

Theoretical fine spectroscopy with symmetry adapted cluster–configuration interaction general-*R* method: First-row *K*-shell ionizations and their satellites

Kei Kuramoto and Masahiro Ehara

Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto-Daigaku-Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

Hiroshi Nakatsuji^{a)}

Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto-Daigaku-Katsura, Nishikyo-ku, Kyoto 615-8510, Japan and Fukui Institute for Fundamental Chemistry, Kyoto University, 34-4 Takano-Nishihiraki-cho, Sakyo-ku, Kyoto 606-8103, Japan

(Received 22 July 2004; accepted 5 October 2004; published online 13 December 2004)

Molecular core ionization spectra and their satellites were studied by the symmetry adapted cluster–configuration interaction (SAC-CI) general-*R* method. The core-electron binding energies of C, N, O, and F atoms of 22 molecules were calculated with an average deviation of 0.11 eV from the experimental values. The energy splittings between *K*-shell gerade and ungerade states were calculated and discussed in relation to the bond length. The satellite spectra of the C 1s and N 1s core ionizations of methane and ammonia were investigated. The SAC-CI general-*R* method gave many shake-up states with moderate intensities, reproducing the general feature of the experimental spectra, and thus enabling the detailed understanding and assignments of the core-electron ionization spectra. © 2005 American Institute of Physics. [DOI: 10.1063/1.1824899]

I. INTRODUCTION

Core-electron ionization spectra contain the information not only about inner-core electrons but also valence electrons and chemical bonds. Extensive experimental studies have given core-electron binding energies (CEBE) of numerous molecules: Siegbahn *et al.*¹ summarized the CEBE data in 1969 and Bakke, Chen, and Jolly² collected them in 1980. They have also clarified the important chemical implications involved in the CEBE data. Recent development of the high-resolution soft x-ray photoelectron spectroscopy has enabled the accurate and detailed experimental characterizations of the core-electron ionization processes.

In the theoretical calculations of CEBE, Δ SCF (self-consistent field) method has been used most frequently, but it usually underestimates the CEBE. Deutsch and Curtiss³ investigated the CEBE of CH₄, NH₃, H₂O, and HF by the Δ SCF method using various basis sets and showed that the Δ SCF method with sufficiently large basis set uniformly underestimated the CEBE. The density functional theory (DFT) is also useful for estimating the CEBE. Slater introduced the transition-state method⁴ and Williams, deGroot, and Sommers proposed the generalized transition-state method.⁵ Chong performed extensive calculations of CEBE by the unrestricted generalized transition-state (uGTS) method, and the average deviation of the calculated values from the experimental ones for over 50 molecules was 0.23 eV.^{6,7} However, the density functional method can describe only one-electron processes and, therefore, is suitable only for the main peaks of the core-electron ionizations; it cannot de-

scribe the satellite peaks associated with the core-electron ionizations, which are basically due to two-electron processes.

The experimental studies of the satellites of the core-electron ionizations have been performed with some help of theoretical calculations. Creber *et al.*⁸ observed the satellite spectra of the core-electron ionizations of methane, ammonia, and water, and assigned them with the $X\alpha$ -SW (SW: scattered-wave) calculations. Moncrieff *et al.*⁹ performed the SDCI calculations for studying the satellite peaks of these molecules, but there were some discrepancies between the theoretical and experimental data, and the assignments of some peaks were still controversial. Then, theoretical studies based on a reliable method with flexible basis sets are necessary for the final assignment of these peaks.

The SAC (symmetry adapted cluster¹⁰)/SAC-CI (SAC-configuration interaction) method^{11–14} has been well established as a useful method for studying molecular spectroscopy in general.^{13–17} For ordinary single-electron excitation and ionization processes, we use SAC-CI SD(singles and doubles)-*R* method, but for multiple-electron processes such as those involved in shake-up satellite peaks, the SD-*R* method is sometimes insufficient and the SAC-CI general-*R* method^{18–20} has been shown to be a powerful tool. With the general-*R* method, we could accurately calculate multiple electron processes and a large number of states appearing in particular in the inner-valence region of the ionization spectra.^{21,22} Through a series of recent applications,²² the SAC-CI general-*R* method has been established as a useful tool for describing fine details of the valence ionizations and their satellite spectra. In the present study, we will show that

^{a)}Fax: +81-75-383-2741. Electronic mail: hiroshi@sbchem.kyoto-u.ac.jp

he method is also useful to describe both the main and satellite peaks in the core-ionization spectra of molecules.

