Cluster expansion of the wave function. Valence excitations and ionizations of pyridine

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The SAC (symmetry-adapted cluster) and SAC-CI theories are applied to the calculations of the valence excitations and the ionizations of pyridine. The active space consists of 85 MOs (35π and 50 σ MOs). For the valence $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ excited states, $S_1(1\,^1B_2)$, $S_2(1\,^1A_1)$, $S_3(2\,^1B_2)$, $S_n(1\,^1B_1)$, $T_1(1\,^3A_1)$, and $T_n(1\,^3B_1)$, the calculated excitation energies are higher than the experimental values by within $\sim$0.7 eV. Although the $S_4(2\,^1A_1)$ state is experimentally considered not to be split from S_3, the present calculation predicted it to be higher than S_3 by 0.31 eV. The average discrepancy from the experimental data is 0.55 eV without including S_4. The transition energies and some other properties are predicted for the valence $\pi\rightarrow\pi^*$ excited states, $T_2(1\,^3B_2)$, $T_3(2\,^3A_1)$, $T_4(2\,^3B_2)$ and for the $n\rightarrow\pi^*$ excited states, $S'_n(1\,^1A_2)$ and $T'_n(1\,^3A_2)$, for which the experimental values are unavailable so far. The following two observations seem to be interesting. (i) The valence $\pi\rightarrow\pi^*$ excited states of pyridine are understood from those of benzene, reported previously, as a result of perturbation, an alteration of one C–H group to an isoelectronic nitrogen atom. The typical V states, S_3 and S_4, show large σ-reorganization effect, which is detected as the change in the transition energy and some one electron properties. (ii) For the relative positions between the $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ excitations, our results are as follows. The lowest singlet excited state is $n\rightarrow\pi^*[S_n(1\,^1B_2)]$. The lowest triplet state is $\pi\rightarrow\pi^*[T_1(1\,^3A_1)]$ and $n\rightarrow\pi^*[T_n(1\,^3B_1)]$ exists higher than T_1 by 0.15 eV. Experimentally, the lowest singlet excitation is confirmed to be $n\rightarrow\pi^*$, but two controversial assignments exist for the lowest triplet state: $\pi\rightarrow\pi^*$ or $n\rightarrow\pi^*$. For the ionization potential, the experimental spectra is reproduced to within $\sim$0.6 eV. The nature of the first three peaks are calculated as $n\pi\pi$, which is supported by some recent experimental studies. The similarity and difference in the satellite peaks of benzene and pyridine are pointed out.

I. INTRODUCTION

Pyridine is a key hetero aromatic compound. The electronic theory for ring conjugated systems has been developed using benzene as a key molecule.[1–4] Pyridine has been used, in the development of these theories, as a first molecule in the hetero aromatics.[5–7] This compound has been extensively investigated experimentally in the organic photophysics as much as benzene.[7–14] There is, however, no theoretical treatment on this key molecule from a strictly *ab initio* point of view.

In this series of articles, we have developed a cluster-expansion-based formalism for the studies of the ground and excited states of molecules. The SAC (symmetry-adapted-cluster) expansion[15] is applied to a closed- or open-shell ground state, and the SAC-CI theory[16] to its excited, ionized, and electron-attached states. The details of the SAC and SAC-CI theories and the algorithm of calculations have already been reported.[15–21] 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,[22] a property probably necessary to describe a large system such as pyridine. 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 the ground and excited states. The orthogonality and Hamiltonian orthogonality are satisfied between the SAC and SAC-CI solutions.[16] This property is required for the wave functions of the ground and excited states.

We are interested in the nature of the electron correlations in the excited states of π-conjugated molecules. Previously, we studied ethylene,[18(a)] formaldehyde,[18(b)] *trans*-, *cis*-butadiene,[18(c)] and five membered ring compounds, pyrrole, furan, and cyclopentadiene.[19] Lastly, we dealt with benzene[20] and naphthalene,[18(d)] key aromatic molecules, on their valence and Rydberg excited and ionized states. We here study the valence excited and ionized states of pyridine. We investigate the similarity and the difference between the benzene aromatics and the pyridine hetero aromatics. Two points are interesting. One is the change in the valence $\pi\rightarrow\pi^*$ excited states, caused by a perturbation of replacing one C–H group by a nitrogen atom. Another is the relative position between these $\pi\rightarrow\pi^*$ states and the $n\rightarrow\pi^*$ states generated from the nitrogen lone pair.

We here summarize some natures of the valence $\pi\rightarrow\pi^*$ excited states of benzene, which are pertinent for understanding those of pyridine.

(i) About the lower three excited states, $T_1(^3B_{1u})$, $T_2(^3E_{1u})$, and $S_1(^1B_{2u})$, the excitation energies are reproduced reasonably well within π-CI.[23] These three states are typical covalent states.

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(ii) The higher two optically forbidden states, $T_3(^3B_{2u})$ and $S_2(^1B_{1u})$, require the inclusion of the σ electron correlation as much as the π one. The π space readjustment after the inclusion of the σ electron correlation is small.

(iii) For the $S_3(^1E_{1u})$ state, the σ correlation effect is very important. This state is optically allowed, and is a typical V state after Mulliken.[24(b)] As in the V state of ethylene,[24–29] the σ-correlation effect is indispensable to obtain a reliable excitation energy. Another important feature, different from the T_3 and S_2 states, is a large π-space readjustment after inclusion of the σ electron correlation. This phenomena is observed in the behavior of the π electron cloud. The theoretical π electron cloud expands like a Rydberg orbital when only π electron correlation is included, but shrinks to the quasivalence one after inclusion of the σ electron correlation. This change is reflected in the theoretical transition dipole moment.

The characteristic correlation between the σ and π spaces in the V state of ethylene were called left–right correlation.[26] For benzene, we call it molecular in–out correlation.[20] In their studies on porphyrin, a big ring conjugated system, Sekino and Kobayashi[27] pointed out that an instantaneous counterpolarization of the σ electron system against the motion of π electrons is especially significant in the strongly allowed ($\pi\pi^*$) excited state. The large $\sigma\pi$ interaction in the optically allowed excited states of the conjugated systems is claimed by Shibuya *et al.*[28] too. Recently, Matos *et al.* studied the excited states of benzene with the CASSCF-CCI (complete active space SCF-contracted CI) method and reported the significance of the $\sigma\pi$ electron correlation in the ionic states of benzene.[29]

The valence orbitals of pyridine are compared in Fig. 1 with those of benzene. The valence $\pi\rightarrow\pi^*$ excitation from π_2 or π_3 MO to π_4^* or π_5^* MO gives eight different states: four singlet states, $1\,^1B_2$, $1\,^1A_1$, $2\,^1B_2$, $2\,^1A_1$, and four triplet

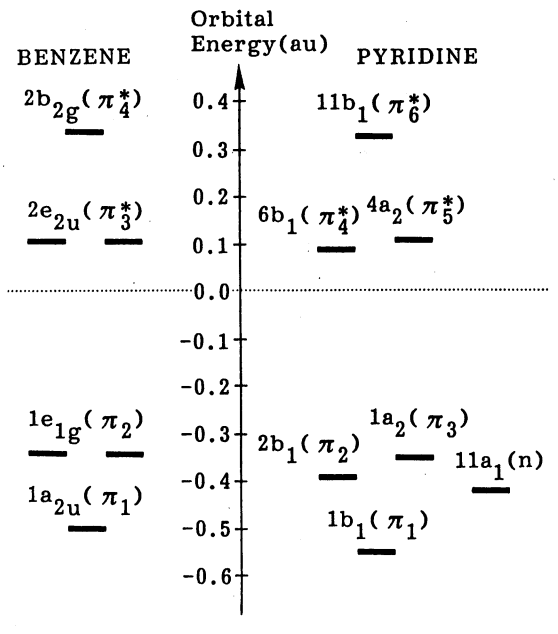

FIG. 1. Comparison of the SCF orbital energies between benzene and pyridine.

