

Electronic excitation and ionization spectra of azabenzenes: Pyridine revisited by the symmetry-adapted cluster configuration interaction method

Jian Wan,^{a)} Masahiko Hada, Masahiro Ehara, and Hiroshi Nakatsuji^{b)}

Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

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Electronic excited and ionized states of pyridine were reinvestigated by the symmetry-adapted cluster configuration interaction (SAC-CI) method using an extended basis set and a wide active space. The present SAC-CI results for the singlet and triplet excited states are greatly improved and agree well with the experimental observations, providing a firm assignment of all low-lying $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ valence excited states observed in the vacuum ultraviolet spectrum and electron energy-loss spectrum. The ionization potentials were reexamined by the SAC-CI general-R (R represents excitation operator) method. The first four ionization potentials are greatly improved compared with our previous results obtained by the SAC-CI single- and double-R (SD-R) method. The present theoretical ionization potentials are in good agreement with the experimental values in high-resolution synchrotron photoelectron spectrum for energy regions up to 25 eV (which contain outer- and inner-valence regions), and give a detailed theoretical assignment for the photoelectron spectra. © 2001 American Institute of Physics. [DOI: 10.1063/1.1351880]

I. INTRODUCTION

Azabenzenes are important parent molecular systems for numerous compounds such as biologically active nicotinic acid and the nucleotides cytosine, uracil, and thymine, and therefore have been the subject of extensive experimental and theoretical studies.¹⁻¹⁷ Azabenzenes are isoelectronic with benzene. The nitrogen atoms introduce perturbations to the benzene energy levels and give rise to new transitions due to excitation of their lone-pair electrons. Their lower electronic excitation spectra in the near and vacuum ultraviolet regions are due to both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ valence transitions, and the lowest-lying transitions are of $n \rightarrow \pi^*$ origin; these are the fundamental differences in the photophysical behavior of azabenzenes and benzene.

A good review of experimental and theoretical studies on the electronic structure of azabenzenes up to 1988 has been given by Innes *et al.*¹ Recently, a series of studies have been reported by Walker and co-workers,²⁻⁵ which include vacuum ultraviolet absorption (VUV) spectra, electron energy loss (EEL) spectra, and the results of multi-reference multi-root configuration-interaction (MRD-CI) calculations. In addition, a comprehensive collection of VUV spectra and theoretical results has also been presented by Bolovinos *et al.*⁶

Pyridine is the simplest azabenzene because only one CH group is replaced by nitrogen atom. In fact, the optical spectrum of pyridine is still experimentally assigned by analogy to that of benzene. The electronic spectrum of pyridine

is dominated by three bands at about 5.0, 6.4, and 7.2 eV, which are associated to the $\pi \rightarrow \pi^*$ valence excitations from the comparison with the three $\pi \rightarrow \pi^*$ valence excitation bands of benzene at 4.9, 6.2, and 7.0 eV, respectively. The valence nature of these transitions was confirmed by their existence in the liquid phase.⁷ The lowest-lying singlet absorption of pyridine contains an $n \rightarrow \pi^*$ excitation on the rising shoulder of the first optical absorption band.^{2,6} The lowest Rydberg-excited state, $n \rightarrow 3s$, has been observed at 6.28 eV by multi-photon ionization.^{8,9} Other Rydberg series have been assigned from the fine structure at 8–9 eV in the optical spectrum.^{2,6}

Optical absorption data for pyridine have been complemented by electron energy-loss spectra. With incident electrons of relatively high energies, the electron-impact excitation spectrum resembles the optical absorption spectrum.¹⁰ When the incident electron energy is reduced to near-threshold values,¹¹ additional transitions emerge, including spin-forbidden ones. Ion-impact (He^+) excitation of pyridine reveals a singlet-triplet excitation, with an onset energy of 3.8 eV and $E_{\text{max}}=4.1$ eV.¹² This is the lowest-lying excited state to have been definitively located in the gas phase. Other singlet-triplet excitations at 4.84 and 5.4 eV were observed in the experimental studies of Walker *et al.*²

The first band in the photoelectron spectrum of pyridine is a composite of two ionization potentials involving an N nonbonding (n) electron and a π electron. High-resolution studies and comparison with the deuterated, D_5 , molecule show that the first ionization potential (IP) is nonbonding ($n, 11a_1$).^{13,14} This is consistent with the observation that the lowest Rydberg state has A_1 symmetry ($n-3s$).^{8,9} Recently, a high-resolution synchrotron photoelectron spectroscopy (PES) study, including the outer- and inner-valence regions,

^{a)}Also at the Department of Chemistry, Central China Normal University, Wuhan 430079, China.