II. COMPUTATIONAL DETAILS

In this study, we examine vertical core-ionization processes, and so the molecular geometries used were the experimental ones for the ground state.²³ The molecules studied were C^{*}H₄, N^{*}H₃, H₂O^{*}, HF^{*}, C₂^{*}H₆, C₂^{*}H₄, C₂^{*}H₂, C^{*}H₃Cl, HC^{*}N, C^{*}H₃F, C^{*}H₂Cl₂, HC^{*}ONH₂, H₂C^{*}O, C^{*}O, C^{*}H₂F₂, C^{*}O₂, N₂^{*}H₄, HCN^{*}, HCON^{*}H₂, ClCN^{*}, N₂^{*}H₂, N^{*}NO, N₂^{*}, CIN^{*}O, and NN^{*}O, where the asterisk designates the atom whose 1s electron ionization was investigated. We chose the basis sets to be flexible enough to describe orbital reorganizations and electron correlations. The valence triple zeta (VTZ), Gaussian type orbitals of Ahlrichs,²⁴ (10s6p)/[6s3p], and (12s9p)/[8s5p] were used for the first-row atoms and Cl atom, respectively, augmented with the two polarization *d* functions²⁵ and the Rydberg functions [2s2p2d] for main line calculations, and [4s4p4d] for the calculations of the shake-up satellites.²⁶ For the atoms, whose 1s electron was ionized, these basis sets were further augmented by the first derivatives^{27,28} of the three *s* functions, which describe the polarizations and the angular correlations of the 1s electrons. It also describes the orbital reorganization due to the core-electron ionizations.^{29,30} We also added two *s*- and *p*-type functions [2s2p] for the calculations of shake-up satellites [$\alpha_s(\text{C})=0.257\,462\,7$; $0.064\,365\,675$, $\alpha_p(\text{C})=0.201\,695\,08$; $0.050\,423\,77$, $\alpha_s(\text{N})=0.358\,794\,28$; $0.089\,698\,57$, $\alpha_p(\text{N})=0.285\,902\,626$; $0.071\,475\,656\,5$]. These were important to describe the valence orbital reorganization induced by the core-electron ionizations. However, these extensive basis sets for the shake-up states had only a small effect on the CEBE and therefore, they were not included in the calculations of CEBE. For H atom, the VTZ (6s1p)/[3s1p] set was used. The resultant basis sets for main line calculations were [8s8p4d] for the atoms whose 1s electron was ionized, and [8s5p4d/10s7p4d/3s1p] for other atoms. For the calculations of the shake-up satellites, we used [12s12p6d] set for C and N atoms.

For the calculations of CEBE, the *R* operators up to triples were included; these higher-order operators are necessary for describing orbital relaxations as well as electron correlations. Furthermore, the satellite states in the present energy region are described mainly by the two-electron processes with considerable contributions of triples, and, therefore, to provide reliable theoretical spectra, we have included the *R* operators up to quadruple excitations.

In the SAC-CI calculations, all the MOs (molecular orbitals) were included in the active space. To reduce the computational effort, perturbation selection¹⁵ was performed in the state-selection scheme. The threshold of the linked terms for the ground state was set to $\lambda_g=1.0\times 10^{-6}$ a.u. The unlinked terms were adopted as the products of the important linked terms whose SDCI coefficients were larger than 0.005. To calculate the CEBE, the thresholds of the linked doubles and triples terms were set to $\lambda_e=1.0\times 10^{-7}$ a.u. for the core-electron ionized states. For the calculation of the

TABLE I. Calculated and observed CEBE (eV) of CH₄, NH₃, H₂O, and HF.

	SAC/SAC-CI	Expt. ^a	ΔSCF^b	DFT ^c
CH ₄ (C 1s ⁻¹)	290.63	290.80	290.97	290.92
NH ₃ (N 1s ⁻¹)	405.50	405.60	405.36	405.83
H ₂ O (O 1s ⁻¹)	539.87	539.88	539.21	540.05
HF (F 1s ⁻¹)	694.00	694.22	693.28	694.28
Average discrepancy	0.13	...	0.51	0.15

^aReference 2.

^bReference 3.

^cReference 7.

satellite spectrum, the threshold of the linked doubles and triples were set to 5.0×10^{-7} a.u. and that of the quadruples was set to 5.0×10^{-6} a.u. The 60 reference states were adopted for the perturbation selection and, therefore, the threshold dependence of the results should be small. The thresholds of the CI coefficients for calculating the unlinked operators in the SAC-CI method were 0.05 and 0.0 for the *R* and *S* operators, respectively. The threshold dependence of the results was examined for the low-lying satellites of CH₄; the difference was as small as $\Delta E=0.03$ eV.

Ionization cross sections were calculated using the monopole approximation³¹ to estimate the relative intensities of the peaks. Both initial-state and final-ionic-state correlations were included.

The SAC/SAC-CI calculations were executed with the GAUSSIAN03 suite of programs³² with some modifications for calculating inner-shell ionization spectra.

III. CEBE OF CH₄, NH₃, H₂O, AND HF

First, the CEBE of CH₄, NH₃, H₂O, and HF are studied by the SAC-CI general-*R* method. The calculated values were presented in Table I along with the experimental values² and other theoretical results.^{3,7} The calculated CEBE of CH₄ (C 1s⁻¹), NH₃ (N 1s⁻¹), H₂O (O 1s⁻¹), and HF (F 1s⁻¹) were 290.63, 405.50, 539.87, and 694.00 eV, respectively, in excellent agreement with the experimental values of 290.80, 405.60, 539.88, and 694.22 eV. The relativistic effects for these molecules were reported to be quite small,⁷ i.e., less than 0.1 eV, except for HF molecule. The average absolute deviation of these four CEBE by the general-*R* method was small (0.13 eV) in comparison with those of the ΔSCF (Ref. 3) and DFT (Ref. 7) methods, 0.51 and 0.15 eV, respectively.

