	$^1A_1(1a_2\rightarrow3a_2)$			6.97	$^1B_2(3d_{xy})$
7.43[d,e,g]	$^1A_1(1a_2\rightarrow4da_2)$	7.52	$2\,^1B_2(\pi_3\rightarrow\pi_4^*,\pi_2\rightarrow3d_{xy})$					7.12	$^1A_1(3d_{xy})$
7.54[d,e,g]	$^1A_1(1a_2\rightarrow5pb_2)$	7.59	$3\,^1B_2(\pi_2\rightarrow3d_{xy},\pi_3\rightarrow\pi_4^*)$			7.70	$^1B_2(1a_2\rightarrow\pi_4^*)$	7.83	$^1B_2(f')$
7.69[d,e,g]	$^1A_1(1a_2\rightarrow5da_2)$								
7.86[d,e,g]	$^1B_1(2b_1\rightarrow4s)$							8.10	$^1B_2(3d_{x^2y})$

[a] Reference 12. [c] Reference 14. [e] Reference 18(a). [g] Reference 16(b).
[b] Reference 13. [d] Reference 16(a). [f] Reference 17.

TABLE III. Rydberg and valence triplet excitations of pyrrole (eV).

Exptl.		SAC-CI		π-CI Tanaka[a]		MRSD-CI Butscher[b]	
ΔE	assign.	ΔE	assign.	ΔE	assign.	ΔE	assign.
4.21	$^3(\pi\rightarrow\pi^*)$[c]	4.65	$1\,^3B_2(\pi_3\rightarrow\pi_4^*)$	4.27	$^3B_2(1a_2\rightarrow 3b_1)$	4.42	$^3B_2(1a_2\rightarrow\pi_4^*)$
5.10	$^3(\pi-\pi^*)$[c]?	5.17	$1\,^3A_2(\pi_3\rightarrow 3s)$			5.25	$^3A_2(1a_2\rightarrow 3s)$
		5.82	$1\,^3B_1(\pi_3\rightarrow 3p_y)$				
		5.84	$1\,^3A_1(\pi_2\rightarrow\pi_4^*,\pi_3\rightarrow\pi_5^*)$	5.45	$^3A_1(1a_2\rightarrow 2a_2,2b_1\rightarrow 3b_1)$	5.71	$^3A_1(2b_1\rightarrow\pi_4^*)$
		5.93	$2\,^3A_2(\pi_2\rightarrow 3p_z)$				
		5.96	$2\,^3B_2(\pi_3\rightarrow 3p_x)$	6.37	$^3B_2(1a_2\rightarrow 4b_1)$		
		6.03	$2\,^3B_1(\pi_2\rightarrow 3s)$			5.99	$^3B_1(1a_2\rightarrow 3pb_2)$
		6.59	$2\,^3A_1(\pi_3\rightarrow 3d_{xy})$				
		6.86	$3\,^3A_2(\pi_2\rightarrow 3p_y)$				
		6.89	$3\,^3A_1(\pi_2\rightarrow 3p_x,\pi_3\rightarrow\pi_5^*,3d_{xy})$	7.14	$^3A_1(1a_2\rightarrow 2a_2,2b_1\rightarrow 3b_1)$	7.10	$^3A_1(1a_2\rightarrow\pi_5^*,2b_1\rightarrow\pi_4^*)$
		7.23	$3\,^3B_2(\pi_2\rightarrow\pi_5^*)$			6.91	$^3B_2(2b_1-\pi_5^*)$

[a] Reference 12.
[b] Reference 13.
[c] Reference 18(a).
[d] Reference 18(b).

shown the singlet and triplet excitation energies, respectively. The present SAC-CI results are relative to the SAC energy of the ground state. We have cited the previous theoretical results of Tanaka *et al.*[12] who performed CI within π MO's, the results of Butcher *et al.*[13] with the MRSD-CI method, and the results of Davidson *et al.*[14] with the Rayleigh–Schrödinger B_k method. Table IV shows some one-electron properties of the ground and singlet excited states, and the oscillator strengths of pyrrole. The second moment is useful to characterize the excited state whether it is valence or Rydberg in nature. In Fig. 1, we displayed the theoretical excitation spectra of pyrrole which is compared with the experimental spectra of Flicker *et al.*[18(a)] observed by the electron-impact spectroscopy. The spectrum observed at the 5.5–9.0 eV region is at low scattering angle ($\theta = 3°$), so that the selection rule is considered to be parallel with that of the UV spectra.[21] The spectra at higher scattering angle ($\theta = 70°$) at the 3.5–5.5 eV region include the spectra for triplet excitations.

We first discuss the singlet excitations. For almost all the states, the present theoretical results agree quite well with the experimental values. They are different from the experimental values to within 0.1 eV. In Fig. 1, the theoretical excitation spectra seem to reproduce well the experimental spectra. For the excitations below 7.0 eV, the assignments of the observed peaks are essentially the same as those given by the experimentalist. However, for the peaks above 7.0 eV, our assignments are different from theirs. The peak observed at 7.22 eV is assigned to the $4\,^1A_1$ state calculated at 7.20 eV. The stronger peaks observed at 7.43 and 7.54 eV are assigned to the $2\,^1B_2$ and $3\,^1B_2$ states, respectively. The relative intensities of these peaks given in Table IV agree reasonably with the experiments. The shoulders at 7.69 and 7.86 eV were not calculated here because it is due to the more diffuse and

TABLE IV. Oscillator strengths and one-electron properties for the ground and singlet excited states of pyrrole (a.u.).

State	Orbital picture		SAC-CI ΔE	Oscillator strength	Dipole moment $-\langle z\rangle$[a]	Electronic part of second moment $\langle x^2\rangle$[b]	$\langle y^2\rangle$	$\langle z^2\rangle$[a]
Ground		Exptl.			0.708 ± 0.003[c]	27 ± 2[d]	138 ± 2[d]	140 ± 2[d]
		Theor. HF			0.788	26	140	140
		SAC			0.834	26	141	140
Excited								
$1\,^1A_2$	$\pi_3\rightarrow 3s$		5.20	0.0	−2.597	42	151	160
$1\,^1B_1$	$\pi_3\rightarrow 3p_y$		5.85	3.22×10^{-2} x	0.199	40	177	152
$2\,^1A_2$	$\pi_3\rightarrow 3p_z$		5.95	0.0	3.900	41	151	178
$1\,^1B_2$	$\pi_3\rightarrow 3p_x$		5.97	4.21×10^{-2} y	0.623	68	149	151
$2\,^1B_1$	$\pi_2\rightarrow 3s$		6.13	1.57×10^{-3} x	−2.217	41	159	157
$2\,^1A_1$	$\pi_3\rightarrow 3d_{xy}$		6.68	1.99×10^{-4} z	0.690	73	182	152
$3\,^1B_1$	$\pi_2\rightarrow 3p_z$		6.70	2.22×10^{-2} x	3.534	41	153	176
$3\,^1A_2$	$\pi_2\rightarrow 3p_y$		6.85	0.0	0.422	40	186	150
$3\,^1A_1$	$\pi_2\rightarrow 3p_x$		6.89	2.44×10^{-3} z	0.368	67	153	148
$4\,^1A_1$	$\pi_2\rightarrow\pi_4^*,\pi_3\rightarrow\pi_5^*$		7.20	2.14×10^{-2} z	0.768	31	143	142
$2\,^1B_2$	$\pi_3\rightarrow\pi_4^*,\pi_2\rightarrow 3d_{xy}$		7.52	8.74×10^{-2} y	0.817	47	159	145
$3\,^1B_2$	$\pi_2\rightarrow 3d_{xy},\pi_3\rightarrow\pi_4^*$		7.59	9.30×10^{-2} y	0.565	57	169	147

[a] z axis is collinear to a main axis.
[b] x axis is perpendicular to the molecular plane.
[c] Reference 19.
[d] Reference 20.