^{b)}Author to whom correspondence should be addressed. Electronic mail: hiroshi@sbchem.kyoto-u.ac.jp

was reported by Moghaddam *et al.*¹⁵ In their report, $1a_2$ was assigned to the first IP using an algebra diagrammatic construction accurate to the third order in electron–electron interaction ADC(3) calculations.

On the other hand, in contrast to this abundant experimental information regarding pyridine, there have been only a few *ab initio* studies (at the electron correlation level) on the excited and ionized states of pyridine: symmetry-adapted cluster (SAC) and SAC configuration interaction (SAC-CI) calculations¹⁶ in 1988, MRD-CI calculations² in 1989, complete active space second-order perturbation (CASPT2) calculations^{17,18} in 1992 and 1995, and ADC(3) calculations¹⁵ in 1996. The SAC/SAC-CI study¹³ was a pioneering work, but due to the limitations in the computational resources available at that time, the rather limited basis sets and relatively small active space impaired the quality of the results. CASPT2¹⁷ has been used to systematically study the singlet valence $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitations of azabenzenes including pyridine, pyrimidine, pyrazine, pyridazine, and *s*-triazine, and the singlet Rydberg transitions ($n=3$, $l=0,1,2$), the triplet excited states and the first three ionized states of pyridine.¹⁸

In this study, we re-examined the singlet and triplet valence and Rydberg excitations of pyridine using an extended basis set and a larger active space by SAC/SAC-CI single- and double-operator (SD-R) calculations.^{19–27} Furthermore, to provide a theoretical interpretation of correlation (satellite) peaks characterized by a multi-electron process in the PES spectrum,¹⁵ the SAC/SAC-CI general-R method²⁵ was also used to accurately calculate the inner-valence region of the ionization spectrum. In Sec. II, we outline the computational details. Calculated results and discussions are presented in Sec. III. A summary is given in Sec. IV.

II. COMPUTATIONAL DETAILS

Details of the SAC/SAC-CI method for calculating ground, excited, and ionized states of molecules have been presented elsewhere.^{19–27} An experimental ground-state equilibrium geometry of pyridine with C_{2v} symmetry²⁸ was used, and the pyridine ring was put on the yz -plane with z as the principle axis. Therefore, the calculated excitation energies are vertical in nature.

One of the major sources of errors in the excitation energies is from incompleteness in the basis set. Most standard basis sets are optimized for ground-state calculations. Since excited states are often considerably more diffuse than ground states, extended basis sets are required. Therefore, we use well-extended basis sets to perform SAC/SAC-CI SD-R calculations to overcome this problem: Dunning's augmented correlation consistent basis set AUG-cc-pVTZ²⁹ was used for nitrogen and carbon atoms with one f polarization function removed for all carbon atoms, and cc-pVTZ³⁰ was used for H atoms. Additionally, a set of molecule-centered diffuse function ($5s5p5d$) selected from the studies of Kaufmann *et al.*³¹ was placed on the N atom, since many n -Rydberg states are targets in pyridine. For convenience, the above basis set is referred to as basis set A. In the SAC/SAC-CI general-R calculations for the ionized states of pyridine, we use basis set B, in which AUG-cc-pVDZ was used

TABLE I. Calculated triplet excitation energies (ΔE , in eV), and second moments for pyridine with basis set A.

| Symmetry | Expt. ^a (eV) | SAC-CI | | CASPT2 ^c | MRD-CI ^d | |
|----------|----------------------------|-----------------|---------------|---------------------|---------------------|-----------------|
| | | ΔE (eV) | Type | S. M. ^b | ΔE (eV) | ΔE (eV) |
| 1^1A_1 | | | Ground | 80.2 | | |
| 1^3A_1 | ~4.1 | 4.06 | $^3\pi-\pi^*$ | 79.9 | 4.05 | 3.95 |
| 2^3A_1 | ~4.84 | 4.91 | $^3\pi-\pi^*$ | 80.7 | 4.73 | 4.93 |
| 1^3B_1 | ~4.1 | 4.25 | $^3n-\pi^*$ | 79.4 | 4.41 | 3.87 |
| 2^3B_1 | | 6.83 | $a_2^3p_y$ | 166.6 | | 7.46 |
| 1^3B_2 | ~4.84 | 4.64 | $^3\pi-\pi^*$ | 80.8 | 4.56 | 4.98 |
| 2^3B_2 | | 6.08 | $^3\pi-\pi^*$ | 81.6 | 6.02 | 6.67 |
| 1^3A_2 | ~5.4 | 5.28 | $^3n-\pi^*$ | 80.1 | 5.10 | 5.43 |
| 2^3A_2 | | 6.26 | a_2^3s | 132.3 | | 8.99 |

^aExperimental values are discussed in the text.