IV. C 1S CEBE

The present method was systematically applied to the C 1s ionizations of 13 molecules and the chemical shift of the CEBE was investigated. The results are summarized in Table II in comparison with the experimental values. Figure 1 shows a comparison between the present theoretical and experimental values. The C 1s CEBE of these molecules range from 290.6 to 297.7 eV. Our method reproduced these CEBE quite accurately, and hence the chemical shifts of these molecules. In general, the CEBE is shifted higher when the adjacent atom is electron withdrawing. The average ab-

TABLE II. Calculated and observed C 1s CEBE (eV) of 13 molecules.

Molecules	SAC/SAC-CI	Expt. ^a
C ₂ H ₆	290.75, ^b 290.76 ^c	290.60
C ₂ H ₄	290.80, ^b 290.85 ^c	290.79
CH ₄	290.63	290.80,290.71 ^d
C ₂ H ₂	291.19, ^b 291.28 ^c	291.17
CH ₃ Cl	292.51	292.40
HCN	293.61	293.50
CH ₃ F	293.68	293.65
CH ₂ Cl ₂	294.05	294.00
HCONH ₂	294.42	294.45
H ₂ CO	294.43	294.47
CO	296.27	296.19
CH ₂ F ₂	296.25	296.40
CO ₂	297.96	297.66
Average discrepancy	0.09	...

^aReference 2.^cGerade state.^bUngerade state.^dReference 8.

solute deviation for these 13 molecules was 0.09 eV, while that of the uGTS model of the DFT method by Chong was also small, 0.16 eV.⁷

The chemical shift of the C 1s ionization has been investigated by several authors. Levy *et al.* studied fluoromethanes and found that the electron correlations were very important for reproducing the chemical shifts.³³ In our results, the chemical shifts of CH₃F and CH₂F₂ relative to CH₄ were calculated to be 3.05 and 5.62 eV, respectively, which are in good agreement with the experimental values of 2.94 and 5.69 eV, respectively.³³

For C₂H₂, C₂, C₂H₄, and C₂H₆, we calculated the K-shell gerade and ungerade states and estimated the energy splitting Δ_{g-u} . This splitting in the core-ionized states have been intensively discussed, and recently, the energy separations were observed for C₂H₂³⁴ and N₂.³⁵ In the present study, we calculated the Δ_{g-u} for C₂H₂, C₂, C₂H₄, and C₂H₆ to see its relationship with the C–C bond length. The energy splittings of these molecules were summarized in Table III. For C₂H₂, C₂, C₂H₄, and C₂H₆, the calculated Δ_{g-u} value decreased with increasing C–C bond length, as expected from a simple MO picture. The Δ_{g-u} value calculated for C₂H₂ was 0.08 eV in comparison with the experimental result of 0.105 eV.³⁴

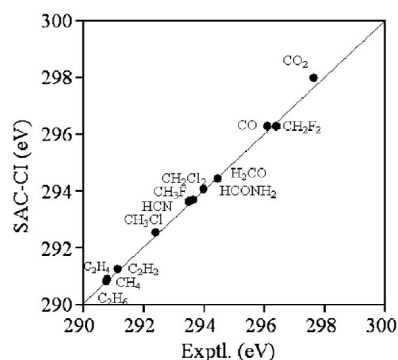


FIG. 1. C 1s CEBE: SAC-CI vs Experiments.

TABLE III. Energy splitting between gerade and ungerade core-hole states.

	R_{C-C} or R_{N-N}	Δ_{g-u} (eV)	Expt. (eV)
C ₂ H ₂	1.203	0.08	0.105 ^a
C ₂	1.243	0.03	...
C ₂ H ₄	1.330	0.02	...
C ₂ H ₆	1.522	0.01	...
N ₂	1.098	0.09	0.097 ^b
N ₂ H ₂	1.252	0.02	...
N ₂ H ₄	1.450	0.01	...

^aReference 34.^bReference 35.

V. N 1S CEBE

We summarized in Table IV the N 1s CEBE of nine molecules and the correspondence between theory and experiment is shown in Fig. 2. The experimental value of CEBE for N₂H₂ was not reported, but, it was calculated for the K-shell gerade and ungerade energy splitting. For N₂O, the N 1s CEBE of the central and edge N atoms were calculated. The N 1s CEBE range from 405.5 to 412.6 eV for these molecules with the chemical shift depending on the electron negativity of the adjacent atom as in the case of C 1s CEBE. The SAC-CI calculated the CEBE of these molecules very accurately: the average absolute deviation from the experimental values was 0.11 eV in comparison with that of the DFT method, 0.26 eV.⁷

For molecules containing two N atoms, N₂, N₂H₂, and N₂H₄, we also calculated the energy splitting Δ_{g-u} between K-shell gerade and ungerade states. As shown in Table III, the relationship between the Δ_{g-u} values and the N–N bond lengths for these molecules is the same as the molecules with two carbon atoms. The energy splitting for N₂H₂, and N₂H₄ were as small as 0.02 and 0.01 eV, respectively. The Δ_{g-u} value of N₂ was calculated to be 0.09 eV in agreement with the experimental value of 0.097 eV.³⁵

VI. SATELLITE PEAKS OF C 1S IONIZATION OF CH₄

Creber, Tse, and Bancroft⁸ observed the core-electron ionization and its satellite spectrum of CH₄ and performed X α –SW calculations for the assignment of the ESCA (electron spectroscopy for chemical analysis) spectrum. Their cal-

TABLE IV. Calculated and observed N 1s CEBE (eV) of nine molecules.