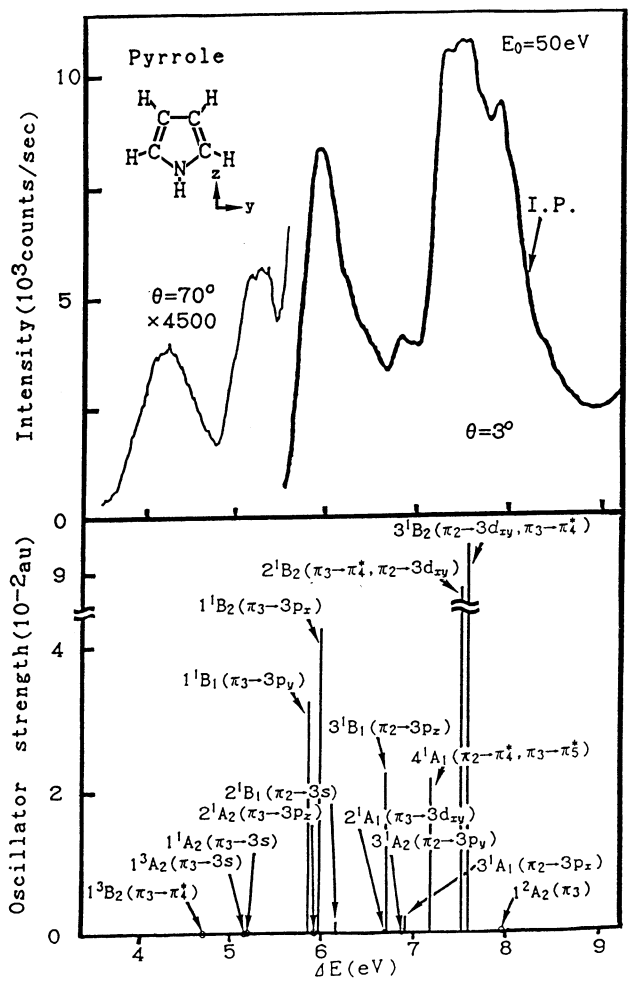

FIG. 1. Experimental and theoretical excitation spectra of pyrrole.

higher Rydberg MO's.

About the assignment of the peak observed at 6.23 eV, there is a controversy between the experimentalists. Derrick *et al.*[16(b)] attributed this peak to the $\pi \rightarrow 3s$ Rydberg transition, but Bavia[16(c)] considered this assignment to be rather unlikely. The present result of the SAC-CI calculation supports the conclusion of Derrick *et al.*, as so were the MRSD-CI and the Rayleigh–Schrödinger B_k calculations.

There is also some controversial situation for the transition observed at 6.78 eV whether it is a valence or Rydberg-type transition. Tanaka *et al.* and Butscher *et al.* assigned this peak to the valence $\pi \rightarrow \pi^*$ excitation. Davidson *et al.* also assigned this peak to the valence excited state, but they suspected their result from a very small absorption coefficient of this transition (0.001 a.u.). From photoelectron spectroscopy, Derrick *et al.*[16(b)] assigned this peak to the Rydberg $^1A_1$ state, which is produced by the excitation from the $1a_2$ MO to the $3d_{xy}$ MO. The electronic part of the second moment in the $\pi(x)$ direction calculated by Tanaka *et al.* is 27 a.u., which may imply that the state is valence. In the SAC-CI calculation, this state is calculated at 6.68 eV and has the second moment of 73 a.u., which implies that the state is Rydberg. Thus, our result supports the Derrick's assignment in contrast to the previous theoretical studies. Further, in our calculations, the valence $\pi \rightarrow \pi^*$ transition was calculated at 7.20 eV.

Now, how does this difference from the previous theoretical studies occur? We assign this peak as an excitaiton from $\pi_3(1a_2)$ MO to the Rydberg $3d_\pi$ MO, which agrees with the Derrick's assignment. For a proper description of this state, we need the Rydberg d basis to be included in the calculation. The present calculation includes the Rydberg d basis explicitly but all the previous calculations did not. They included diffuse Rydberg basis function of up to s and p symmetries only. However, we note that more recent *ab initio* SCF CI calculations of Tanaka *et al.*[15] seem to give a similar assignment to the present one.

The peaks observed at the 7.0–8.0 eV region were assigned experimentally to the higher Rydberg excitations. However, the intensity of these peaks[16(a),18(a)] seems to be too strong to be purely Rydberg in nature. An example is seen in Fig. 1 from the electron-energy loss spectroscopy.[18(a)] In the present calculations, we found a considerable admixture of the Rydberg and valence configurations for the states calculated at 7.52 (2 $^1B_2$) eV and 7.59 (3 $^1B_2$) eV. The 4 $^1A_1$ peak calculated at 7.20 eV is essentially valence $\pi \rightarrow \pi^*$ excitation in nature, as shown in the assignment of Table II. This trend is also seen in the oscillator strength and the second moment shown in Table IV. The lowest three states have relatively large oscillator strengths and small second moments. Especially, the last two states, which both have $^1B_2$ symmetry, were calculated to be the strongest peaks within the calculated ones. This trend seems to agree with the experimental spectra shown in Fig. 1.

For the triplet excitations, the experimental informations are still very limited. In Table III we have given the results of the SAC-CI calculations not only for the observed states but also for those states which are not yet observed experimentally. They are given there for prediction. Our result for the 1 $^3B_2$ valence state of pyrrole is higher than Flicker's electron impact data by 0.4 eV. This is the valence $\pi_3 \rightarrow \pi_4^*$ excited state.