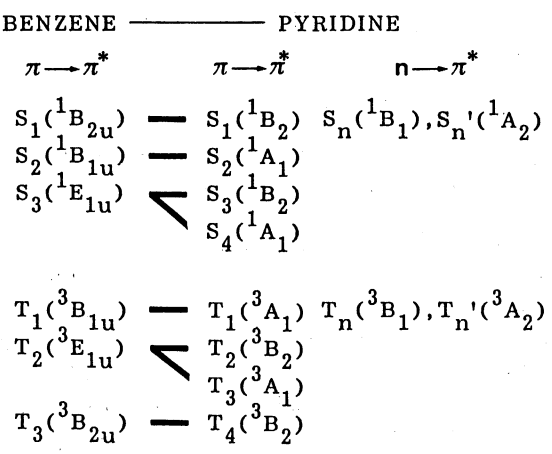

FIG. 2. Correspondence of the electronic excited states between benzene and pyridine.

states, $1\,^3A_1$, $1\,^3B_2$, $2\,^3A_1$, $2\,^3B_2$, which are referred to in this paper as S_1, S_2, S_3, S_4, and T_1, T_2, T_3, T_4, respectively. These electronic states correspond to the S_1–S_3 and T_1–T_3 states of benzene as summarized in Fig. 2. As seen in Fig. 1, the nitrogen lone pair MO ($11a_1$) is located in the vicinity of the two highest π MOs. It is therefore expected that the $n\rightarrow\pi^*$ excited states exist in the same energy region as the $\pi\rightarrow\pi^*$ ones. In this study, we deal with four $n\rightarrow\pi^*$ states: $^1B_1$, $^1A_2$, $^3B_1$, and $^3A_2$. These states are referred to in this paper as S_n, S_n', T_n, and T_n', respectively.

Now what is the present status of the theoretical studies on the valence excited states of pyridine? In conclusion, there are no reliable theoretical studies. Although many semiempirical results have been published,[5,7] no *ab initio* calculation has been reported except for one by Takekiyo.[6] His calculation is based on the VB method and uses the GMS (Goeppert-Mayer and Sklar) approximation[3] in the integral evaluations with the minimal-class basis function. We collect some representative theoretical and experimental results in Table I. RZ (Ridley and Zerner)[5(h)] and LA (Lindholm

TABLE I. Comparison of the past semiempirical and *ab initio* results for the valence excitation energies of pyridine (eV).

	Semiempirical		*Ab initio*	
State	RZ[a]	LA[b]	T[c]	Exptl.
S_1 ($1\,^1B_2$)	4.79	4.9	5.12	4.99[d]
S_2 ($1\,^1A_1$)	6.16	6.2	9.72	6.38[d]
S_3 ($2\,^1B_2$)	7.05	7.5	10.82	7.22[d]
S_4 ($2\,^1A_1$)	7.05	7.1	11.28	...[e]
S_n ($1\,^1B_1$)	4.30	4.9	...	4.59[f]
S_n' ($1\,^1A_2$)	5.45	...	...	...

[a] Reference 5(h).
[b] Reference 7. The values are read from their schematic summary.
[c] Reference 6.
[d] Reference 8.
[e] See the text.
[f] Reference 9.

and Asbrink)[7] are due to the semiempirical methods, INDO and HAM, respectively. The abbreviation T stands for Takekiyo.[6] Experimental results correspond to the band maxima of the UV spectra by Bolovinos *et al.*[8] and Goodman.[9] The semiempirical data are consistent with the experimental ones. It is, however, evident that these data are not theoretically produced from the first principle. *Ab initio* results by Takekiyo are higher than the experimental results by 3–4 eV except for the lowest singlet excited state. This situation is similar to the one in the VB study of benzene by Tantardini *et al.*[30]

Wadt *et al.*[31] studied pyradine, para-diazabenzene, with the GVB-π-CI method. Their calculational level corresponds to that of the π-CI of benzene by Hay and Shavitt.[32] Their results may be summarized as:

(i) The lowest $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ states were reproduced to within ~ 0.2 eV of the experimental values.

(ii) The higher excited $\pi \rightarrow \pi^*$ states, namely, more polar states, were calculated to be higher than the experimental results by ~ 2 eV.

This result seems to imply that the theoretical characteristics obtained for benzene[23] hold even for the diazabenzene.

Experimentally the assignments of the singlet excited states of pyridine are well established.[8,9,12] There is, however, a controversial situation on the assignment of the first and second triplet excited states.[13,14] Highly reliable theoretical studies are required to resolve such a problem. It is also our main interest whether our knowledge on benzene, especially on the role of the σ electron correlations, hold for the azabenzene.

For the ionization spectra of pyridine, von Niessen, Cederbaum *et al.* reported the theoretical spectra for the outer and inner valence ionizations.[33] Their Green function method seems to be useful to investigate these properties.[34] Using the VB method, Tantardini and Simonetta calculated the ground and several doublet states.[35] Experimentally several photoelectron spectra have been reported, but some problems still remain on the assignment of the peaks, especially on whether it is n character or π character.[36–45] A reliable theoretical assignment is necessary to resolve this problem.

In this paper, we systematically study the valence excitations and ionizations of pyridine by the SAC and SAC-CI methods, 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 excited states, and ionized states. The conclusion of the present study is given in the last section.

II. CALCULATIONAL DETAILS

The ground state of pyridine is calculated by the SAC theory.[15] The SAC-CI theory[16] is used for the calculations of the singlet, triplet, and ionized states. We use a slightly modified version of the SAC85 program.[21] As reference orbitals, we use Hartree–Fock SCF MOs of the ground state for all the states studied here. They are calculated by the HONDO program.[46]

The geometry of the ground state of pyridine was determined by the microwave study.[47] 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 z axis, as pictured in Fig. 3.

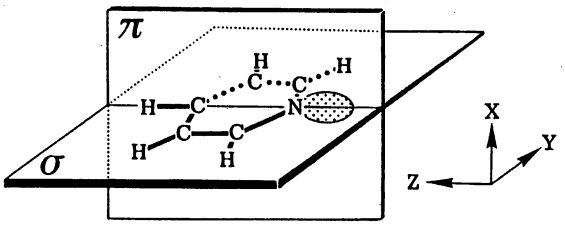

FIG. 3. Geometry of pyridine.

The quality of the basis set we used is similar to that for benzene[20]: the [4*s*2*p*/2*s*] set of Huzinaga–Dunning[48,49] plus diffuse p_π functions (0.034 77, 0.010 75) on each carbon and nitrogen atom. This set is argumented by the polarization d_π function (0.75) on each carbon atom and d function (0.80) on a nitrogen atom.[50]

These 98 AOs give 97 MOs, $35\pi + 62\sigma$, because of a linear dependence among these AOs. We consider the following three active spaces.

(i) 35π: all valence and Rydberg π MOs.

(ii) $35\pi + 1N$: (i) plus one occupied MO of lone pair (n) character.

(iii) $35\pi + 50\sigma$: (i) plus all the valence and Rydberg σ MOs.

To diminish the size of calculations, we select the linked operators by a perturbation selection technique.[17(a)] Main reference configurations are those which have large coefficients (>0.1) in the SE (single excitation)-CI. For those states 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

TABLE II. Dimensions of the matrices involved in the SAC/SAC-CI calculations of pyridine.

State	35π	$35\pi + 1N$	$35\pi + 50\sigma$
Ground $^1A_1$	598	636	1710
Excited			
$^1A_1$	855	882	3158
$^1A_2$	···	546	2220
$^1B_1$	···	644	3575
$^1B_2$	1112	1133	5282
$^3A_1$	1143	1160	4678
$^3A_2$	···	909	3831
$^3B_1$	···	1069	7569
$^3B_2$	1182	1196	5446
Ionized			
$^2A_1$			1120
$^2A_2$			216
$^2B_1$			441
$^2B_2$			1089

of the present calculations. For the configurations arising additionally in the $\pi+\sigma$ calculations, we adopt the thresholds 8×10^{-5} a.u. Since the π configurations used in the 35π calculations are completely included in the $\pi+\sigma$ calculations, we can quantitatively discuss the σ electron correlation effect. Table II shows the dimensions of the SAC and SAC-CI calculations for the valence excitations and ionizations.