Molecules	SAC/SAC-CI	Expt. ^a
NH ₃	405.50	405.60
N ₂ H ₄	405.89, ^b 405.90 ^c	406.1
HCN	406.35	406.36
HCONH ₂	406.41	406.39
CICN	406.51	406.45
N ₂ H ₂	408.65, ^b 408.67 ^c	...
NNO	408.88	408.66
N ₂	409.76, ^b 409.85 ^c	409.83
CINO	411.20	411.48
NNO	412.79	412.57
Average discrepancy	0.11	...

^aReference 2.^bUngerade state.^cGerade state.

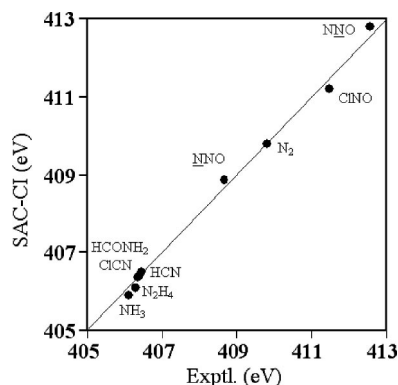
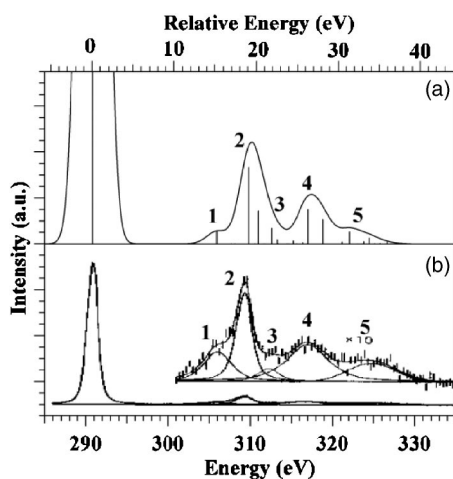


FIG. 2. N 1s CEBE: SAC-CI vs experiments.

culations gave, however, much lower values in comparison with the experimental ones, especially in the higher energy region. Moncrieff *et al.*⁹ used the SDCI method to calculate the C 1s shake-up satellites of CH₄.

We have used in the present study the SAC-CI general-*R* method in which the *R* operators up to quadruples are included and the results are given in Fig. 3 to compare with the experimental satellite spectrum⁸ of the *K*-shell ionization of CH₄. In the theoretical spectrum, the calculated monopole intensities were shown by the solid vertical lines and convoluted with the Gaussian envelopes using the FWHM (full width at half maximum) of 2.4 eV. Table V summarizes the IPs, monopole intensities and the main configurations of the satellite peaks of CH₄ whose relative intensities were larger than 0.001. We note that many other states with negligible intensities existed in this energy region, though they were not listed here. Five remarkable satellite bands were identified by the ESCA experiment⁸ and the peak numbers 1–5 were cited from their work. In the following discussions, the peak positions are given relative to the main peak ($1a_1$)⁻¹ state since the previous experimental and theoretical works^{8,9} did in that manner. We note, however, that our results are comparable with the experimental values in their absolute values.

As shown in Fig. 3, the theoretical spectrum roughly reproduces the shape of the observed satellite spectrum.

FIG. 3. C 1s ionization and its satellite spectrum of CH₄ by (a) SAC-CI general-*R* method and (b) ESCA (Ref. 8).

Creber, Tse, and Bancroft assigned the first satellite peak to the shake-up state of the $(1t_2^{-1}3s)$ transition.⁸ However, this state is 2T_2 , which has no final-state interaction with the $(1a^{-1})$ state and, therefore, it should have a negligible intensity. We assigned this peak to the shake-up state of the $(1t_2^{-1}3p)$ transition calculated at 15.13 eV in comparison with the experimental value of 15.66 eV. The relative pole strength was calculated to be 0.008, which was smaller than the experimental relative peak area of 0.04.⁸ The SDCI work of Moncrieff *et al.* calculated this state at 16.6 eV with very small intensity.⁹

The strongest satellite peak 2 was assigned to the shake-up state characterized by the $(1t_2^{-1}3p)$ transition.^{8,9} This peak was found to be composed of several split peaks owing to the strong electron correlation effects. All of these shake-up states were described mainly by the $(1t_2^{-1}3p)$ transitions in agreement with the previous assignment. The total pole strength was calculated to be 0.070, which was close to the experimental value of 0.10.⁸ The calculated relative binding energies of these states, the strongest one being at 19.01 eV, were larger than the experimental value of 18.91 eV.