There is a problem with the assignment of the peak found at 5.10 eV. From the electron energy-loss spectra, van Veen[18(b)] attributed this peak to the valence excitation because this peak is broad and has no singlet-triplet splitting which is expected for the Rydberg excitation. On the other hand, Flicker *et al.*[18(a)] reported that the peak around 5.22 eV is a spin allowed but electron dipole-forbidden excitation from the low energy, variable-angle electron impact technique of the electron energy-loss spectra. This is the singlet Rydberg $\pi \rightarrow 3s$ excitation as already shown in Table II. Due to the SAC-CI and MRSD-CI calculations, there is no valence excitations near 5.20 eV. The second valence excitation is calculated at 5.84 eV by the SAC-CI method and 5.71 eV by the MRSD-CI method. Both calculations agree in that the peak around 5.10 eV is the triplet $\pi \rightarrow 3s$ Rydberg excitation. This is the triplet counterpart of the singlet $\pi \rightarrow 3s$ Rydberg transition observed at 5.22 eV. Due to the SAC-CI method, the triplet counterpart is calculated to be lower that the singlet one by 0.03 eV, very small as expected for the Rydberg-type transition. However, the results of the MRSD-CI calculations by Butcher *et al.* show different or-

TABLE V. Rydberg and valence singlet excitations of furan (eV).

Exptl.		SAC-CI		MRSD-CI Thunemann[a]	
ΔE	assign.	ΔE	assign.	ΔE	assign.
5.94[b]	$^1A_2(1a_2\rightarrow 3sa_1)$	6.27	$1\ ^1A_2(\pi_3\rightarrow 3s)$	5.94	$1A_2(1a_2\rightarrow 3sa_1)$
6.04[c],6.06[d]	$^1B_2$	7.32	$2\ ^1A_1(\pi_2\rightarrow\pi_4^*,\pi_3\rightarrow\pi_5^*)$	6.79–7.08	$^1A_1(\pi\rightarrow\pi^*)$
6.44[c],6.47[d],6.61[d]	$^1(1a_2\rightarrow 3p)$	6.74	$1\ ^1B_1(\pi_3\rightarrow 3p_y)$	6.52	$^1B_1(1a_2\rightarrow 3pb_2)$
		6.80	$1\ ^1B_2(\pi_3\rightarrow 3p_x)$	6.52	$^1B_2(1a_2\rightarrow 3pb_1)$
7.28[e]	$^1(1a_2\rightarrow 3d)$	7.59	$3\ ^1A_1(\pi_3\rightarrow 3d_{xy})$	7.46	$^1A_1(1a_2\rightarrow 3da_2)$
7.38[c,f],7.39[e],7.42[d]	$^1(2b_1\rightarrow 3s)$	6.98	$2\ ^1A_2(\pi_3\rightarrow 3p_z)$	7.27	$^1B_1(2b_1\rightarrow 3sa_1)$
7.79[c],7.82[d]	$^1A_1$ or $^1B_2$[d]	7.50	$2\ ^1B_2(\pi_3\rightarrow\pi_4^*)$	7.58	$^1B_2(\pi\rightarrow\pi^*)$
		7.62	$2\ ^1B_1(\pi_2\rightarrow 3s)$		
8.01[f],8.05[d]	Rydberg	8.19	$3\ ^1A_2(\pi_2\rightarrow 3p_y)$	7.85	$^1A_2(2b_1\rightarrow 3pb_2)$
		8.24	$3\ ^1B_1(\pi_2\rightarrow 3p_z)$		
		8.27	$4\ ^1A_1(\pi_2\rightarrow 3p_x)$		
8.50[f],8.52[d]	Rydberg	8.91	$3\ ^1B_2(\pi_2\rightarrow 3d_{xy})$	8.60	$^1B_2(2b_1\rightarrow 3da_2)$

[a] Reference 22.
[b] Reference 17.
[c] Reference 23(a).
[d] Reference 18(a).
[e] Reference 23(c).
[f] Reference 23(b).

dering of the singlet and triplet states because of the different quality of the calculations for each state.

In Fig. 1, the lowest two triplet states are also shown by arrows, and compared with the experimental electron energy-loss spectra. For the higher triplet excited states, our results are rather close to the MRSD-CI results of Butcher *et al.*, except for the last two states shown in Table III. The ordering of these states is different between these theories mainly because of an admixture of the $3d_{xy}$ basis, in the present calculation, into the $3\ ^3A_1$ state. Butcher *et al.* did not include this function into the calculation.

B. Furan

The energy of the ground state of furan was calculated to be $-228.557\ 15$ a.u. at the Hartree-Fock level and $-228.810\ 55$ a.u. at the SAC level. The calculated correlation energy is $-0.253\ 40$ a.u. In Tables V and VI, we have shown the singlet and triplet excitation energies, respectively. The present SAC-CI results are relative to the SAC energy of the ground state. We have cited the previous theoretical results of Thunemann *et al.* obtained by the MRSD-CI method.[22] In Fig. 2, we compared the spectra obtained by the present theory with the electron energy-loss spectra due to Flicker *et al.*[18(a)]

First, we discuss the results of the singlet states. The SAC-CI results agree with the experimental values to within 0.3 eV in almost all the states. However, the singlet valence $\pi\rightarrow\pi^*$ excitation to the $2\ ^1A_1$ state calculated at 7.32 eV is higher than the experimental data by 1.26 eV. Referring to Fig. 2, we see that the electron energy-loss spectra[18(a)] is relatively well reproduced by the theory, except for this transition. The third column of Table V shows the MRSD-CI results of Thunemann *et al.*[22] They also show a similar tendency; this $^1A_1$ excited state was calculated higher than the experimental value by about 1.0 eV. These two calculations used almost the same basis set and geometry. Table VII shows the oscillator strengths and some one-electron properties of the ground and singlet excited states of furan. The $2\ ^1A_1$ state under consideration has relatively small oscillator strength (4.40×10^{-3} a.u.). This state is, however, valence in nature as seen from the electronic part of the second

TABLE VI. Rydberg and valence triplet excitations of furan (eV).

Exptl.		SAC-CI		MRSD-CI Thunemann[a]	
ΔE	assign.	ΔE	assign.	ΔE	assign.
4.02[b]	valence	4.40	$1\ ^3B_2(\pi_3\rightarrow\pi_4^*)$	4.08	$^3B_2(1a_2\rightarrow b_1)$
5.22[b]	valence	5.75	$1\ ^3A_1(\pi_2\rightarrow\pi_4^*,\pi_3\rightarrow\pi_5^*)$	5.44–5.76	$^3A_1(1a_2\rightarrow a_2,2b_1\rightarrow b_1)$
		6.20	$1\ ^3A_2(\pi_3\rightarrow 3s)$	5.82	$^3A_2(1a_2\rightarrow 3sa_1)$
		6.68	$2\ ^3B_1(\pi_3\rightarrow 3p_y)$	6.45	$^3B_1(1a_2\rightarrow 3pb_2)$
		6.87	$2\ ^3B_2(\pi_3\rightarrow 3p_x)$		
		6.95	$2\ ^3A_2(\pi_3\rightarrow 3p_z)$		
		7.42	$2\ ^3A_1(\pi_3\rightarrow\pi_5^*,3d_{xy},\pi_2\rightarrow\pi_4^*)$	7.25	$^3A_1$
		7.57	$2\ ^3B_1(\pi_2\rightarrow 3s)$		
		7.58	$3\ ^3A_1(\pi_3\rightarrow 3d_{xy})$		
7.75[c]	valence	7.90	$3\ ^3B_2(\pi_2\rightarrow\pi_5^*)$	7.54	$^3B_2(2b_1\rightarrow a_2)$
		8.29	$3\ ^3A_2(\pi_2\rightarrow 3p_y)$	7.82	$^3A_2(2b_1-2pb_2)$

[a] Reference 22.
[b] Reference 18(a).
[c] Reference 17.