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 include 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 the 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 coefficient in the SD-CI for the ground state is larger than 1×10^{-3}, and the main reference configurations are selected as those whose coefficient in the SD-CI for each state is larger than 1×10^{-1}.

TABLE III. SCF result for the ground state of pyridine (a.u.).

MO	Orbital energy		$\langle z\rangle$[a]	$\langle x^2\rangle$[b]	$\langle y^2\rangle$	$\langle z^2\rangle$
$5a_1$	−1.259 178		1.479	0.7	2.0	4.1
$6a_1$	−1.091 824		−1.160	0.8	2.7	5.4
$3b_2$	−1.039 239		0.156	0.8	6.5	2.5
$7a_1$	−0.862 566		−0.672	0.7	6.0	5.5
$4b_2$	−0.858 247		0.173	0.6	5.9	5.5
$8a_1$	−0.726 942		−0.417	0.6	6.5	7.2
$5b_2$	−0.661 671		−0.058	0.5	4.5	4.5
$9a_1$	−0.655 440		−0.716	0.6	11.6	5.3
$6b_2$	−0.601 190		−0.025	0.6	9.7	3.7
$10a_1$	−0.578 723		−1.199	0.6	2.3	10.8
$1b_1$	−0.543 890	π_1	0.557	2.3	3.2	4.0
$7b_2$	−0.516 445		−0.118	0.5	9.1	4.9
$11a_1$	−0.417 511	n	2.067	0.6	3.2	9.3
$2b_1$	−0.385 977	π_2	−0.376	2.3	2.1	6.3
$1a_2$	−0.354 882	π_3	−0.075	2.5	6.2	2.2
$3b_1$	0.025 987	R_π	−2.796	85.9	29.5	34.4
$2a_2$	0.034 558	R_π	−1.715	78.3	80.7	28.3
$4b_1$	0.036 057	R_π	0.121	78.5	32.8	73.8
$3a_2$	0.045 834	R_π	1.726	74.4	76.7	73.8
$5b_1$	0.046 210	R_π	2.472	74.5	66.0	83.3
$6b_1$	0.091 405	π_4^*	−0.721	9.1	9.8	11.7
$4a_2$	0.105 494	π_5^*	−0.219	9.7	13.1	10.8
$7b_1$	0.129 045	R_π	−2.025	41.3	14.1	17.1
$5a_2$	0.142 775	R_π	−0.019	33.0	34.6	11.6
$8b_1$	0.150 166	R_π	1.747	31.8	13.1	30.0
$9b_1$	0.171 619	R_π	−2.083	22.7	29.0	31.3
$6a_2$	0.188 074	R_π	0.284	22.9	25.1	23.6
$10b_1$	0.189 312	R_π	2.632	23.7	23.0	29.8
$12a_1$	0.272 435		0.740	1.0	4.1	4.9
$13a_1$	0.277 568		1.816	2.3	3.0	11.7
$8b_2$	0.308 115		−2.295	3.2	14.2	13.7
$14a_1$	0.308 706		−1.866	3.5	12.4	16.2
$15a_1$	0.327 856		0.438	3.7	15.4	14.2
$11b_1$	0.334 237	π_6^*	−0.059	4.7	8.2	7.6
$9b_2$	0.348 017		−1.627	1.1	14.2	11.7

[a] The z axis includes the nitrogen atom.
[b] The x axis is perpendicular to the molecular plane.

TABLE IV. Total energies for the ground state of pyridine (a.u.).

Method	35π	$35+1N$	$35\pi+50\sigma$
HF	−246.664 03		
SAC	−246.754 16	−246.755 96	−246.869 43

III. RESULTS AND DISCUSSIONS

A. Ground state

The SCF orbital energy sequence of pyridine is shown in Table III, in which the dipole moment and the electronic part of the second moment calculated on these SCF orbitals are given. This table involves only valence occupied orbitals and lower virtual orbitals up to around the π_6^* MO. Among these, the main orbitals describing the valence excitations are shown in Fig. 1. In pyridine, the degenerate two valence π MOs, $1e_{1g}(\pi_2)$ and $2e_{2u}(\pi_3^*)$, of benzene are split into $2b_1(\pi_2)$ and $1a_2(\pi_3)$ and $6b_1(\pi_4^*)$ and $4a_2(\pi_5^*)$, respectively. The MOs of b_1 symmetry are slightly lower than the counter MOs of a_2 symmetry. The gap is 0.85 eV for the occupied pair and 0.38 eV for the unoccupied one. This value for the former becomes slightly small after including electron correlation: 0.57 eV. The experimental value is 0.74[36] and 0.76 eV.[51] (For more detail, see Table IX.) The MO stabilization in the b_1 symmetry is explained by the larger electronegativity of a nitrogen atom than that of a carbon one, for the MO of the a_2 symmetry has a node at nitrogen atom and the MO of the b_1 symmetry does not. Note that the lone-pair $11a_1$ MO is close to the pair of the occupied π MOs. The existence of this MO makes the spectroscopy of pyridine extremely more complicated than that of benzene.

The total energy of the ground state of pyridine is shown in Table IV. The HF energy calculated with the $[4s2p/2s]$ set alone is −246.549 069 a.u.,[33(a)] then the lowering by the polarization d_π function on carbon and d on nitrogen is $\sim$0.11 a.u. This is larger than $\sim$0.02 a.u. in benzene.[20] The HF energy calculated with the $[4s2p1d/2s1p]$ set is −246.697 261 a.u.,[52] then the polarization function on hydrogen atom plays a little role as in benzene.[20] The correlation energy is only −0.086 36 a.u. by the 35π SAC calculation, but −0.201 40 a.u., more than twice, by the $35\pi+50\sigma$ SAC calculation. This situation is similar to the case of benzene.[20] The ground state energy referred to in the following calculations of the excitation energies is −246.869 43 a.u.

The second moment calculated with this SAC wave function is 29 a.u. for $\langle x^2\rangle$, 203 a.u. for $\langle y^2\rangle$, and 205 a.u. for $\langle z^2\rangle$. The experimental values are 28 ± 3, 203 ± 3, and 204 ± 3 a.u., respectively.[53] The agreement between the theory and experiment is excellent. The calculated dipole moment is 0.940 a.u. at the SAC level, which is slightly larger than the experimental value, 0.862 a.u.[54] The direction is, of course, from nitrogen to carbon.

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

In this and the next paragraph, we discuss the calculational and experimental results on the valence excited states

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

State	SAC-CI $35\pi(\Delta^a)$	SAC-CI $35\pi+1N(\Delta)$	SAC-CI $35\pi+50\sigma(\Delta)$	Expt.
S_1 $(1\,^1B_2)$	5.37(0.38)	5.37(0.38)	5.44(0.45)	4.99[b]
S_2 $(1\,^1A_1)$	7.64(1.26)	7.63(1.25)	7.04(0.66)	6.38[b]
S_3 $(2\,^1B_2)$	8.66(1.44)	8.66(1.44)	7.85(0.63)	7.22[b]
S_4 $(2\,^1A_1)$	8.85	8.85	8.16	...[c]
S_n $(1\,^1B_1)$		5.89(1.30)	5.24(0.65)	4.59[d]
S'_n $(1\,^1A_2)$		6.58	5.69	
T_1 $(1\,^3A_1)$	3.94(0.14)	3.95(0.15)	4.34(0.54)	3.69,[e] 3.8[f]
T_2 $(1\,^3B_2)$	5.07	5.08	5.09	
T_3 $(2\,^3A_1)$	5.17	5.17	5.32	
T_4 $(2\,^3B_2)$	7.03	7.03	6.60	
T_n $(1\,^3B_1)$		5.21(1.11)	4.49(0.39)	4.1[f]
T'_n $(1\,^3A_2)$		6.47	5.69	

[a] Δ shows the difference from the experimental value.
[b] Reference 8.
[c] See the text.
[d] Reference 9.
[e] Reference 10.
[f] Reference 11.

of pyridine. We use the notations, S_1–S_4, S_n, S'_n, T_1–T_4, T_n, and T'_n in the following text and related tables and figures. The definition of these electronic states is given in the previous section and in Table V. The single excitation from the occupied π_3 MO ($1a_2$) or π_2 MO ($2b_1$) to the unoccupied π_4^* MO ($6b_1$) or π_5^* MO ($4a_2$) give eight excited states, S_1–S_4 and T_1–T_4. In Table V, we collect the results of the SAC-CI calculations and experimental data. The active spaces are 35π MOs, $35\pi+1N$ MOs, and $35\pi+50\sigma$ MOs. The experimental results for the singlet excitations are taken from the UV spectra by Bolovinos *et al.*[8] and Goodman[9] and the cited values correspond to the band maxima. The triplet data are taken from the UV spectra by Japar and Ramsay[10] and EELS (electron energy loss spectroscopy) by Doering and Moor[11] and the cited values are onset, namely adiabatic data. A schematic description of the present result is given in Fig. 4. A comparison of the energy levels between benzene and pyridine is given in Fig. 5. The SAC-CI theoretical excitation spectra are compared with the experimental spectra of Doering and Moor[11] in Fig. 6.