Between the two strong peaks 2 and 4, a weak peak 3 was observed. We might assign this peak to be composed of the many shake-up states characterized as the excitations to the Rydberg 3d and 4p orbitals accompanying the C 1s ionization. These shake-up satellites were distributed in a broad energy region from 21.82 to 25.59 eV. Creber, Tse, and Bancroft⁸ calculated the C 1s satellite spectrum without including the *d*-type Rydberg basis functions and concluded that these peaks were assigned to the $(1t_2^{-1}4p)$ transitions. We calculated $(1t_2^{-1}3d)$ and $(1t_2^{-1}4p)$ transitions at 21.82 and 22.49 eV, respectively, and assigned these transitions to this peak 3, though the intensity of the $(1t_2^{-1}3d)$ transition was evaluated to be small. The total pole strength of these shake-up states was 0.011 in comparison with the experimental peak area of 0.02. The SDCI calculations also gave the shake-up states in this energy region, though their intensities were very small.⁹

In the region of the broad peak 4, we calculated several shake-up states. The two prominent peaks calculated in this energy region were attributed to the $(2a_1^{-1}3s)$ transitions calculated at 26.22 and 28.02 eV and both peaks had relatively large intensities of 0.022 and 0.016, respectively. The experimental peak also had a large intensity with the relative area of 0.10 (Ref. 8) and Creber, Tse, and Bancroft also assigned this peak as the $(2a_1^{-1}3s)$ transition. Finally, peak 5 was assigned to the $(2a_1^{-1}4s)$ transitions whose IPs were calculated at 31.29, 33.68, and 35.71 eV, while the experimental peak was centered at 34.83 eV. The $X\alpha$ -SW calculation estimated this state at 29.65 eV,⁸ while the CISD calculated two candidates at 32.0 and 36.8 eV with very small intensities.⁹

The present calculations did not give the shake-up states with considerable intensities in the energy region higher than peak 5.

VII. N 1S SATELLITE SPECTRUM OF NH₃

Finally, we discuss the satellite spectrum of the N 1s core-electron ionization of NH₃. The satellite spectrum of

TABLE V. Ionization potential (IP) (eV), monopole intensity, and main configurations of the C 1s ionization and its satellite states of CH₄ calculated by the SAC-CI general-*R* method.

Expt. ^a				Theory		SAC-CI general- <i>R</i>			
No.	IP (eV)	ΔE^c (eV)	Intensity	$X\alpha$ -SW ^a ΔE^c (eV)	CISD ^b ΔE^c (eV)	IP (eV)	ΔE^c (eV)	Intensity	Main configurations ($ C >0.2$)*
0	290.7	0.0	1.000	290.80	0.00	1.000	$0.83(1a_1^{-1}) - 0.21(1t_2^{-1}3p1a_1^{-1}) - 0.21(1t_2^{-1}3p1a_1^{-1}) - 0.21(1t_2^{-1}3p1a_1^{-1})$
1	306.4	15.66	0.04	15.23 (16.58)	(16.6)	305.93	15.13	0.008	$0.42(1a_1^{-1}3p1t_2^{-1}) + 0.42(1a_1^{-1}3p1t_2^{-1}) + 0.42(1a_1^{-1}3p1t_2^{-1})$
2	309.6	18.91	0.10	17.79	19.8 19.9	309.81	19.01	0.049	$0.35(1t_2^{-1}3p1a_1^{-1}) + 0.35(1t_2^{-1}3p1a_1^{-1}) + 0.35(1t_2^{-1}3p1a_1^{-1}) - 0.25(1a_1^{-1}3p1t_2^{-1}) - 0.25(1a_1^{-1}3p1t_2^{-1}) - 0.25(1a_1^{-1}3p1t_2^{-1})$
						310.99	20.19	0.021	$0.42(1a_1^{-1}3p1t_2^{-1}) + 0.42(1a_1^{-1}3p1t_2^{-1}) + 0.42(1a_1^{-1}3p1t_2^{-1}) + 0.35(1t_2^{-1}3p1a_1^{-1}) + 0.35(1t_2^{-1}3p1a_1^{-1}) + 0.35(1t_2^{-1}3p1a_1^{-1})$
3	312.7	22.01	0.02	18.40	...	312.62	21.82	0.010	$0.29(1t_2^{-1}3d1a_1^{-1}) + 0.28(1a_1^{-1}3d1t_2^{-1}) - 0.25(1t_2^{-1}3p1a_1^{-1}) + 0.24(1t_2^{-1}3p1a_1^{-1})$
						313.29	22.49	0.001	$0.35(1a_1^{-1}4p1t_2^{-1}) - 0.27(1t_2^{-1}4p1a_1^{-1}) + 0.27(1a_1^{-1}4p1t_2^{-1}) - 0.20(1t_2^{-1}4p1a_1^{-1})$
4	317.6	26.89	0.10	23.35	27.1 29.5	317.02	26.22	0.022	$0.33(1a_1^{-1}3s2a_1^{-1}) - 0.28(1a_1^{-1}3s2a_1^{-1}) - 0.26(2a_1^{-1}4s1a_1^{-1})$
						318.82	28.02	0.016	$0.48(2a_1^{-1}3s1a_1^{-1}) - 0.48(1a_1^{-1}3s1a_1^{-1}) + 0.45(1a_1^{-1}4s2a_1^{-1})$
						322.09	31.29	0.008	$0.33(1a_1^{-1}4s2a_1^{-1}) - 0.25(2a_1^{-1}3s1a_1^{-1}) - 0.25(2a_1^{-1}4s1a_1^{-1}) + 0.22(1a_1^{-1}3s2a_1^{-1})$
5	325.5	34.84	0.05	29.65	(32.0) (36.8)	324.48	33.68	0.004	$0.51(1a_1^{-1}4s2a_1^{-1}) + 0.47(2a_1^{-1}4s1a_1^{-1}) + 0.44(2a_1^{-1}3s1a_1^{-1}) + 0.35(1a_1^{-1}3s2a_1^{-1})$
						326.51	35.71	0.001	$0.51(2a_1^{-1}4s1a_1^{-1}) + 0.51(1a_1^{-1}4s2a_1^{-1}) - 0.47(2a_1^{-1}3s1a_1^{-1}) - 0.47(1a_1^{-1}4s2a_1^{-1})$

^aReference 8.^bReference 9.^c ΔE means relative energy to $(1a_1^{-1})$ state.