^bSecond moment.

^cReference 18.

^dReference 2.

for nitrogen and carbon atoms, and cc-pVDZ was used for H atoms, since the computing dimension is considerably increased in the general-R method, and these were then augmented by the molecule-centered diffuse functions ($2s2p2d$) above the molecular center of gravity. All SCF calculations were performed with the GAUSSIAN 98 package.³²

The present SAC/SAC-CI calculations were performed with the local version of the SAC/SAC-CI module.²⁷ The active space consists of the complete molecular orbital space except that $1s$ core orbitals were frozen. In the SAC ground-state calculation, all single-excitation and selected double-excitation operators S_I^+ were included in the linked term. The energy threshold λ_g for perturbation selection²⁴ (PS) was 1.0×10^{-5} a.u. For the unlinked term, we included only the products of the double-excitation operators $S_I^+ S_J^+$ when the coefficients C_I and C_J , estimated by SD-CI in practice, were larger than 1.0×10^{-3} .

In the SAC-CI SD-R calculations of excited states, all single-excitation operators and selected double-excitation operators were included in the linked operators R_K^+ . Perturbation selection was performed as follows. First, we selected the main reference configurations from SE-CI with a coefficient greater than 0.1, and then selected the double-excitation operator whose second-order perturbation matrix element with one of the main reference configurations is greater than the threshold λ_e (1.0×10^{-6} a.u.). In the unlinked term $\sum_{K,I} d_K C_I R_K^+ S_I^+ |0\rangle$, we included double-excitation operators $\{S_I^+\}$ whose coefficients (C_I) were larger than 1.0×10^{-3} in the SAC ground-state calculation, and as the R_K^+ operator, we included single- and double-excitation operators whose coefficients (taken from SD-CI in practice) were greater than 0.05.

In the SAC-CI general-R calculations of the outer- and inner-valence ionization potentials of pyridine, a preliminary SD-CI calculation was performed to select operators for the exponential generation (EG) scheme²⁶ by which we can construct important triple- and quadruple-excitation operators required for a quantitative description of the multi-electron process in the ionization spectrum. The generated higher-order excitation operators were further selected by the per-

TABLE II. SAC-CI results for the singlet excited states, compared with the experimental excitation energies (in eV) and other theoretical results for pyridine.