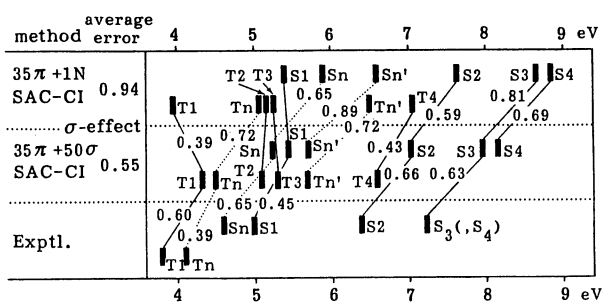

FIG. 4. Schematic summary of the SAC-CI results for the valence $\pi\rightarrow\pi^*$ (real lines) and $n\rightarrow\pi^*$ (broken lines) excitations of pyridine. The experimental results are taken from Refs. 8 and 9 for singlet excitations and from Refs. 10 and 11 for triplet ones. The values show the differences.

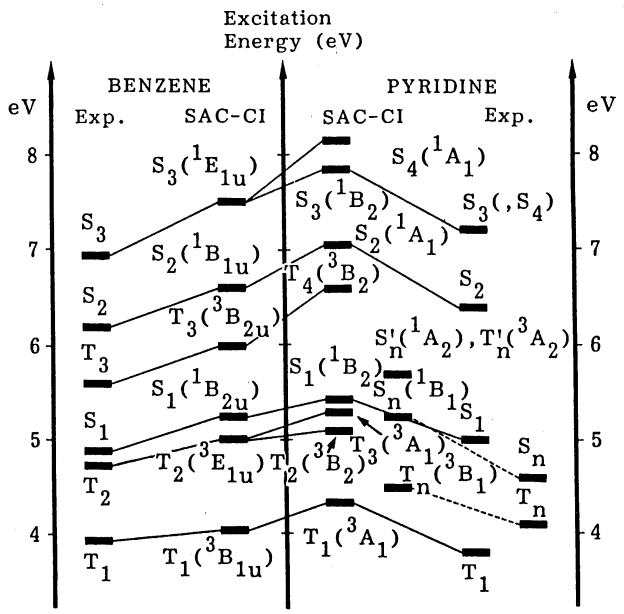

FIG. 5. Comparison of the experimental and theoretical excitation energies between benzene and pyridine.

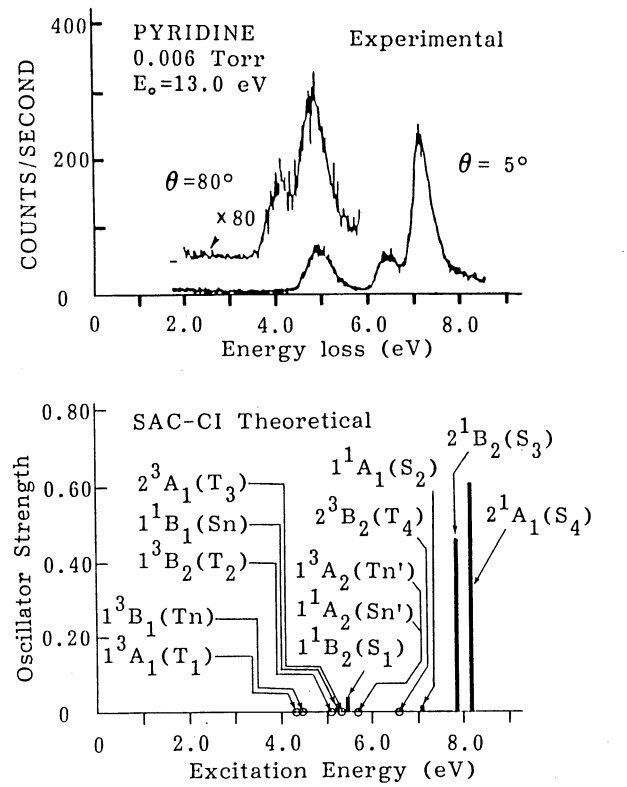

FIG. 6. Experimental (above) and theoretical (below) excitation spectra of pyridine. The experimental results are taken from Ref. 11.

TABLE VI. Electronic part of the second moment for the valence excited states of pyridine calculated by the SAC/SAC-CI method (a.u.).

	35π			$35\pi + 1N$			$35\pi + 50\sigma$		
State	$\langle x^2\rangle$[a]	$\langle y^2\rangle$	$\langle z^2\rangle$[b]	$\langle x^2\rangle$	$\langle y^2\rangle$	$\langle z^2\rangle$	$\langle x^2\rangle$	$\langle y^2\rangle$	$\langle z^2\rangle$
S_0[c]	29[c]	203[c]	205[c]	29[c]	203[c]	205[c]	29[c]	203[c]	205[c]
S_1	29	203	206	29	203	206	30	203	206
S_2	32	205	207	32	205	207	31	205	207
S_3	62	212	228	62	212	228	55	209	228
S_4	64	231	234	64	231	234	48	211	214
S_n				31	203	202	32	204	202
S'_n				31	205	201	32	206	201
T_1	29	203	205	29	203	205	29	204	206
T_2	29	202	207	29	202	207	30	202	207
T_3	29	204	205	29	204	205	30	204	206
T_4	30	205	205	30	205	205	30	206	204
T_n				31	203	202	31	204	202
T'_n				31	205	201	32	206	201

[a] The x axis is perpendicular to the molecular plane.
[b] The z axis includes the nitrogen atom.
[c] The experimental values for the ground state are $\langle x^2\rangle = 28 \pm 3$, $\langle y^2\rangle = 203 \pm 3$, $\langle z^2\rangle = 204 \pm 3$ a.u. (Ref. 53).

First we discuss the lowest excited state T_1 ($1\,^3A_1$). The excitation energy is calculated higher by 0.54 eV than the adiabatic experimental data. The discrepancy from the experimental value is large in comparison with the corresponding T_1 state ($1\,^3B_{1u}$) of benzene. The potential surface of the T_1 state is experimentally expected to have double minima owing to the perturbation from the nearly degenerate T_n state.[13(e)] This may explain the possibility that the adiabatic excitation energy is rather lower than the calculated vertical excitation energy. The detailed discussion is given in the next section in relation with the relative position between the $T_1(^3A_1{:}\pi\rightarrow\pi^*)$ and $T_n(^3B_1{:}n\rightarrow\pi^*)$ states. Here we would like to note the change in the excitation energy due to the inclusion of the σ correlation. The excitation energy is higher by 0.39 eV in the $\pi+\sigma$ calculation than in the π one. This is similar to the T_1 state of benzene, where this change is 0.26 eV. The contribution of the σ electron correlation depends on the ionicity of the electronic state under consideration.[24] The above observation indicates that the T_1 state is less polar than the ground state. For the T state of ethylene, a similar discussion was given by Ryan and Whitten.[26(a)] The calculated one-electron properties are summarized in Tables VI and VII. The σ correlation gives little effect to this state. This state is typically valence in nature.