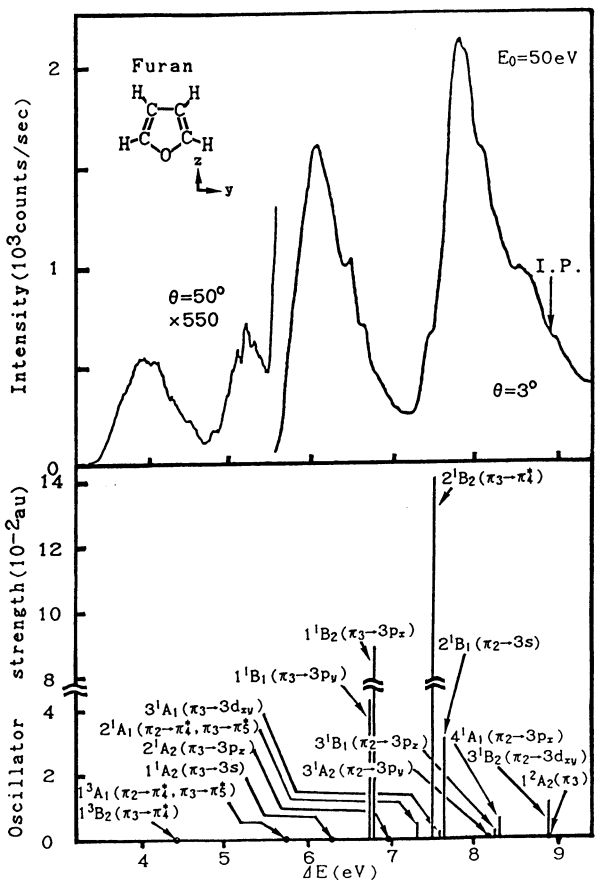

FIG. 2. Experimental and theoretical excitation spectra of furan.

moment in the $\pi(x)$ direction (26 a.u. compared with 25 a.u. for the ground state). These two observations seems to be in contrast with the case of ethylene, where the $\pi\rightarrow\pi^*$ excited state is more diffuse than the ground state, though it is not a genuine Rydberg state.[4] Thunemann also observed no admixture of diffuse configurations to the $2\ ^1A_1$ state.

What is the reason for the discrepancy between theory and experiment for the singlet $\pi\rightarrow\pi^*$ $2\ ^1A_1$ excited state? Probably, one reason is the basis set. The basis set we and Thunemann used can not well describe the reorganization of electron cloud along the z axis. We note that this $\pi\rightarrow\pi^*$ excited state, $2\ ^1A_1$, has the oscillator strength along the z axis. The dipole moment, which has also the orientation along the z axis, was poorly reproduced by the present basis set as shown in Table VII. Along this line of investigation, we also performed the SAC and SAC-CI calculations, within only π space, using the basis set which is augmented to the previous basis set by the valence d-polarization function on the oxygen atom. Table VIII shows the result. Probably because of a smallness of the active MO space, we could not see a drastic improvement. It was an improvement of only about 0.1 eV. However, we think that an improvement along this line would be necessary for an adequate description of this state.

On the other hand, we can also expect a nonvertical nature of the transition due to a bond-alternating change in the geometry as shown in Fig. 3. This is expected especially from the valence nature of the excitation and the nodal property of the π MO's involved in the excitation, and actually has been ascertained by Mishra and Jug by a semiempirical calculation.[26]

In the region of 7.20–7.50 eV, there is a discrepancy between theory and experiment about the ordering of the two Rydberg excitations, $\pi\rightarrow 3d$ and $\pi\rightarrow 3s$ transitions. Derrick *et al.*[23(c)] reported that the Rydberg series of $3d$ lie lower than those of $3s$, but the reverse was the result of the SAC-CI calculation. The MRSD-CI method also gave the same tendency as the SAC-CI method.

TABLE VII. Oscillator strengths and one-electron properties for the ground and singlet excited states of furan (a.u.).

State	Orbital picture		SAC-CI ΔE	Oscillator strength	Dipole moment $-\langle z\rangle$[a]	Electronic part of second moment $\langle x^2\rangle$[b]	$\langle y^2\rangle$	$\langle z^2\rangle$[a]
Ground		Exptl.		0.260 ± 0.002[c]	24 ± 2[d]	135 ± 2[d]	129 ± 2[d]	
		Theor. HF[e]			0.498	25	134	133
		HF[f]			0.342	25	134	133
		SAC[e]			0.409	25	135	134
$1\ ^1A_2$	$\pi_3\rightarrow 3s$		6.27	0.0	−0.367	42	146	149
$1\ ^1B_1$	$\pi_3\rightarrow 3p_y$		6.74	4.26×10^{-2} x	0.601	38	173	146
$1\ ^1B_1$	$\pi_3\rightarrow 3p_x$		6.80	8.91×10^{-2} y	0.894	58	141	143
$2\ ^1A_2$	$\pi_3\rightarrow 3p_z$		6.98	0.0	1.591	38	144	176
$2\ ^1A_1$	$\pi_2\rightarrow\pi_4^*, \pi_3\rightarrow\pi_5^*$		7.32	4.40×10^{-3} z	0.590	26	136	135
$2\ ^1B_2$	$\pi_3\rightarrow\pi_4^*$		7.50	1.40×10^{-1} y	0.239	34	136	138
$3\ ^1A_1$	$\pi_3\rightarrow 3d_{xy}$		7.59	2.83×10^{-6} z	0.698	72	178	147
$2\ ^1B_1$	$\pi_2\rightarrow 3s$		7.62	3.09×10^{-2} x	−0.896	42	149	148
$3\ ^1A_2$	$\pi_2\rightarrow 3p_y$		8.19	0.0	0.921	38	177	144
$3\ ^1B_1$	$\pi_2\rightarrow 3p_z$		8.24	2.35×10^{-3} x	2.689	38	146	173
$4\ ^1A_1$	$\pi_2\rightarrow 3p_x$		8.27	6.09×10^{-3} z	0.930	66	145	143
$3\ ^1B_2$	$\pi_2\rightarrow 3d_{xy}$		8.91	1.06×10^{-2} y	0.919	72	180	145

[a] z axis is collinear to a main axis.
[b] x axis is perpendicular to the molecular plane.
[c] Reference 24.
[d] Reference 25.
[e] The basis set is [4*s*2*p*/2*s*] set plus Rydberg *spd* sets.
[f] The basis set is [4*s*2*p*/2*s*] set plus Rydberg *spd* sets plus valence *d* polarization function.