| Symmetry | Nature | SAC-CI ^a | | | Expt. ^b (eV) | CASPT2 ^c | | MRD-CI ^b | |
|-----------------------------|-----------------------------|---------------------|---------|------------|----------------------------|---------------------|---------|---------------------|-------|
| | | $f(r)$ | S.M. | ΔE | | ΔE | $f(r)$ | ΔE | |
| ¹ A ₁ | Ground | | 80.17 | | | | | | |
| | π - π^* | 0.0195 | 93.93 | 6.26 | 6.38 | 6.42 | 0.005 | 6.990 | |
| | a_23d_{-2} | 0.0001 | 217.12 | 7.62 | | | | | |
| | π - π^* | 0.6174 | 97.61 | 7.18 | 7.22 | 7.23 | 0.82 | 8.178 | |
| | b_13p_x | 0.0001 | 175.90 | 7.65 | | 8.05 | | | |
| | $n3s$ | 0.0008 | 126.69 | 6.17 | 6.28 | 6.70 | 0.021 | 6.188 | |
| | a_24d_{-2} | 0.0001 | 725.16 | 8.20 | | | | | |
| | $n5p_z$ | 0.0004 | 974.84 | 8.21 | 8.17 | | | | |
| | $n4s$ | 0.0003 | 361.37 | 7.59 | | | | | |
| | $n4p_z$ | 0.0002 | 493.77 | 7.82 | 8.07 | | | 8.20 | |
| | $n3p_z$ | 0.0756 | 170.11 | 6.83 | 6.93 | 7.21 | | 6.701 | |
| | ¹ A ₂ | a_23s | forbid. | 131.19 | 6.21 | | 6.75 | forbid. | |
| | | n - π^* | forbid. | 80.03 | 5.11 | | 5.17 | forbid. | 5.280 |
| a_23p_z | | forbid. | 164.74 | 6.97 | | 7.52 | forbid. | | |
| a_23d_{+2} | | forbid. | 160.00 | 7.33 | | 7.98 | forbid. | | |
| a_23d_0 | | forbid. | 197.09 | 7.58 | | 8.17 | forbid. | | |
| a_24s | | forbid. | 357.73 | 7.73 | | | | | |
| b_13p_y | | forbid. | 186.11 | 7.64 | | | | | |
| a_24p_z | | forbid. | 501.61 | 7.98 | | | | | |
| a_24d_{+2} | | forbid. | 526.46 | 8.09 | | | | | |
| a_24d_0 | | forbid. | 624.60 | 8.19 | | | | | |
| ¹ B ₁ | | n - π^* | 0.0054 | 79.76 | 4.59 | 4.44/4.59 | 4.91 | 0.009 | 4.503 |
| | b_13s | 0.0011 | 140.29 | 6.92 | | 7.39 | 0.001 | | |
| | a_23p_y | 0.0347 | 154.48 | 6.77 | 6.93 | 7.25 | | | |
| | a_23d_{-1} | 0.0000 | 200.13 | 7.53 | | 8.03 | | | |
| | b_13p_z | 0.0045 | 168.21 | 7.66 | | 8.16 | | | |
| | a_24p_y | 0.0047 | 473.16 | 7.93 | | | | | |
| | a_24d_{-1} | 0.0000 | 625.38 | 8.19 | | | | | |
| | a_25p_y | 0.0030 | 1044.01 | 8.36 | | | | | |
| | b_13d_{+2} | 0.0153 | 172.97 | 8.10 | | 8.71 | | | |
| | b_14s | 0.0006 | 408.12 | 8.43 | | | | | |
| | ¹ B ₂ | π - π^* | 0.0400 | 81.04 | 4.85 | 4.99 | 4.84 | 0.018 | 4.762 |
| π - π^* | | 0.4072 | 114.90 | 7.27 | 7.22 | 7.48 | 0.64 | 7.699 | |
| a_23d_{+1} | | 0.0097 | 246.17 | 7.71 | | 8.18 | | | |
| a_23p_x | | 0.2098 | 134.63 | 6.83 | 6.93 | 7.41 | 0.039 | | |
| a_24p_x | | 0.0019 | 462.03 | 7.95 | | | | | |
| a_24d_{+1} | | 0.0010 | 701.11 | 8.23 | | | | | |
| a_25p_x | | 0.0002 | 1020.43 | 8.36 | | | | | |
| a_25d_{+1} | | 0.0009 | 883.56 | 8.59 | | | | | |
| b_13d_{-2} | | 0.0005 | 249.16 | 8.33 | | 8.77 | | | |
| a_26p_x | 0.0001 | 981.56 | 8.71 | | | | | | |

^aWith basis set A; $f(r)$ denotes oscillator strength; S.M. denotes second moment.

^bReference 2.

^cReference 18.

turbation selection²⁴ procedure with an energy threshold of 1.0×10^{-6} hartree. Therefore, all single (ionization) operators and selected higher operators (SDTQ) were included in the linked term of the SAC-CI general-R equation. In the unlinked term, we included all of the double-excitation operators $\{S_I^+\}$ in the SAC ground-state calculation, and as the R_K^+ operator, we included all single operators and selected higher-order operators up to quadruple.

III. RESULTS AND DISCUSSIONS

Oscillator strengths and excited-state properties, such as second moments, are important for characterization of the excited electronic states and give information that is useful for the qualitative assignment of the excited states, for ex-

ample in terms of valence and Rydberg states. These points have been illustrated in our previous calculations on five-membered ring compounds. The triplet excitation energies and second moments calculated by the SAC-CI SD-R method are shown in Table I, and compared with the experimental values and the CASPT2 and MRD-CI results. Table II shows the singlet excitation energies, oscillator strengths, and second moments calculated by the SAC-CI SD-R method, together with the experimental values, and the CASPT2 and MRD-CI results. Figure 1 shows a comparison of the experimental VUV spectrum⁴ and the theoretical SAC-CI spectrum of pyridine. The ionization potentials calculated by the SAC-CI general-R method are listed in Table III, together with the PES data and other theoretical