Second we discuss the next three states, S_1, T_2, and T_3. As summarized in Fig. 5, the S_1 state ($1\,^1B_2$) corresponds to the S_1 state ($1\,^1B_{2u}$) of benzene. The excitation energy of this state calculated by the present theory is larger than the experimental value by 0.45 eV. The degenerate T_2 state ($1\,^3E_{1u}$) of benzene splits into the $T_2(1\,^3B_2)$ and $T_3(2\,^3A_1)$ states of pyridine. For these states, there is no experimental results, as far as we know. We, however, expect that the present SAC-CI values would be higher than the future experimental values by within 0.3 eV, which is the corresponding deviation in benzene. As seen from Fig. 4 and Table V, the S_1, T_2, and T_3 states show only a small change after inclusion of the σ electron correlation: viz., 0.07, 0.01, and 0.15 eV, respectively. These three states have the σ electron correlation similar to that of the ground state. This situation is the same as that of the corresponding states of benzene.[20] A small difference between the T_2 and the T_3 states is caused by the difference in the perturbation of changing the C–H group to the nitrogen atom. The wave function of the $T_2(^3B_2)$ state has the node at the nitrogen atom, but that of the $T_3(^3A_1)$ state does not. Therefore, the change from benzene to pyridine affects more the T_3 state than the T_2 one. As seen from Fig. 5, the deviation from benzene is larger for the T_3 state than for the T_2 state.

In Tables VI and VII, we summarize the calculated values of the electronic part of the second moment, and the

TABLE VII. Dipole moment for the ground and valence excited states of pyridine calculated by the SAC/SAC-CI method (a.u.).

State	35π $\langle z\rangle$[a]	$35\pi + 1N$ $\langle z\rangle$	$35\pi + 50\sigma$ $\langle z\rangle$
S_0[b]	0.944[b]	0.941[b]	0.940[b]
S_1	0.826	0.825	0.823
S_2	1.037	1.032	0.896
S_3	3.482	3.472	− 1.216
S_4	2.267	2.255	0.571
S_n[c]		− 0.242[c]	− 0.466[c]
S'_n		− 0.468	− 0.571
T_1	0.871	0.870	0.886
T_2	0.795	0.792	0.780
T_3	0.999	0.996	0.979
T_4	1.398	1.386	1.262
T_n		− 0.181	− 0.470
T'_n		− 0.427	− 0.531

[a] The z axis is the molecular axis passing through the nitrogen atom.
[b] Exptl. $\langle z\rangle = 0.862$ a.u. (Ref. 54). The value calculated from the HF wave function is 0.966 a.u.
[c] Exptl. $\langle z\rangle = -0.393$ a.u. (Ref. 59).

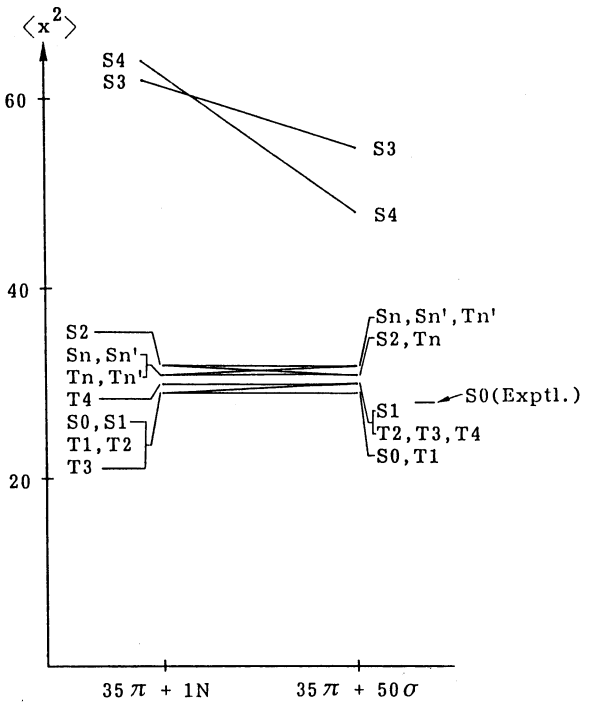

FIG. 7. Schematic summary of the SAC-CI results for the electronic part of the second moment (a.u.).

dipole moment. The change in these one-electron properties owing to the inclusion of the σ electron correlation is pictured in Figs. 7 and 8. We see that the excited states, S_1, T_2, and T_3, are unambiguously valence in nature. The oscillator strength is given in Table VIII. The S_1 state of pyridine is optically allowed and the oscillator strength is observed to be 0.029[8] or 0.04.[55] The calculated value, 0.038 is in good agreement with the experimental value. The corresponding S_1

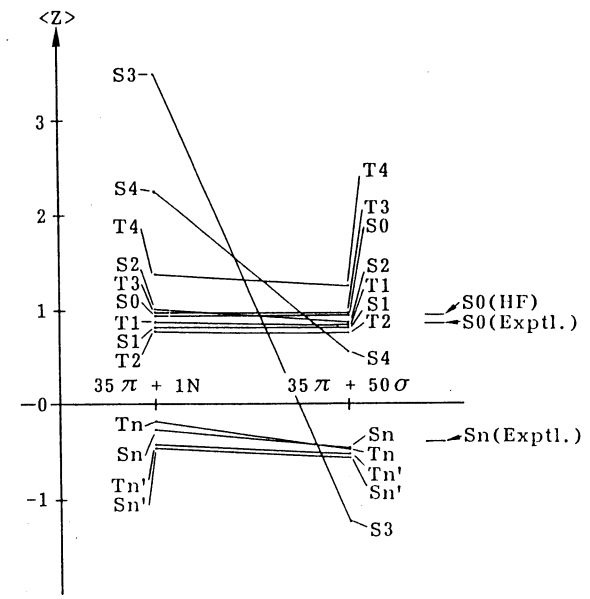

FIG. 8. Schematic summary of the SAC-CI results for the dipole moment (a.u.).

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

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

[a] Reference 8.
[b] Reference 55.
[c] The molecule is placed on the yz plane with the z axis being the molecular axis.
[d] Reference 56.
[e] Not calculated.

state in benzene is optically forbidden but has a nonzero oscillator strength, 0.0013,[8] by borrowing the strength from the upper optically allowed S_3 state. The peak of the S_1 state of pyridine thus seems to be almost owing to the lowering in symmetry from D_{2h} to C_{2v}.

Figures 9 and 10 show the contour maps of the difference density on the π plane of Fig. 3 due to each excitation. The maps (a), (b), (c), and (d) show the differences in 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. The contour map for the S_1 state is displayed on the left-hand side of Fig. 9. The map (a) owing to the π SAC-CI and the map (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 electron reorganization. This observation explains why the excitation energy is little affected by the inclusion of the σ electron correlation. The same was true for the case of the S_1 state of benzene, the left side of Fig. 4 of Ref. 20.

Next we discuss the S_2 and T_4 states. These states correspond to the S_2 and T_3 states of benzene, respectively. By the inclusion of the σ electron correlation, the excitation energies of these two states are lowered by 0.59 and 0.43 eV, respectively. The S_2 state is calculated higher by 0.66 eV than the experimental value. Although no experimental data is reported for the T_4 state, the discrepancy would be of this order, for the difference about the corresponding T_3 state of benzene was 0.42 eV.