NH₃ lies in a broader energy region than that of CH₄, since the $t_2 \rightarrow t_2$ transition in CH₄ splits into $a_1 \rightarrow a_1$ and $e \rightarrow e$ transitions in NH₃.⁸ The ESCA spectrum observed by Creber, Tse, and Bancroft showed such feature⁸ and the CISD calculations by Moncrieff *et al.* also gave such distributed peaks.⁹ In Fig. 4, the N 1s satellite spectrum of NH₃ calculated by the SAC-CI method is compared with the ESCA spectrum.⁸ The calculated pole strengths shown by the solid vertical lines were convoluted with Gaussians using the FWHM of 2.4 eV. The IPs, monopole intensities, and the main configurations of the satellite peaks whose relative intensities were larger than 0.001 were listed in Table VI and many other states with smaller intensities were not given. As

in the ESCA work,⁸ the peak numbers 1–4 were used and the energies were shown again relative to the IP of the N 1s main peak.

The first small peak 1 was observed at 11.02 eV.⁸ In this energy region, the shake-up states of $(3a_1^{-1}3s)$ transition were calculated at 10.46 and 12.34 eV. We attribute these states to the peak 1. For CH₄, these states correspond to the symmetry-forbidden 2T_2 state. This assignment is consistent with the earlier one by the ESCA and $X\alpha$ -SW works,⁸ though the $X\alpha$ -SW method calculated this peak in the higher energy at 14.29 eV. In the work of UHF (unrestricted Hartree–Fock) calculation,³⁶ the peaks below 15 eV were assigned as due to the inelastic scattering, but, the SD-CI calculation⁹ gave a shake-up state at about 14 eV. Since we do not include the inelastic scattering in the present calculations, we cannot exclude the contribution of inelastic scattering for the peak 1.

To examine the low-lying shake-up states, we also calculated the O 1s satellite spectra of H₂O. The first satellite peak of H₂O was observed at ~ 16.7 eV.³⁷ We calculated the shake-up states at 16.84 and 18.75 eV and assigned these states to this first peak. We did not obtain the shake-up states in the energy region lower than 16 eV, where other experiments observed the inelastic scatterings.^{9,38} Thus, the assignment of the low-lying satellite states of these three molecules has been confirmed: the satellite peaks of NH₃ exist from the low energy region compared with those of CH₄ and H₂O because of the lower symmetry and nuclear charge. The detailed SAC-CI results of the entire O 1s spectrum of H₂O will be reported elsewhere in the literature.

For the peak 2 observed at 17.22 eV in the shoulder of

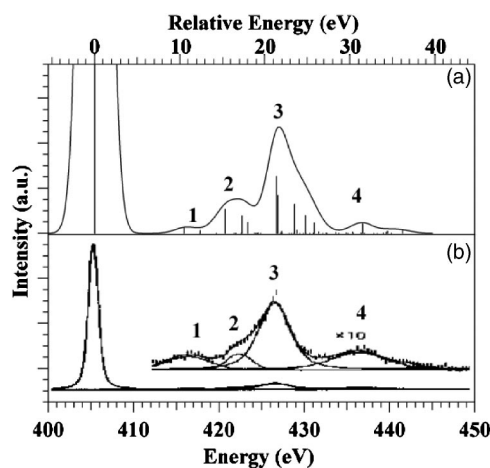
FIG. 4. N 1s ionization and its satellite spectrum of NH₃ by (a) SAC-CI general-*R* method and (b) ESCA (Ref. 8).

TABLE VI. Ionization potential (IP) (eV), monopole intensity, and main configurations of the N 1s ionization and its satellite states of NH₃ calculated by the SAC-CI general-*R* method.