TABLE VIII. Effect of *d*-polarization function on the excitation energy of furan within the π approximation (a.u.).

State	Exptl.[a]		SAC-CI Basis I[b]	SAC-CI Basis II[c]	Effect of *d*-fn[d]	Difference from exptl.[e]
$2\,^1A_1$	6.06	*V*	7.07	6.97	0.10	0.91
$1\,^1B_2$	6.61	*R*	7.09	6.91	0.18	0.30
$3\,^1A_1$	7.42	*R*	7.87	7.70	0.18	0.28
$2\,^1B_2$	7.82	*V*	8.12	8.00	0.12	0.18
$4\,^1A_1$			8.56	8.44	0.12	
$3\,^1B_2$			9.23	9.11	0.12	
$1\,^3B_2$	4.02	*V*	3.98	3.97	0.01	− 0.05
$1\,^3A_1$	5.22	*V*	5.52	5.47	0.05	0.25
$2\,^3B_2$			7.12	6.93	0.19	
$2\,^3A_1$			7.77	7.59	0.18	
$3\,^3B_2$	7.75	*V*	7.81	7.71	0.10	− 0.04
$3\,^3A_1$			8.02	7.94	0.08	
$1\,^2A_2$	8.87	*V*	9.21	9.02	0.19	0.15
$1\,^2B_1$	10.38	*V*	10.54	10.41	0.13	0.03
$2\,^2B_1$	15.2	*V*	14.53	14.39	0.14	0.81

[a] See footnotes of Tables VII, VIII, and XIII.
[b] The basis set is (4*s*2*p*/2*s*) set plus Rydberg *spd* sets.
[c] The basis set is (4*s*2*p*/2*s*) set plus Rydberg *spd* sets plus valence *d* polarization function on oxygen atom.
[d] Difference between the results of the basis II calculation and the basis I calculation.
[e] Difference between the result of the basis II calculation and the experimental value.

Flicker *et al.*[18(a)] reported that the peak around 7.80 eV would involve the $^1A_1$ or $^1B_2$ transition. Thunemann *et al.*[22] assigned this peak to the valence $^1B_2$ ($\pi - \pi^*$) transition calculated at 7.58 eV. Due to the present SAC-CI calculation this peak is considered to be composed of the valence $2\,^1B_2$ ($\pi_3 \rightarrow \pi_4^*$) transition and Rydberg $2\,^1B_1$ ($\pi_2 \rightarrow 3s$) transition. The calculated excitation energies were 7.50 and 7.62 eV, respectively.

There is no detailed analysis for the transitions in the region of 8.0–9.0 eV. They are considered to be Rydberg in nature. The present SAC-CI calculation shows some candidates of the excited states for these peaks. They are shown in Table V.

Although the electron energy-loss spectra of furan resemble that of pyrrole as a whole, there are some interesting differences in nature. We studied pyrrole and furan using almost the same basis set including Rydberg *spd* set. However, in all the region, a remarkable difference was that in furan there was little admixture between valence and Rydberg configurations in contrast to the case of pyrrole. This was especially so for the mixing between the $\pi \rightarrow \pi^*$ and the $\pi \rightarrow d_\pi$ configurations. These points are also seen from the one-electron properties shown in Tables IV and VII.

Next, we examine the results for the triplet states. For furan, as for pyrrole, the experimental information about the triplet excitations is very limited. Table VI includes many states which has not yet observed experimentally.

For the first triplet valence excitation, both pyrrole and furan resemble benzen. The result from both experiments and calculations support the aromatic ring model of these two molecules.

The triplet $\pi \rightarrow \pi^*$ excitation to the $1\,^3A_1$ state observed at 5.22 eV was calculated at 5.75 eV. The deviation is as large as 0.53 eV. This triplet excitation is the partner of the singlet $\pi \rightarrow \pi^*$ excitation which deviated largely, as discussed above, from the experimental value. The nature of this second triplet state of furan is very different from that of pyrrole. It is the valence $\pi \rightarrow \pi^*$ excitation in furan but the Rydberg $\pi \rightarrow 3s$ excitation in pyrrole.

Lastly, we compare the result calculated within only π MO's shown in Table VIII with those calculated with both σ and π MO's shown in Tables V and VI. For the singlet states, the calculated values of the former is 0.3–0.6 eV higher than those of the latter. The differences of − 0.4 to + 0.3 eV are seen for the triplet states. These values mean that the reorganization of the σ electrons following the π excitation is significant. The largest difference was seen for the $3\,^1B_2$ excitation.

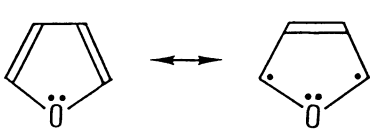

FIG. 3. Bond-alternating change in geometry in the $\pi \rightarrow \pi^*$ excited state of furan.

C. Cyclopentadiene

The energy of the ground state of cyclopentadiene was calculated to be − 192.737 32 a.u. at the Hartree-Fock level and − 192.965 84 a.u. at the SAC level. The calculated correlation energy is − 0.228 52 a.u. Tables IX and X show,

TABLE IX. Rydberg and valence singlet excitations of cyclopentadiene (eV).

Exptl.[a]		SAC-CI			
ΔE	assign.	ΔE	assign.	Oscillator strength (a.u.)	
5.26,5.34[b]	$N\rightarrow V_1(a_1\rightarrow b_2)$	6.48	$1\,^1B_2(\pi_3\rightarrow\pi_4^*)$	1.59×10^{-1}	y
5.68,5.77,5.94	$\pi\rightarrow3s$	5.76	$1\,^1A_2(\pi_3\rightarrow3s)$	0.0	
6.28	$\pi\rightarrow3p$	6.33	$1\,^1B_1(\pi_3\rightarrow3p_y)$	3.10×10^{-2}	x
		6.38	$2\,^1A_2(\pi_3\rightarrow3p_z)$	0.0	
6.41		6.42	$2\,^1B_2(\pi_3\rightarrow3p_x)$	4.42×10^{-3}	y
6.80,7.05	Rydberg	7.12	$2\,^1A_1(\pi_3\rightarrow3d_{xy})$	1.41×10^{-5}	z
7.61,7.84					
8.03	$N\rightarrow V_2,V_3(a_1\rightarrow a_1)$	7.81	$3\,^1A_1(\pi_2\rightarrow\pi_4^*,\pi_3\rightarrow\pi_5^*)$	1.93×10^{-2}	z
8.19,8.13	Rydberg	8.17	$2\,^1B_1(\pi_2\rightarrow3s)$	2.02×10^{-2}	x
8.28,8.36	Rydberg	8.63	$3\,^1A_2(\pi_3\rightarrow4s)$	0.0	
		8.69	$3\,^1B_1(\pi_2\rightarrow3p_z)$	1.61×10^{-2}	x
		8.77	$4\,^1A_1(\pi_2\rightarrow3p_z)$	3.53×10^{-2}	z
		8.80	$4\,^1A_2(\pi_2\rightarrow3p_y)$	0.0	
		8.81	$5\,^1A_2(2p_y\rightarrow\pi_4^*)$	0.0	
9.2	Rydberg				
10.4	Rydberg				
11.8,14.0	Rydberg				