The effect of the σ electron correlation on the second moment and dipole moment of the S_2 and T_4 states is small as seen from Tables VI and VII. These values are similar to that of the ground state, showing that these states are typically valence in nature. This is also similar to the S_2 state and T_3 state of benzene. As seen in Table VIII, the S_2 state of pyridine is optically allowed and the oscillator strength is calculated as 0.021. The experimental value is 0.90[8] and 1.36,[56] so that the difference between theory and experiment is extraordinarily large. The corresponding S_2 state of benzene is optically forbidden but has the nonzero oscillator strength, 0.09,[57] owing to the intensity borrowing due to the vibronic coupling with the upper strongly optically allowed S_3 state of

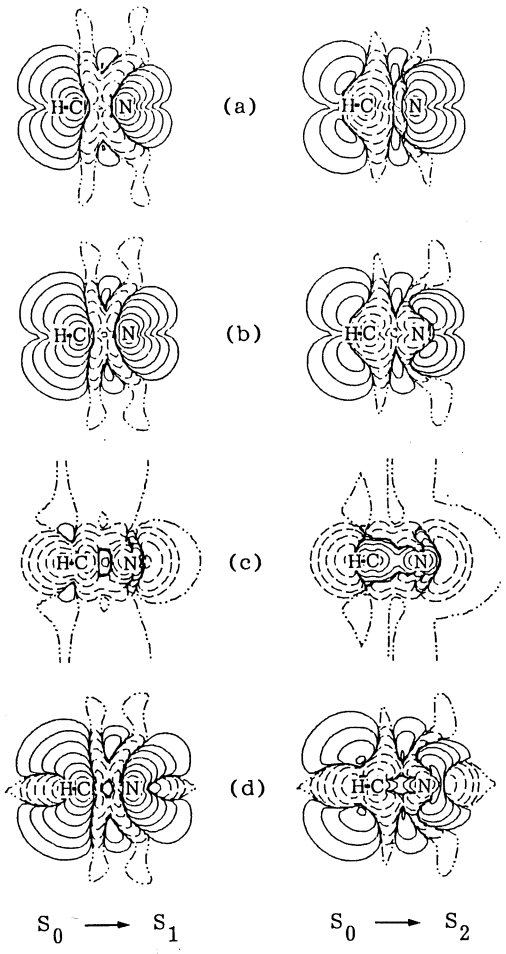

FIG. 9. Contour maps of the density differences for the singlet $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ excitations. These maps show the contours on the π plane defined in Fig. 3. Maps for (a) π SAC-CI, (b) π space in $\pi + \sigma$ SAC-CI, (c) σ space in $\pi + \sigma$ SAC-CI, (d) $\pi + \sigma$ 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, $\pm 1\times10^{-8}$, $\pm 1\times10^{-7}$, $\pm 1\times10^{-6}$, $\pm 1\times10^{-5}$, $\pm 1\times10^{-4}$, $\pm 1\times10^{-3}$, $\pm 1\times10^{-2}$, $\pm 1\times10^{-1}$ a.u.

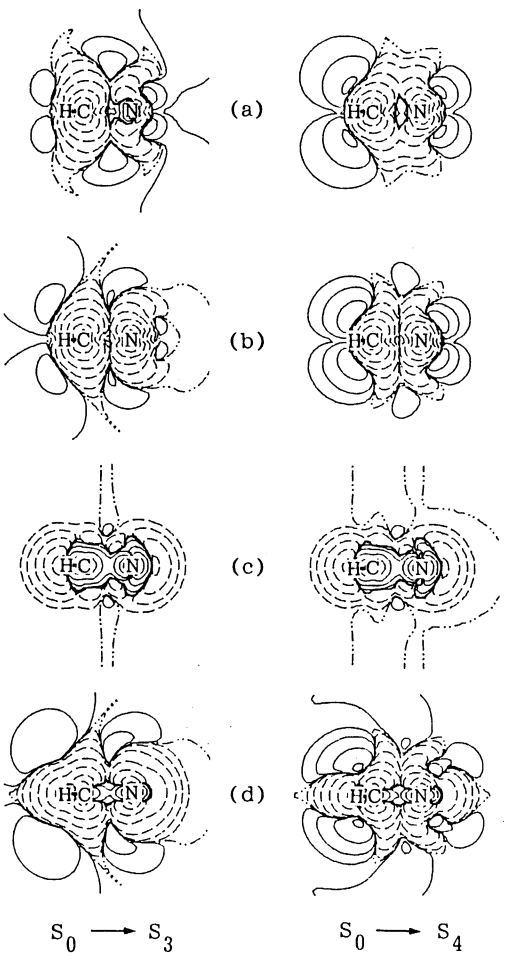

FIG. 10. Contour maps of the density differences for the singlet $S_0 \rightarrow S_3$ and $S_0 \rightarrow S_4$ excitations. Other definitions are the same as those in Fig. 9.

this molecule. This fact suggests that the intensity of the S_2 state of pyridine is owed mainly to the intensity borrowing from the upper strong peaks for the S_3 and S_4 states. Therefore, there seems to be an interesting contrast between the origin of the intensity for the S_1 and S_2 peaks of pyridine.

In these two electronic states, the σ electron correlation plays an important role for the transition energy, but gives only a small effect for the one-electron property. This behavior is similar to that of the S_2 and T_3 states of benzene, in which the σ effect on the excitation energy was 0.71 eV for S_2 and 0.71 eV for T_3, respectively. In benzene, such a large σ electron correlation effect was explained with the simple VB theory.[24] These two states, $^1B_{1u}$ and $^3B_{2u}$, are expressed only with the ionic structures, for the nonpolar structure belongs to the irreducible representation, $^1A_{1g}$, $^1B_{2u}$, or $^1E_{2g}$ for singlet state and $^3A_{2g}$, $^3B_{1u}$, $^3E_{1u}$, or $^3E_{2g}$ for triplet one. For pyridine, however, such a clear discussion does not hold owing to the lowering in molecular symmetry. Nevertheless, the importance of the σ correlation effect is shown with the aid of the differential density maps given on the right-hand side of Fig. 9. Some characteristics points are similar between this figure and the middle of Fig. 4 of Ref. 20. A remarkable difference is the density distribution around the nitrogen atom in the π plane. The increase around the nitrogen atom in (c) map, the σ-reorganization map, leads to a decrease in the density from (a) map to (b) map around the same region. In the benzene case, maps (a) and (b) were similar.

Lastly we discuss the S_3 and S_4 states. These two states correspond to the degenerate S_3 state of benzene. The S_3 state of benzene is a typical V state and very interesting as described in the previous paper.[20] As the S_3 state of benzene, these two states show the typical behaviors of the V state, after inclusion of the σ electron correlation.[20] One is the considerable lowering in transition energy and the other is a large change in the nature of the wave function. The inclusion of the σ correlation effect lowers the excitation energy by 0.81 eV for the S_3 state and 0.69 eV for the S_4 state. The present calculation reproduces the S_3 state to within 0.63 eV. Experimentally the peak of the S_4 state is believed to collapse with that of the S_3 state.[11] If this is true, the present value is higher by 0.94 eV than the experimental data. This difference is very large in our experiences with the calculation of benzene and pyridine. This situation is very mysterious,[58] for

the $^2E_{2g}$ ionic state of benzene is detected to be split into two components separated by up to ~0.7 eV from the photoelectron spectra.[36] Based on our theoretical results, we expect a splitting of about 0.31 eV between the S_3 and S_4 peaks, so that a detailed experimental examination is waited for. This splitting is similar to the splitting of the benzene T_2 state into the T_2 and T_3 states of pyridine. There, the difference between the T_2 and T_3 state was 0.23 eV. The B_2 states (T_2 and S_3) which have a node on nitrogen are lower and closer to the original benzene states than the A_1 states (T_3 and S_4) which do not have a node there.