Expt. ^a				Theory		SAC-CI general- <i>R</i>			
No.	IP (eV)	ΔE^c (eV)	Intensity	$X\alpha$ -SW ^a ΔE^c (eV)	CISD ^b ΔE^c (eV)	IP (eV)	ΔE^c (eV)	Intensity	Main configurations ($ C > 0.2$)*
0	405.6	0.0	1.00	405.45	0.00	1.000	$0.84(1a_1^{-1}) - 0.20(1e^{-1}3p1a_1^{-1}) - 0.20(1e^{-1}3p1a_1^{-1})$
1	416.6	11.02	0.03	14.29	...	415.91	10.46	0.003	$0.30(3a_1^{-1}4a_1(\sigma^*)1a_1^{-1}) - 0.28(1a_1^{-1}3s3a_1^{-1})$
						417.79	12.34	0.002	$0.55(1a_1^{-1}4a_1(\sigma^*)3a_1^{-1}) + 0.53(3a_1^{-1}4a_1(\sigma^*)1a_1^{-1})$
2	422.8	17.22	0.02	17.38	17.2	420.69	15.24	0.016	$0.43(1a_1^{-1}3p3a_1^{-1}) - 0.34(3a_1^{-1}3p1a_1^{-1})$
						422.70	17.25	0.012	$0.45(1a_1^{-1}3p1e^{-1}) + 0.45(1a_1^{-1}3p1e^{-1}) + 0.45(1e^{-1}2e1a_1^{-1})$ $+ 0.45(1e^{-1}3p1a_1^{-1})$
						423.37	17.92	0.007	$0.64(3a_1^{-1}3p1a_1^{-1}) + 0.64(1a_1^{-1}3p3a_1^{-1})$
3	426.7	21.13	0.13	20.21		426.75	21.30	0.038	$0.39(1e^{-1}3p1a_1^{-1}) + 0.39(1e^{-1}3p1a_1^{-1}) + 0.36(1a_1^{-1}3s3a_1^{-1})$
				21.12	22.3	426.92	21.47	0.025	$0.38(3a_1^{-1}3s1a_1^{-1}) + 0.36(1a_1^{-1}3s3a_1^{-1})$
				21.25	23.1	428.85	23.40	0.020	$0.39(1a_1^{-1}3p1e^{-1}) + 0.39(1a_1^{-1}3p1e^{-1})$
					23.3	430.12	24.67	0.012	$0.38(1e^{-1}4p1a_1^{-1}) + 0.38(1e^{-1}4p1a_1^{-1}) + 0.32(1e^{-1}3p1a_1^{-1})$ $+ 0.32(1e^{-1}3p1a_1^{-1})$
					25.6	431.13	25.68	0.007	$0.37(1a_1^{-1}4p1e^{-1}) + 0.29(1a_1^{-1}4p1e^{-1})$
						436.83	31.38	0.006	$0.38(2a_1^{-1}4a_1(\sigma^*)1a_1^{-1}) - 0.35(2a_1^{-1}3s1a_1^{-1})$
4	436.6	31.01	0.07	27.54	32.0	439.74	34.29	0.001	$0.38(2a_1^{-1}3s1a_1^{-1}) - 0.35(1a_1^{-1}4a_1(\sigma^*)2a_1^{-1})$
				30.63	34.8	441.51	36.06	0.002	$0.35(2a_1^{-1}4s1a_1^{-1}) - 0.32(1a_1^{-1}4s2a_1^{-1})$ $- 0.29(2a_1^{-1}4a_1(\sigma^*)1a_1^{-1})$

^aReference 8.^bReference 9.^c ΔE means relative energy to $(1a_1^{-1})$ state.

the strongest peak, we attributed the $(1e^{-1}3p)$ and $(3a_1^{-1}3p)$ transitions calculated at 15.24, 17.25, and 17.92 eV with the intensities of 0.016, 0.012, and 0.007, respectively; these states correspond to the first peak of CH₄, namely, the lower-energy transition of $(t_2^{-1}3p)$. The previous calculations^{8,9} also gave the $(3a_1^{-1}3p)$ transition at about 17.2–17.4 eV, but the $(1e^{-1}3p)$ state was calculated in the higher energy region.

For the strongest peak 3 centered at 21.13 eV, we obtained two prominent shake-up states at 21.30 and 21.47 eV with the relative intensities of 0.038 and 0.025, respectively. These shake-up states were characterized as the transitions $(3a_1^{-1}3s)$ and $(1e^{-1}3p)$. In the higher energy region of these states, some shake-up states were also calculated at 23.40, 24.67, and 25.68 eV with considerable intensities, which contribute to the higher-energy tail of peak 3. These states were dominantly characterized as the transitions from 1e MO to 3p and 4p MOs. For peak 3, the $X\alpha$ -SW calculations gave only the transitions from 1e MO and the SDCI gave the transitions from both $3a_1$ and 1e MOs.^{8,9}

For peak 4 observed at 31.01 eV, the present results assign the shake-up states at 31.38, 34.29, and 36.06 eV that were described by the linear combination of the $[2a_1^{-1}4a_1(\sigma^*)]$, $(2a_1^{-1}3s)$, and $(2a_1^{-1}4s)$ transitions.

VIII. SUMMARY

The SAC-CI general-*R* method was systematically applied to the calculations of the CEBE of C, N, O, and F atoms of 22 molecules and of the satellite spectra of the C 1s and N 1s core-ionizations of methane and ammonia.

The CEBE of molecules were accurately calculated by the present method and, in particular, for the C 1s and N 1s

ionizations, the theoretical chemical shifts of the CEBE were in good agreement with the experimental values. The average absolute discrepancy from the experimental values was only 0.11 eV. The energy splittings between *K*-shell gerade and ungerade states, that have been intensively studied in the recent works, were calculated and discussed in relation to the bond length.