[a] Reference 28.
[b] Reference 23(a).

respectively, the singlet and triplet excitation energies of cyclopentadiene. As far as we know, no *ab initio* calculations of the excited states have been reported so far for this system. The present work is the first calculation to assign theoretically the valence and Rydberg excitations except for the semiempirical ones.[27]

The results of the SAC-CI calculation agree with the experimental values to within ~0.2 eV. However there is again a large disagreement for the singlet and triplet $\pi\rightarrow\pi^*$ ($1B_2$) valence excitations. The discrepancy is as large as 1.14 eV for the singlet state and 0.42 eV for the triplet state, as was seen for the excited $2A_1$ states of furan. Probably the same reasons as the case of furan may be considered for these remarkable gaps.

In Fig. 4, we displayed the calculated excitation spectra below the electron energy loss spectra reported by Kuppermann *et al.*[28] The agreement between theory and experiment is reasonable except for the $1\,^1B_2$ state.

In the region of 5.5–6.5 eV, the Rydberg excitations to the 3*s* and 3*p* MO's are reported.[28] The SAC-CI results supported this assignment as shown in Table IX. The excitation $\pi_3\rightarrow3s$ observed at 5.68 or 5.77 eV was calculated at 5.76 eV. The Rydberg 3*p* MO's were calculated at 6.33, 6.38, and 6.42 eV above the ground state in the order of $3p_y$, $3p_z$, and $3p_x$ MO's, where *z* is the principal axis and *x* is perpendicular to the molecular plane. Experimentally, only two of these three states were observed at 6.28 and 6.41 eV. We assign them to the $1\,^1B_1$ ($\pi_3\rightarrow3p_y$) and $2\,^1B_2$ ($\pi_3\rightarrow3p_x$) states, because the

TABLE X. Rydberg and valence triplet excitation of cyclopentadiene (eV).

Exptl.[a]		SAC-CI	
ΔE	assign.	ΔE	assign.
3.1	$N\rightarrow T(a_1\rightarrow b_2)$	3.52	$1\,^3B_2(\pi_3\rightarrow\pi_4^*)$
above 4.7		5.50	$1\,^3A_1(\pi_2\rightarrow\pi_4^*,\pi_3\rightarrow\pi_5^*)$
		5.82	$1\,^3A_2(\pi_3\rightarrow3s)$
		6.36	$1\,^3B_1(\pi_3\rightarrow3p_y)$
		6.37	$1\,^3B_2(\pi_3\rightarrow3p_x)$
		6.44	$2\,^3A_2(\pi_3\rightarrow3p_z)$
		7.08	$2\,^3A_1(\pi_3\rightarrow3d_{xy})$
		8.12	$2\,^3B_1(\pi_2\rightarrow3s)$
		8.23	$3\,^3A_1(\pi_2\rightarrow\pi_4^*,\pi_3\rightarrow\pi_5^*)$
		8.57	$3\,^3A_2(\pi_3\rightarrow4s)$
		8.92	$3\,^3B_2(\pi_3\rightarrow4p_x)$

[a] Reference 28.

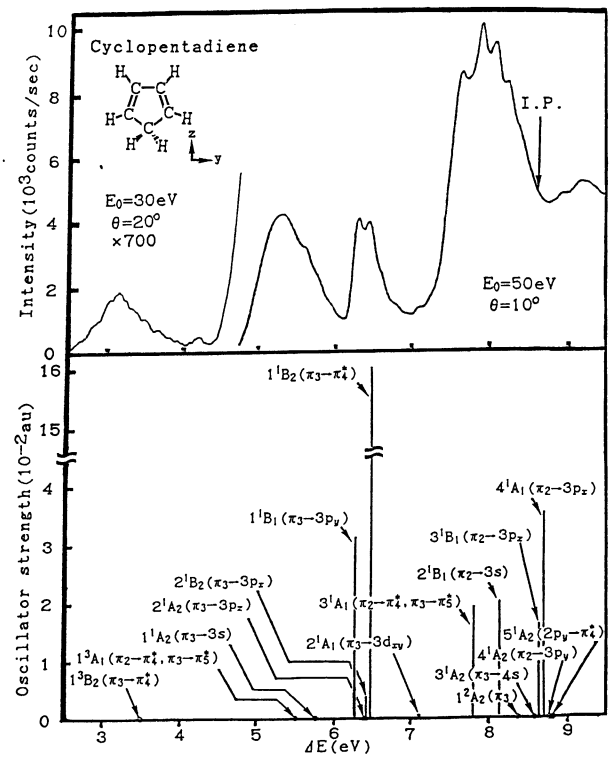

FIG. 4. Experimental and theoretical excitation spectra of cyclopentadiene.

transition to the $2\ ^1A_2$ ($\pi_3 \rightarrow 3p_z$) state is optically forbidden. Kuppermann *et al.*[28] considered the peak observed at 7.05 eV to be the Rydberg one. Our calculation support them and assign the peak to the $2\ ^1A_1$ ($\pi_3 \rightarrow 3d_{xy}$) state. The Rydberg-valence mixing seems to be small for this state. The second valence excitation was observed at 8.03 eV and the corresponding theoretical one is $3\ ^1A_1$ ($\pi_2 \rightarrow \pi_4^*$, $\pi_3 \rightarrow \pi_5^*$) state calculated at 7.81 eV. In the region of 8.1–8.8 eV, the Rydberg excitations from the π_2 MO (next HOMO) to the $3s$ and $3p$ MO's are calculated. The ordering was $3s$, $3p_z$, $3p_x$, and $3p_y$ which is slightly different from that of the corresponding Rydberg excitations from the π_3 MO (HOMO). The Rydberg excitation $\pi_3 \rightarrow 4s$ ($^1A_2$) was also calculated in this region. Experimentally, the spectra in this region is rather complicated and the detailed assignments are difficult. The present theoretical results will be useful when more detailed spectral information is obtained in the future.

In comparison with pyrrole and furan, cyclopentadiene has the highest occupied σ orbital in rather higher energy region. In Table XI, we compared the highest three occupied orbitals of pyrrole, furan, and cyclopentadiene. It is expected for cyclopentadiene that the $\sigma \rightarrow \pi^*$ excitation may occur close to the $\pi \rightarrow \pi^*$ excitation. This is confirmed by the SAC-CI calculation. The $\sigma \rightarrow \pi_4^*$ ($5\ ^1A_2$) excitation was calculated at 8.81 eV. Such tendency was already reported for butadiene from experiments.[17]

In the system of butadiene and its derivatives, it was reported[17,29] that the ratio of the oscillator strength between $N \rightarrow V_1$ and $N \rightarrow V_2, V_3$ absorption bands is a function of the dihedral angle of the two ethylenic parts. The value of $f(N \rightarrow V_1)/f(N \rightarrow V_2, V_3)$ is large in the *trans* system, but small in the *cis* system. Experimentally, cyclopentadiene has the same tendency as the *cis* system, as expected. However, the ratio of the oscillator strength calculated by the SAC-CI theory resembles that of the *trans* system. Probably, this is related with the failure of the present calculation to reproduce the position of the lowest $\pi \rightarrow \pi^*$ excitation.