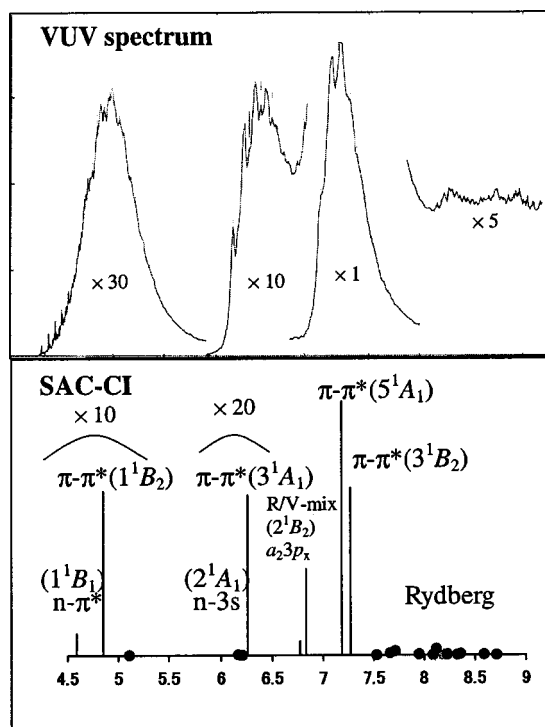


FIG. 1. VUV spectrum and calculated excitation energies and oscillator strengths of pyridine.

results. A comparison of the PES spectrum with the SAC-CI general-R theoretical spectrum is illustrated in Fig. 2.

A. Electronic excited states

In the energy region of 3.5–5.8 eV in pyridine, there are five electronic excitations with firmly identified E_{\max} values by spectroscopic studies,^{2,6,11,33} three of which are optically forbidden singlet-triplet excitations at 4.1, 4.84, and 5.43 eV, while the remaining two at 4.44³³ and 4.99 eV are optically allowed singlet-singlet $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excited states, respectively.

Our present results for triplet excitation energies are listed in Table I, along with the experimental values, CASPT2 and MRD-CI results. The present calculations gave two nearly degenerate triplet excited states $1^3A_1(\pi \rightarrow \pi^*)$ and $1^3B_1(n \rightarrow \pi^*)$ at 4.06 and 4.25 eV, respectively, which are responsible for the absorption at 4.1 eV. At a slightly higher energy region, we gave $1^3B_2(\pi \rightarrow \pi^*)$ and $2^3A_1(\pi \rightarrow \pi^*)$ at 4.64 and 4.91 eV, respectively, which are responsible for the absorption at 4.84 eV. In addition, we gave $1^3A_2(n \rightarrow \pi^*)$ at 5.28 eV, which is responsible for the absorption at 5.43 eV. It is clear from the second moments shown in Table I that these states are all valence excitations. Note that while an absorption spectrum showed two very weak absorptions at about 3.7 eV, impurity effects could not be excluded under the extreme experimental conditions.³⁴ Our present calculations did not give any triplet excitations in this energy region.

The present singlet excitation results are listed in Table II, where they are compared with the experimental values and the results of theoretical CASPT2 and MRD-CI studies. The lowest two optically allowed singlet excitations

are observed at 4.44(1^1B_1) and 4.99 eV(1^1B_2).² Our present computed results gave the 1^1B_1 state at 4.59 eV with a weak oscillator strength of 0.0054, and the 1^1B_2 state at 4.85 eV with an oscillator strength of 0.04. The 1^1B_1 state is $n \rightarrow \pi^*$, while the 1^1B_2 state is $\pi \rightarrow \pi^*$ in nature. MRD-CI calculations gave these at 4.50(1^1B_1) and 4.76 eV(1^1B_2), respectively, while CASPT2 calculations put them at 4.91(1^1B_1) and 4.84 eV(1^1B_2), respectively. Note that the CASPT2 calculations¹⁸ suggested the lowest $n \rightarrow \pi^*$ transition corresponded to an adiabatic transition.

The maximum of the second optically allowed absorption band (5.8–6.8 eV) is observed at 6.38 eV, which is assigned to valence $\pi \rightarrow \pi^*$ excitation (1^1A_1).^{2,6} The present calculations give the 3^1A_1 state at 6.26 eV with an oscillator strength of 0.02. The second moment (93.9) and main configurations clearly defined it as a valence $\pi \rightarrow \pi^*$ excitation. CASPT2 calculations gave this at 6.42 eV with a weak oscillator strength of 0.005, while MRD-CI calculations put it at 6.99 eV. Close to the maximum, the Rydberg $n-3s$ excitation is determined by two-photon absorption^{8,9} at 6.28 eV. Our present results gave the $2^1A_1(n-3s)$ Rydberg state at 6.17 eV with a weak oscillator strength of 0.0008. MRD-CI gave a calculated value of 6.19 eV, while CASPT2 gave this state at 6.70 eV.