The large changes in the one electron properties of the S_3 and S_4 states are seen in Figs. 7 and 8, and in Tables VI–VIII. The change in the second moment is larger for the S_4 state than for the S_3 state. The change in the S_4 state of pyridine is similar to that of the S_3 state of benzene in both molecular σ plane and π plane. On the other hand, for the dipole moment, the change is larger for the S_3 state than for the S_4 state. In the π-CI level, both of these states have large positive values, but after inclusion of the σ correlation effect, both states suffer remarkable changes and for the S_3 state even the sign is altered. By the inclusion of the σ electron correlation, the oscillator strength for the $S_0 \rightarrow S_3$ transition becomes small and that for the $S_0 \rightarrow S_4$ transition becomes large: viz., 0.619 → 0.458 for the former and 0.513 → 0.604 for the latter. As a result, the sum of the oscillator strengths is about 1.0, reproducing well the experimental value: 0.90,[8] 1.36.[56]

We would like to consider the change in the calculated one-electron properties after including the σ electron correlation. The general trend is as follows: the electronic part of the second moment decreases and the dipole moment shifts to the negative direction on the z axis. From the investigation on the description of the wave function, the weight of the $\pi \rightarrow R^*_\pi$ configuration, in which the R^*_π orbital is of the f_π type, $5b_1$ for S_3 and $3a_2$ for S_4 (see, Table III), drastically decreases. The difference between these two states is understood from the absence or the presence of the node on the nitrogen atom. The $S_4(2A_1)$ state does not have a node on the nitrogen atom and suffers larger $\sigma\pi$ interaction than the $S_3(2B_2)$ state, in which the node exists on the nitrogen atom. This effect is reflected in the larger extent of the shrink of the S_4 state than the S_3 one, as seen in Fig. 7. Figure 8 indicates that the S_3 state is more polar than the S_4 state in both π SAC-CI and $\pi + \sigma$ SAC-CI calculations. The differential density contour maps for these two states are given in Fig. 10. The left-hand side shows the maps for the $S_0 \rightarrow S_3$ transition and the right-hand side shows those for the $S_0 \rightarrow S_4$ transition. As a whole, the characteristics in these maps on the π plane are similar to those for benzene given in the right-hand side of Fig. 4 of Ref. 20. It is interesting to note that the alteration of the C–H group to the nitrogen atom causes relatively small change in the electron density distributions. For the S_3 state of pyridine, the increase in (a) map and the decrease in (b) one are seen in the region very near to the nitrogen atom. This is different from the S_4 state of pyridine and the S_3 state of benzene. The node on the nitrogen atom causes such a change. A large change in the dipole moment from the π-SAC-CI to the $\pi + \sigma$-SAC-CI calculations is explained from a large decrease in the electron density in (b) map near the nitrogen atom. These changes are reflected in the change of the dipole moment of these states.

Thus, these S_3 and S_4 states are typical V states as the S_3 state of benzene. The inclusion of the σ electron correlation considerably reduces the transition energy and affects much on other one-electron properties. The final out-of-plane second moment indicates that these states are quasivalence in nature as the S_3 state of benzene. A similar behavior was also observed for the ^1B_u state of *trans*-butadiene.[18(c)]

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

The occupied lone-pair orbital of pyridine exists near the occupied π_2 and π_3 orbitals. Therefore, the $n\pi^*$ excitations appear near the $\pi\pi^*$ excitations. Here we study the lowest states belonging to the $^{1,3}B_1$ and $^{1,3}A_2$ symmetries, which are called S_n, T_n, S'_n, and T'_n, respectively. We also discuss the relative position of the lowest $n \rightarrow \pi^*$ (T_n:$1\,^3B_1$) and lowest $\pi \rightarrow \pi^*$ (T_1:$1\,^3A_1$) states.

Experimentally, it is established that the lowest singlet excited state is $^1B_1(n\pi^*)$.[12] There is, however, no *ab initio* theoretical study so far. Our results are given in Table V and Fig. 4. The final result including σ electron correlation is 5.24 eV above the ground state and the difference from the experimental value is 0.65 eV. The σ electron correlation effect is as large as 0.65 eV, which is natural since the $n \rightarrow \pi^*$ excitation involves the orbitals belonging to the σ and π spaces. There is no experimental report for the second $n\pi^*$ excited state. This state is also reduced by 0.89 eV by the inclusion of the σ electron correlation. As seen in Fig. 4, the final result (that the lowest singlet excited state is of $n \rightarrow \pi^*$ character) is obtained only after the inclusion of the σ electron correlation. The $35\pi + 1N$ result gives incorrect ordering. The oscillator strength for the $S_0 \rightarrow S_n$ transition is calculated to be 0.007 in good agreement with the experimental value, 0.003.[8] The calculated second moments of the S_n and S'_n states are almost the same as that of the ground state with a little shrink along the z axis; viz., 205 → 202,201 a.u. Of course this is because one electron is out of the nitrogen lone pair MO. The dipole moment is calculated to be negative for both $n \rightarrow \pi^*$ states: viz, the direction is reverse to that of the ground state. This trend is enlarged by the inclusion of the σ electron correlation, especially for the S_n state: viz., $-0.242 \rightarrow -0.466$ a.u. Hochstrasser determined experimentally the dipole moment of the S_n state as -0.393 a.u.[59] Our theoretical value agrees reasonably well with the experimental one, though we did not take account of the change in geometry due to the excitation.

There is now a controversial situation in the assignment of the lowest triplet state. Recently Sushida *et al.*[13(e)] reported that the $^3A_1(\pi\pi^*)$ state is lowest, but Bos and Buma *et al.*[14] claimed that the $^3B_1(n\pi^*)$ state is lowest. Historically, the $^3A_2(n\pi^*)$[60] state was once considered as a candidate, but not now. We here report the first *ab initio* theoretical results and assign the lowest triplet state as $T_1(^3A_1)$ with the $\pi \rightarrow \pi^*$ character. We see from Fig. 4 that this conclusion is obtained in both $35\pi + 1N$ and $35\pi + 50\sigma$ calculations. The T_1–T_n energy separation is, however, very sensitive to the σ-correlation effect. It is 1.26 and 0.15 eV before and after inclusion

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

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

[a] Reference 51. Values in parentheses are from Ref. 61.
[b] Reference 36.
[c] These results are based on the calculation with the $S_2{*}I_1$ integrals. See the text.
[d] Reference 33.
[e] Reference 35.

of the σ correlation. The difference in the experimental value is 0.3–0.4 eV.[10,11]

There is no experimental report for the T_n' state. This state is reduced by 0.72 eV after inclusion of the σ correlation effect. The second moment and the dipole moment of the T_n and T_n' states are almost the same as those of the S_n and S_n' states.

D. Ionization potential

The outer valence ionization potentials of pyridine are collected in Table IX. We compare the results of the present SAC-CI method, Green function method,[33] VB method,[35] and Koopmans' method and the experimental data.[36,51,61] The SAC-CI results are due to the calculation including only the $S_2{*}I_1$ integrals in the unlinked term.[16(a)] The experimental results are taken from the photoelectron spectra by Kimura *et al.*[51] The experimental and theoretical spectra are compared in Fig. 11. Since we want to discuss the satellite peaks in the deeper region, they are calculated including the $S_2{*}I_2$ integrals as well as the $S_2{*}I_1$ ones in the unlinked term.[16(a)] The intensity of the peaks is calculated with the monopole approximation.[62] The alphabet on each peak shows the MO from which one electron is annihilated in the ionization under consideration.

In the SCF-MO level, the upper three MOs are $\pi(a_2)$, $\pi(b_1)$, and $n(a_1)$ in order as shown in Table III. The Koopmans' values are 9.66, 10.50, and 11.36 eV, respectively: the HOMO is $\pi(a_2)$ in character. However, there is a controversial situation in the identification of the first ionization peak. An interesting history on this assignment has been briefly summarized by Turner *et al.*[37] and by von Niessen *et al.*[33] The first electron impact treatment by Higashi *et al.*[38] showed the $n\pi\pi$ ordering. This conclusion has been once supported by Watanabe *et al.*[39] from the photoionization yield curves, but once objected later by several experimentalists. From the detailed analysis of the photoelectron spectrum, Turner *et al.*[37] considered two possible ordering of the states: i.e., $\pi\pi n$ and $\pi n\pi$. The former assignment was denied by Baker *et al.*[40] and by Heilbronner *et al.*[41] on the basis of the study on the substituent effects. El-Sayed *et al.*[42] supported the latter assignment based on the investigation of the Rydberg series. This assignment was supported by some other experiments: Basila and Clancy[43] from the electron impact study, Krishana and Chowdhury[44] from the analysis on the charge transfer band. In order to settle this problem, Utsunomiya *et al.*[36] investigated the angular distributions in the HeI photoelectron spectra and concluded the $n\pi\pi$ ordering. From the multiphoton ionization spectroscopy converg-