Kuppermann *et al.* commented that cyclopentadiene must be considered as a dienyl π-electron system and hyperconjugation would not play an important role in the lowest triplet state for the following two reasons.[28] One is that the lowest triplet excitation energies of cyclopentadiene, 1,3-cyclohexadiene, and 1,3-cycloheptadiene are rather insensitive to the ring size. Second is that the splitting of the triplet excitation energies of cyclopentadiene is larger (> 1.6 eV) than those of the other five-membered conjugated molecules for which the aromatic ring model is adequate (e.g., 0.87 eV for pyrrole, 1.23 eV for furan). Experimentally, the second triplet state of cyclopentadiene was not observed due to a masking by the singlet valence excitation and therefore the discussion due to Kuppermann *et al.* was based on the estimate from the spectra of other molecules. Here, however, our calculation predicts the second triplet excitation at the energy of 5.50 eV, as shown in Table X, and the gap between the two lowest triplet states are calculated to be as large as 2.0 eV. This result supports the conclusion due to Kuppermann *et al.* Further, the separation of the two lowest triplet states was calculated to be 0.52 eV for pyrrole and 1.35 eV for furan, in agreement with the experimental values 0.87 and 1.23 eV, respectively.

TABLE XI. MO energy of five-membered ring compounds (HF, a.u.).

MO	Pyrrole	Furan	Cyclopentadiene
π_3	−0.2998	−0.3315	−0.3103
π_2	−0.3504	−0.4059	−0.4140
HO σ	−0.5304	−0.5420	−0.5013

IV. IONIZATION POTENTIAL

A. Pyrrole

In Table XII, we summarized the valence ionization potential of pyrrole. Along with the Koopmans' values and the results of the Green function method due to von Niessen *et al.*,[30] the present SAC-CI results are compared with experiments.[16(b),31] The present assignments of the ionization potentials are the same as those due to the Green function method. The Koopmans' values are too large to compare with experiments except for the lowest ionization. As for the calculations including electron correlations, the calculated results tend to be higher than the experimental ones. The maximum deviation is about 0.5 eV in our SAC-CI method and about 0.8 eV in the Green function method.

TABLE XII. Valence ionization potential of pyrrole (eV).

State	MO	Koopmans	SAC-CI	Exptl.		Green fn.[c]
			3-excited	Derrick[a]	Klasinc[b]	
$1\ ^2A_2$	$1a_2(\pi_3)$	8.16	7.95	8.21	8.02	8.17
$1\ ^2B_1$	$2b_1(\pi_2)$	9.54	8.73	9.20	9.05	8.92
$1\ ^2A_1$	$6a_1$	14.43	12.68	12.60	12.85	12.98
$1\ ^2B_2$	$4b_2$	14.91	13.18	~13.0	12.85	13.39
$2\ ^2B_1$	$1b_1(\pi_1)$	15.56	13.62	~13.7	13.57	13.70
$2\ ^2B_2$	$3b_2$	15.92	14.12	~14.3	14.27	14.37
$2\ ^2A_1$	$5a_1$	16.29	14.41	~14.8	14.80	14.86
$3\ ^2A_1$	$4a_1$	20.19	17.94	~17.5	...	18.17
$3\ ^2B_2$	$2b_2$	20.96	18.65	~18.1	18.20	18.96
$4\ ^2A_1$	$3a_1$	21.78	19.41	~18.8	18.90	19.64

[a] Reference 16(b).
[b] Reference 31.
[c] Reference 30.

TABLE XIII. Valence ionization potential of furan (eV).

State	MO	Koopmans	SAC-CI 3-excited	SAC-CI 3,4-excited	Exptl.[a]	Green fn.[c] OVT	Transition operator[d]
$1\,^2A_2$	$1a_2(\pi_3)$	9.20	8.90	8.90	8.87	8.87	8.00
$1\,^2B_1$	$2b_1(\pi_2)$	11.05	10.16	10.15	10.38	10.36	9.29
$1\,^2A_1$	$6a_1$	14.75	12.61	12.55	12.94	13.30	12.13
$2\,^2A_1$	$5a_1$	15.61	13.68	13.60	13.84	14.10	14.20
$1\,^2B_2$	$4b_2$	15.96	14.26	14.24	14.47	14.69	14.94
$2\,^2B_2$	$3b_2$	16.63	14.88	14.85	15.20	15.17	15.06
$2\,^2B_1$	$1b_1(\pi_1)$	17.40	15.10	14.76	(15.2)	15.47	15.51
$3\,^2A_1$	$4a_1$	20.38	18.03	17.81	17.77	18.48	19.64
$4\,^2A_1$	$3a_1$	21.39	19.04	18.80	18.8[b]	19.25	20.69
$3\,^2B_2$	$2b_2$	22.16	19.83	19.73	~19.7[b]	20.17	21.19

[a] Reference 32.
[b] Reference 33.
[c] Reference 34.
[d] Reference 35.

In the present SAC-CI calculation, the larger discrepancy between theory and experiment occurs for the higher ionization peaks for which the mixing with the shake up configurations is expected to become more important. Indeed, Tanaka *et al.*[12] noted that a significant mixing of shake up configurations with the third π-electron ionized state. In their π-CI calculations, this state consists of a mixture of three configurations. The weight of the main Koopmans' type configuration was 47%. In the "3-excited" level of calculations of the SAC-CI theory, we have included only up to three-electron excitations including ionization. Therefore, it is not well suited for the calculation of the shake up states and this is the reason of larger discrepancy in the deeper region of the ionization potential.

B. Furan

Table XIII shows the valence ionization potentials of furan. The experimental values[32,33] are compared with the result of Koopmans' theorem. Green function results of von Niessen *et al.*,[34] the results of transition operator method,[35] and the results of our SAC-CI method. For the SAC-CI calculations, we reported two types of calculations which differ each other in the unlinked term. One is the "3-excited" calculation in which the unlinked terms are composed of the double excitations from the Koopmans' type ionized configurations. In the "3,4-excited" calculations, we considered further the double excitations from the simultaneous ionization-excitation configurations. The unlinked terms of 3-excited calculation are composed of triple excitations (one ionization plus two excitations) and those of "3,4-excited" calculations are composed of triple and quadruple excitations. The 3,4-excited calculations are more reliable and can be compared not only with the ordinary ionizations but also with the shake-up ionization processes.[3,36]

From Table XII, we see that the present results confirms the assignments of the ionization spectra due to von Niessen *et al.*, though there were some controversial situations for the assignments due to the semiempirical method.[34] The present SAC-CI results show good overall agreement with experiments. The agreement is best for our SAC-CI theory. Our results agree with experiments to within 0.4 eV. The Green function approach[30] gives an agreement to within 0.9 eV and the transition operator method[31] to within 1.1–1.9 eV. Further, a good improvement due to the 3,4-excited calculations are seen particularly in the relatively high ionization potential region. There, the mixing of simultaneous ionization-excitation processes to an ordinary Koopmans' type process becomes increasingly important.