The maximum of the strongest optical absorption band is experimentally observed at 7.22 eV.^{2,6} This absorption corresponds to the benzene 1^1E_{2u} excitation, which becomes $1^1A_1+1^1B_2$ in pyridine. Our present calculations gave two nearly degenerate singlet excited states $4^1A_1(\pi \rightarrow \pi^*)$ and $3^1B_2(\pi \rightarrow \pi^*)$ at 7.18 and 7.27 eV, with large oscillator strengths of 0.62 and 0.41, respectively, which are certainly responsible for the strongest absorption at 7.22 eV. The second moment of the 4^1A_1 state is 97.6 while that of the 3^1B_2 state 114.9, which shows a somewhat diffuse character due to mixing of the Rydberg state, particularly in the 3^1B_2 state. *Vice versa* when the Rydberg state is strongly influenced by valence excitations, the former will borrow some intensity from the latter. This is why the calculated Rydberg 2^1B_2 state had a relatively intense oscillator strength (0.21). MRD-CI gave these two valence excitations at 8.18 eV(1^1A_1) and 7.70 eV(1^1B_2), respectively, while CASPT2 gave them at 7.23 eV(1^1A_1), with a CASSCF oscillator strength of 0.82, and 7.48 eV(1^1B_2), with a CASSCF oscillator strength of 0.64.

In this energy region, two other weak absorptions are visible at 6.93 and 7.6 eV,² which were associated with Rydberg states by Walker *et al.* In the higher energy region of 8–9 eV, a broad optical absorption band is observed, which is caused by transitions to Rydberg states. Our present results gave many Rydberg excitations in these energy regions, and an assignment is given in Table II.

B. Ionized states and assignment of the photoelectron spectrum

The ground-state valence electronic configurations of pyridine (C_{2v}) in order of increasing orbital energy is $5a_1, 6a_1, 3b_2, 7a_1, 4b_2, 8a_1, 5b_2, 9a_1, 6b_2, 10a_1, 1b_1, 7b_2, 11a_1, 2b_1, 1a_2$.

TABLE III. Calculated ionization potentials (IP, in eV), monopole intensities (M.I.), and main configurations with the basis set B for pyridine.