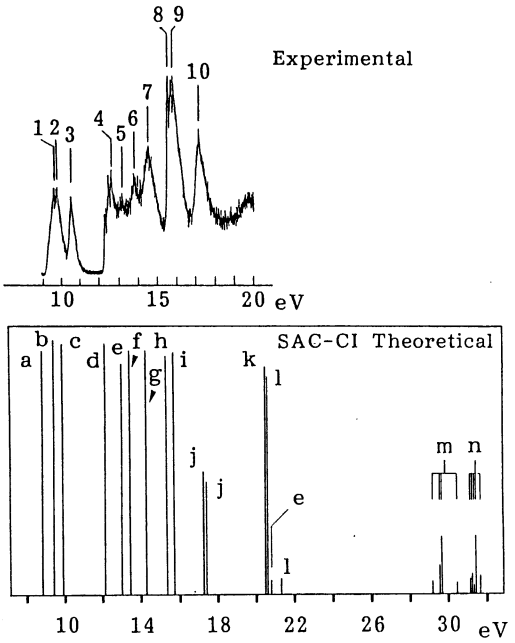

FIG. 11. Experimental (above) and theoretical (below) valence ionization spectra of pyridine. The experimental results are taken from Ref. 51. a: $11a_1$, b: $1a_2$, c: $2b_1$, d: $7b_2$, e: $1b_1$, f: $10a_1$, g: $6b_2$, h: $5b_2$, i: $9a_1$, j:$8a_1$, k: $4b_2$, l: $7a_1$, m: $3b_2$, n: $6a_1$.

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

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

[a] Reference 51. Values in parentheses are from Ref. 61.
[b] Reference 33(b).
[c] $(a)^{-1}(b)^{-1}(c)$ means $(a\rightarrow\infty, b\rightarrow c)$.
[d] These values are read from Fig. 12 of Ref. 33(b).

ing to the 3*s* state, Berg *et al.*[45] arrived at the same conclusion.

As seen in Table IX, the past theoretical treatments beyond Hartree–Fock approximation, the Green function method by von Niessen *et al.*[33] and the VB method by Tantardini *et al.*[35] have supported the $\pi n\pi$ ordering. The present SAC-CI calculation, on the other hand, shows the $n\pi\pi$ ordering. Our conclusion is consistent with the recent experimental results.[36,45] Despite the many differences among these three theoretical treatments, we guess that the main reason for the different ordering is attributed to the basis set difference. Von Niessen *et al.*[33] used the [4*s*2*p*/2*s*] set and Tantardini *et al.*[35] the 4-31G set. Among these three calculations, our basis set is of the highest quality, which is the double-zeta class basis set augmented with the polarization functions. The SAC-CI and Green function results are also different in the ordering of the eight and ninth peaks, though the difference is small. The SAC-CI calculation reproduces the experimental results to within ~0.6 eV.

Differently from benzene, the peaks in the relatively lower energy region of 17 eV are not explainable by the Koopmans' model. In Table X, we summarize the present SAC-CI results for the satellite peaks from 15 to 22 eV. The data based on the 2ph-TDA (two-particle–hole Tamm–Dancoff approximation) are due to von Niessen *et al.*[33(b)] Although both SAC-CI and 2ph-TDA calculation give many satellite peaks in the relatively lower energy region, the details are different between these two theories. The satellite peaks *j* around 17 eV and *l* around 20 eV are owing to the nitrogen atom and are considered to be characteristic to aza-benzenes.[33,63] This is because these peaks borrow their intensities from peak a of *n* character: a_1 symmetry. This explanation does not necessarily hold in the results of von Niessen *et al.*[33,63]

Peak e calculated around 21 eV in Fig. 11 is a satellite peak, which is described as $(\pi\rightarrow\pi^*, \pi\rightarrow\infty)$ as the main configuration and borrows the intensity from the third π peak. The peaks of the same character are seen in the photoelectron spectra of benzene around the similar energy region.[20] Although there is no experimental reports for pyridine beyond 20 eV, the ESCA spectrum on benzene shows the satellite peaks around 30 eV.[64] This theoretical study on pyridine predicts satellite peaks around 30 eV, which may be observed in future by an experimental study. These satellite peaks were also claimed to exist from the theoretical study of von Niessen *et al.*[33]

IV. CONCLUSION

In this paper, we have applied the SAC and SAC-CI theories to the calculations of the valence excitations and the ionizations of pyridine, a key molecule in the hetero aromatics. This is probably the first paper which deals with the excited states of pyridine from the strict *ab initio* viewpoint. Since our treatment is done with the large π and σ active space: viz., $35\pi + 50\sigma$ MOs, the present results would represent the most reliable theoretical study reported so far. By virtue of the SAC-CI formalism, the dimensions of the matrices handled in this calculations were less than 7600, in which we could efficiently include the electron correlations of the quality up to triple excitations, relative to the HF configuration, generated within the 85 active MOs.

About the valence $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ excited states, $S_1(1\,^1B_2)$, $S_2(1\,^1A_1)$, $S_3(2\,^1B_2)$, $S_n(1\,^1B_1)$, $T_1(1\,^3A_1)$, and $T_n(1\,^3B_1)$, the experimental results are reproduced to within ~0.7 eV. The theoretical value is always higher than the experimental one. The $S_4(2\,^1A_1)$ state is experimentally considered not to be split from the S_3 state but is calculated to be

higher by 0.31 eV than the S_3 state from our calculation. The average discrepancy from the experimental data is 0.55 eV without including the S_4 state. There are no experimental data for the valence $\pi\rightarrow\pi^*$ excited states, $T_2(1\,^3B_2)$, $T_3(2\,^3A_1)$, $T_4(2\,^3B_2)$ and the $n\rightarrow\pi^*$ excited states, S'_n $(1\,^1A_2)$ and $T'_n(1\,^3A_2)$. We predict the experimental excitation energy for these unmeasured states to be about 0.3–0.6 eV lower than the present theoretical values. This is based on the comparison between the present theoretical results on pyridine and the corresponding experimental results on benzene as seen in Fig. 5.

Two main features were observed in the investigations of the excited states of the hetero aromatics. One is the perturbation to the $\pi\rightarrow\pi^*$ excited states of benzene by one alteration of the CH group by a nitrogen atom. The other is the existence of the $n\rightarrow\pi^*$ excitations and their positions relative to the $\pi\rightarrow\pi^*$ transitions. As seen in Fig. 5, the valence $\pi\rightarrow\pi^*$ excited states of pyridine are well corresponded to the $\pi\rightarrow\pi^*$ excited states of benzene. However the details are, of course, different between these two isoelectronic aromatic ring compounds. The lowest electronic state T_1 is calculated relatively higher than the experimental value in considering the corresponding T_1 state of benzene. This is probably due to the interaction with the nearly degenerate T_n state. Experimentally, the existence of the T_n potential surface is considered to make the T_1 surface double minimum, so that the adiabatic excitation to this T_1 state is lower than the vertical excitation. The lower electronic states, S_1, T_2, and T_3 are quite similar to the corresponding S_1 and T_2 states of benzene. These states show the characteristics of the so-called covalent state. The higher electronic states, S_2 and T_4, on the other hand, are ionic and the σ correlation effect is important for the transition energy but affects little to the second moment and the dipole moment. This is expected from the corresponding S_2 and T_3 states of benzene. The S_3 and S_4 states of pyridine are the typical V state as the corresponding degenerate S_3 state of benzene. The σ-correlation effect is very important for both transition energy and the one-electron properties such as second moment, dipole moment, and oscillator strength. This effect has been investigated by the differential density contour maps.

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

For the ionization potential, the outer valence part is reproduced to within $\sim$0.6 eV of the experimental value. There is a controversial situation about the identification of the upper three peaks. Our theoretical results display the order, $n\pi\pi$, and these results are supported by the recent experimental results. The satellite peaks exist at a relatively lower region, $\sim$17 eV, in contrast to benzene, and is supposed to be caused by the existence of nitrogen atom. Our results agree, in general, with that of von Niessen *et al.* due to the Green function method. We have predicted several satellite peaks in the inner valence region of pyridine.

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