C. Cyclopentadiene

Table XIV shows the valence ionization potentials of cyclopentadiene. Our SAC-CI results are compared with the experimental data[37] and the Green function results of von Niessen *et al.*[38]

Again, the present results support the assignment of the ionization spectra due to von Niessen *et al.* On the other hand, semiempirical calculations have given some controversial situation between theory and experiment and among theories.[37,39] However the HAM/3 theory developed by Asbrink, Lindholm *et al.* seems to give rather reliable and consistent interpretations of the electronic spectra.[33,40] The Koopmans' values are too large to be able to be used for accurate assignment. The Δ SCF method tends to give smaller values than experiments. Considering the results of pyrrole, furan, and cyclopentadiene, we conclude that for a reliable assignment of the ionization spectra, we need an *ab initio* calculation which includes sufficient amount of electron correlations. For the five-membered compounds stud-

TABLE XIV. Valence ionization potential of cyclopentadiene (eV).

State	MO	Koopmans	SAC-CI 3-excited	Exptl.[a]	Green fn.[b]
$1\,^2A_2$	$1a_2(\pi_3)$	8.53	8.38	8.57	8.38
$1\,^2B_1$	$2b_1(\pi_2)$	11.53	10.68	10.72	10.86
$1\,^2B_2$	$4b_2$	13.60	12.14	~12.2	12.40
$1\,^2A_1$	$6a_1$	13.90	12.21	~12.6	12.71
$2\,^2A_1$	$5a_1$	14.52	12.76	13.2	13.22
$2\,^2B_2$	$3b_2$	15.45	13.68	13.8	14.11
$2\,^2B_1$	$1b_1(\pi_1)$	16.22	14.82	14.8	15.12
$3\,^2A_1$	$4a_1$	19.12	17.08	16.4	17.44
$3\,^2B_2$	$2b_2$	19.76	17.75	17.5	18.04
$4\,^2A_1$	$3a_1$	20.49	18.40	18.4	18.73

[a] Reference 36.
[b] Reference 37.

ied here, the calculations due to von Niessen *et al.* established the assignments of the spectra. The present SAC-CI method supports their assignment. The agreement with experiments is again better for our SAC-CI calculations (within 0.7 eV) than for the Green function calculations (within 1.1 eV), showing a superiority of our method for general cases. Further, only the SAC-CI method is applicable for both excitation spectra and ionization spectra.

V. CONCLUSION

In this paper, we have applied the SAC and SAC-CI theory to the calculations of the valence and Rydberg excitations and ionizations of pyrrole, furan, and cyclopentadiene. These molecules are larger than those to which the SAC and SAC-CI theories have been applied so far. One of the purposes of the present calculation was to confirm the continuous applicability of our theory to larger systems. From the present results, such applicability seems to be confirmed.

For almost all cases, the experimental values were reproduced to within 0.3 eV for excitation energies, and to within 0.5–0.7 eV for ionization potentials.

However, there was a few remarkable disagreements of the order of 1.2 eV for the singlet $\pi \rightarrow \pi^*$ valence excitation of $2\ ^1A_1$ state of furan and $1\ ^1B_2$ state of cyclopentadiene. The MRSD-CI calculations with almost the same basis set and geometry have also given a similar disagreement for furan. Therefore we think that this large discrepancy is not due to the defect of the SAC and SAC-CI theory itself but due to the defects in the basis set and/or to the change in geometry between the ground and the valence excited state.

For pyrrole, our calculation included explicitly the Rydberg *d* basis set, in contrast to the previous ones. We found that the transition observed at 6.78 eV is the Rydberg transition to the $3d_\pi$ MO, in agreement with the experimental estimate. We have ascertained the indispensability of the diffuse *d* basis set for an appropriate description of the excited states and the one-electron properties of this system.

For furan, we have also given several assignments of the spectra. For example, the peaks observed at 7.79 and 7.82 eV were assigned to the $2\ ^1B_2\ (\pi_3 \rightarrow \pi_4^*)$ and $2\ ^1B_1\ (\pi_2 \rightarrow 3s)$ states, respectively. In comparison with pyrrole, there was little admixture of valence and Rydberg configurations in all the regions of the excitation spectra.

This is the first calculation of the excited states of cyclopentadiene by the *ab initio* method including electron correlation. We have given several new and detailed assignments of the spectra. We have supported the dienyl π electron model as given by Kuppermann *et al.* from the analysis of experimental spectra.

For ionization potential, the SAC-CI calculations for pyrrole, furan, and cyclopentadiene reproduced well the ionization spectra. In the semiempirical calculation, some controversial situations have been seen for the assignment. For these three molecules Koopmans' method offers the same ordering as the results of the *ab initio* calculations including electron correlation. The value based on this method is too large to be used to assign correctly the ionization potential even when all the peaks are measured, because of the existence of the shake up bands. On the other hand, Δ SCF method has the tendency of giving too small ionization potential. Then, for a correct assignment we need an *ab initio* method which includes a sufficient amount of electron correlation. For pyrrole, furan, and cyclopentadiene, we think that the Green function calculations due to von Niessen *et al.* have established the assignment of the ionization potential. The present SAC-CI calculations support their assignments and give better overall agreement with the experimental values. Further, the SAC-CI method is applicable to both excited and ionized states in contrast to the Green function method.

TABLE XV. Computer times for the SAC and SAC-CI calculations (min per solution).

Step	Pyrrole	Furan	Cyclopentadiene
SAC	16.9	18.3	17.6
SAC-CI			
singlet state			
3-excited	5.1	6.5	5.7
3,4-excited		3.5	
triplet state			
3-excited	13.4	9.7	4.8
3,4-excited		5.9	
ionized state			
3-excited	4.8	5.6	3.7
3,4-excited		5.5	

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APPENDIX

The referee suggested to mention the computer time. We summarized the computer time used for the SAC and SAC-CI calculations in Table XV. We used the HITAC M-200H computer and its average velocity for the Lawrence Livermore loop is 4.56 MFLOPS[41] (cf. 1.43 MFLOPS for IBM 3033 and 3.41 MFLOPS for CDC 7600).

For furan we have done two types of calculations, namely 3-excited calculation and 3,4-excited one. In the latter case, we used the converged solution of the former as an initial guess. For the single and triplet states we gave the results of only the latter method in the text and in the tables.

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