| Sym. | SAC-CI general-R | | | Expt. ^a (eV) | CASPT2 ^b ADC(3) ^c | | MRD-CI ^d | |
|-----------------------------|---|--------|----------|----------------------------|---|-------|---------------------|--------|
| | Main configuration | M.I. | IP | | IP | IP | IP | |
| ² A ₁ | 0.91(11a ₁) - 0.12(2b ₁ b ₁ ; 11a ₁) | 0.8476 | 9.23 | 9.60(1) | 9.54 | 9.78 | 8.843 | |
| | 0.90(10a ₁) + 0.14(2b ₁ b ₁ ; 11a ₁) | 0.8385 | 13.56 | 13.8(6) | | | 13.92 | 13.696 |
| | 0.89(9a ₁) - 0.17(1a ₂ a ₂ ; 11a ₁) - 0.17(11a ₁ a ₂ ; 1a ₂) | 0.8018 | 15.70 | 15.9(9) | 17.4(10) | 17.60 | 16.02 | 16.048 |
| | | 0.0221 | 15.79 | | | | | |
| | | 0.0135 | 16.50 | | | | | |
| | -0.87(8a ₁) + 0.16(2b ₁ b ₁ ; 10a ₁) | 0.7687 | 17.10 | | | | | |
| | | 0.0309 | 17.92 | | | | | |
| | | 0.1175 | 19.82 | | | | | |
| | -0.63(7a ₁) + 0.31(10a ₁ a ₂ ; 1a ₂) - 0.29(10a ₁ b ₁ ; 2b ₁) | 0.4022 | 20.05 | 19.8(11) | | | 20.08 | |
| | | 0.0447 | 20.54 | | | | | |
| | | 0.0956 | 20.21 | | | | | |
| | | 0.0865 | 19.47 | | | | | |
| | | 0.0101 | 21.66 | | | | | |
| | | 0.0129 | 21.24 | | | | | |
| | 0.0263 | 22.20 | | | | | | |
| | 0.0124 | 22.59 | | | | | | |
| | 0.0102 | 21.97 | | | | | | |
| | 0.0173 | 22.96 | | | | | | |
| | 0.0172 | 22.71 | | | | | | |
| | 0.1954 | 23.27 | 23.4(13) | | | | | |
| ² A ₂ | -0.41(6a ₁) - 0.24(1a ₂ a ₂ ; 10a ₁) - 0.19(10a ₁ b ₁ ; 2b ₁) | 0.8989 | 9.36 | 9.75(2) | 9.65 | 9.44 | 9.526 | |
| | -0.94(1a ₂) | 0.8907 | 10.12 | 10.51(3) | | | 10.15 | 10.127 |
| ² B ₁ | 0.94(2b ₁) + 0.10(2b ₁ b ₁ ; 1b ₁) | 0.8907 | 10.12 | 10.51(3) | 10.37 | 10.15 | 10.127 | |
| | 0.87(1b ₁) - 0.28(1a ₂ b ₁ ; 1a ₂) + 0.22(2b ₁ b ₁ ; 2b ₁) | 0.7636 | 13.06 | 13.1(5) | | | 13.18 | 13.044 |
| | | 0.0135 | 17.67 | | | | | |
| ² B ₂ | 0.93(7b ₂) | 0.8806 | 12.48 | 12.61(4) | 20.6(12) | 20.44 | 12.73 | 12.908 |
| | 0.91(6b ₂) - 0.16(1a ₂ b ₁ ; 11a ₁) | 0.8490 | 14.41 | 14.5(7) | | | 14.65 | 14.636 |
| | -0.86(5b ₂) - 0.31(1a ₂ b ₁ ; 11a ₁) | 0.7610 | 15.60 | 15.9(8) | | | 16.18 | 15.947 |
| | | 0.1187 | 16.84 | | | | | |
| | | 0.0307 | 20.66 | | | | | |
| | | 0.0200 | 23.46 | | | | | |
| | | 0.0203 | 24.07 | | | | | |
| | | 0.0161 | 21.94 | | | | | |
| | | 0.0134 | 24.51 | | | | | |
| | -0.87(4b ₂) - 0.16(1a ₂ b ₁ ; 11a ₁) | 0.7629 | 20.43 | | | | | |
| | | 0.0236 | 24.30 | | | | | |
| | | 0.0294 | 21.72 | | | | | |
| | -0.52(3b ₂) - 0.27(1a ₂ a ₁ ; 2b ₁) - 0.24(2b ₁ a ₁ ; 1a ₂) | 0.2792 | 24.35 | 24.3(14) | | | 24.20 | |
| | | 0.0852 | 24.22 | | | | | |
| | 0.0180 | 24.09 | | | | | | |
| | 0.0110 | 22.76 | | | | | | |

^aReferences 2 and 6, the order of peaks (binding energies) is given in parenthesis.

^bReference 18.

^cReference 15.

^dReference 2.

Synchrotron PES experiments with pyridine have recently been conducted by Moghaddam *et al.*¹⁵ up to 25 eV, which includes both outer- and inner-valence regions (Fig. 2). Table III shows the SAC-CI general-R theoretical ionization energies (binding energies), monopole intensities, and assignments of the ionization peaks observed in PES. The present SAC-CI general-R calculations are in good agreement with the experimental values. In Fig. 2, the experimental PES and the present theoretical spectrum calculated by the SAC-CI general-R method are compared.

Most early assignments in the pyridine photoelectron spectrum were based on Koopman's theorem, i.e., $IP_i = -\varepsilon_i$ where ε_i is the orbital energy. Koopmans' values deviate strongly from the experimental values except for those in the two states associated with 1a₂ and 2b₁. As previously mentioned (Sec. I), the first band in PES contains

two ionizations, IP order 11a₁(n) < 1a₂(π), which have been separated in high-resolution studies.^{13,14} Koopmans' results put the IP order 1a₂(π) < 11a₁(n). Our present SAC-CI general-R calculations computed these two states at 9.23[11a₁(n)] and 9.36 eV[1a₂(π)], respectively, which are effectively degenerate compared to the Koopmans' values: 9.46[1a₂(π)] and 11.42[11a₁(n)] eV. Our present results support the experimental studies.^{8,9,13,14} MRD-CI gave 8.96[11a₁(n)] and 9.38 eV[1a₂(π)]. However, ADC(3) gave a different IP order: 9.44[1a₂(π)] and 9.78[11a₁(n)].

The third IP peak is observed at 10.51 eV. Our present calculations gave this state at 10.12 eV with a monopole intensity of 0.89. The nature of this state is, from the main configurations shown in Table III, dominated by a one-electron process of the orbital 2b₁. Note that CASPT2 gave

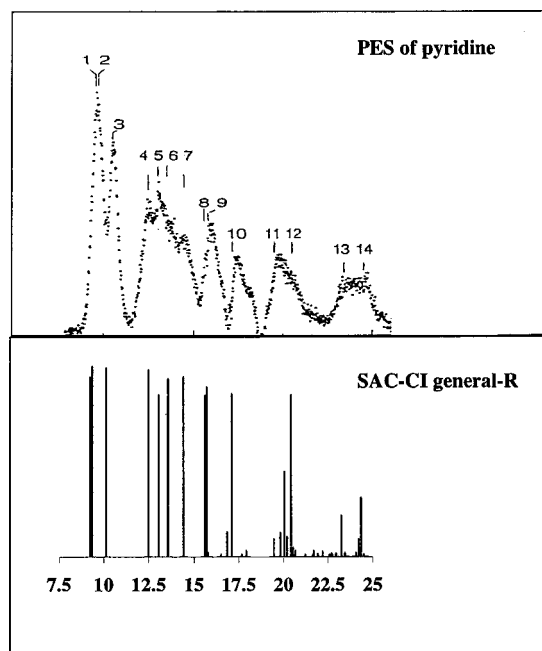


FIG. 2. PES spectrum and calculated ionization energies and monopole intensities of pyridine.

the first three ionization potentials at 9.54 eV[$1a_1(n)$], 9.65 eV[$1a_2(\pi)$], and 10.37 eV($2b_1$).

Following the third IP peak, there are four sequential ionization peaks (4th, 5th, 6th, and 7th) observed at 12.61, 13.1, 13.8, and 14.5 eV. Our present results gave the corresponding ionized states at 12.48, 13.06, 13.56, and 14.41 eV, with monopole intensities of 0.88, 0.76, 0.84, and 0.85, respectively. From the main configurations of each ionized state, the 12.61 eV peak was associated with the ionization from the orbital $7b_2$, and dominated by a one-electron process. The 13.1 eV peak was assigned to the ionization from the orbital $1b_1$, and was affected by a two-electron process. The 13.8 eV peak was assigned to ionization from the orbital $10a_1$, while the 14.5 eV peak was associated with the ionization from the orbital $6b_2$, which is dominated by a one-electron process. Note that Koopmans' order of ionizations is maintained within these states.

The next two ionization peaks (8th and 9th) are observed at 15.9 eV, which overlap with each other. Our present calculations gave two almost degenerate states at 15.60 and 15.70 eV with monopole intensities of 0.76 and 0.80, respectively. We assigned the 15.9 eV peak to ionizations from the orbitals $5b_2$ and $9a_1$. Note that Koopmans' order broke down again in this energy region.

The 10th ionization peak is located at 17.4 eV. Our present results associated it with ionization from the orbital $8a_1$, which was computed at 17.10 eV with a monopole intensity of 0.77. In our present calculations, some satellite peaks occurred in this peak region. The detailed numerical results are listed in Table III.

In the energy region of 20 to 25 eV, two groups of broad peaks with satellite characteristics (11th, 12th, and 13th, 14th) are observed. These ionized states are strongly influenced by multi-electron processes. The detailed numerical

results, the nature of the ionized states, and the corresponding assignments are shown in Table III. Generally, our present results agree well with all PES peaks up to 25 eV.

IV. CONCLUSION

In the present study, singlet and triplet excited states and ionized states of pyridine were re-investigated by the SAC/SAC-CI method with an extended basis set and a large active orbital space. The 48 low-lying singlet and triplet excited states were calculated and a reliable assignment for VUV and EEL spectra up to 8 eV was made using the calculated excitation energies and oscillator strengths. The valence $n-\pi^*$, $\pi-\pi^*$, and Rydberg excited states were discussed separately in detail. Furthermore, the SAC-CI general-R method, along with both the exponential generation and perturbation selection schemes for including higher-order excitation operators, was applied to the ionized states of pyridine up to 25 eV. The experimental PES spectrum and our present calculations show good agreement in terms of the binding energies and peak intensities in both the outer- and inner-valence regions.

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