The satellite spectra of the C 1s and N 1s ionizations of CH₄ and NH₃ were reasonably well reproduced by the present method. The present general-*R* method included the triples and quadruples *R* operators as well as the singles and doubles operators in order to accurately describe the multi-electron processes involved in the core-electron ionization processes. The shake-up states were dominantly described by the two-electron processes, but the three-electron processes also mixed considerably to these shake-up states. These higher excitation operators were important to describe the electron correlation effects of the many-electron processes and the orbital reorganization effects accompanying the core-electron ionizations. The calculations reproduced the shape of the experimental satellite spectrum rather well, though the monopole approximation used for the intensity calculation was not necessarily a good approximation of the real process: more refined theory of the intensity is certainly necessary. We could clarify the detailed electronic origins of the satellite peaks.

We may conclude that the present SAC-CI general-*R* method can describe both the electron correlations and the orbital reorganizations associated with the core-electron ionization processes. The present method provides a general useful theoretical tool for studying fine molecular spectroscopy including core-electron ionization processes.

ACKNOWLEDGMENT

This study was supported by a Grant for Creative Scientific Research from the Ministry of Education, Science, Culture, and Sports of Japan.

- ¹K. Siegbahn, C. Nordling, G. Johansson *et al.*, *ESCA Applied to Free Molecules* (North-Holland, Amsterdam, 1969).
- ²A. A. Bakke, A. W. Chen, and W. L. Jolly, *J. Electron Spectrosc. Relat. Phenom.* **20**, 333 (1980).
- ³P. W. Deutsch and L. A. Curtiss, *Chem. Phys. Lett.* **39**, 588 (1976).
- ⁴J. C. Slater, *Adv. Quantum Chem.* **6**, 1 (1972).
- ⁵A. R. Williams, R. A. deGroot, and C. B. Sommers, *J. Chem. Phys.* **63**, 628 (1975).
- ⁶D. P. Chong, *Chem. Phys. Lett.* **232**, 486 (1995).
- ⁷D. P. Chong, *J. Chem. Phys.* **103**, 1842 (1995).
- ⁸D. K. Creber, J. S. Tse, and G. M. Bancroft, *J. Chem. Phys.* **72**, 4291 (1980).
- ⁹D. Moncrieff, I. H. Hiller, S. A. Pope, and M. F. Guest, *Chem. Phys.* **82**, 139 (1983).
- ¹⁰H. Nakatsuji and K. Hirao, *J. Chem. Phys.* **68**, 2053 (1978).
- ¹¹H. Nakatsuji, *Chem. Phys. Lett.* **59**, 362 (1978).
- ¹²H. Nakatsuji, *Chem. Phys. Lett.* **67**, 329, 334 (1979).
- ¹³H. Nakatsuji, *Acta Chim. Hung.* **129**, 719 (1992).
- ¹⁴H. Nakatsuji, *Computational Chemistry—Review of Current Trends* (World Scientific, Singapore, 1997), Vol. 2, pp. 62–124.
- ¹⁵H. Nakatsuji, *Chem. Phys.* **75**, 425 (1983).
- ¹⁶H. Nakatsuji, J. Hasegawa, and M. Hada, *J. Chem. Phys.* **104**, 2321 (1996).
- ¹⁷H. Nakatsuji, J. Hasegawa, and K. Ohkawa, *Chem. Phys. Lett.* **296**, 499 (1998).
- ¹⁸H. Nakatsuji, *Chem. Phys. Lett.* **177**, 331 (1991).
- ¹⁹H. Nakatsuji, *J. Chem. Phys.* **83**, 713 (1985).
- ²⁰H. Nakatsuji, *J. Chem. Phys.* **83**, 5743 (1985).
- ²¹M. Ehara and H. Nakatsuji, *Chem. Phys. Lett.* **282**, 347 (1998).
- ²²M. Ehara, M. Ishida, K. Toyota, and H. Nakatsuji, in *Reviews in Modern Quantum Chemistry*, edited by K. D. Sen (World Scientific, Singapore, 2002), pp. 293–319.
- ²³J. H. Callomon, E. Hirota, K. Kuchitsu, W. J. Lafferty, A. G. Maki, and C. S. Pote, *Landolt-Bornstein Numerical Data and Functional Relationships in Science and Technology*, edited by K.-H. Hellwege and A. M. Hellwege, Landolt-Börnstein, New Series, Group II, Vol. 7 (Springer, Berlin, 1976).
- ²⁴A. Shafer, H. Horn, and R. Ahlrichs, *J. Chem. Phys.* **97**, 2571 (1992).
- ²⁵T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).
- ²⁶T. H. Dunning, Jr., and P. J. Hay, in *Methods of Electronic Structure Theory*, edited by H. F. Schaefer III (Plenum, New York, 1977).
- ²⁷H. Nakatsuji, K. Kanda, and T. Yonezawa, *Chem. Phys. Lett.* **75**, 340 (1980).
- ²⁸H. Nakatsuji, K. Kanda, M. Hada, and T. Yonezawa, *J. Chem. Phys.* **77**, 3109 (1982).
- ²⁹H. Nakatsuji, *J. Am. Chem. Soc.* **95**, 345 (1973).
- ³⁰H. Nakatsuji and T. Koga, in *The Force Concept in Chemistry*, edited by B. M. Deb (van Nostrand Reinhold, New York, 1981), Chap. 3.
- ³¹R. I. Martin and D. A. Shirley, *J. Chem. Phys.* **64**, 3685 (1976).
- ³²M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 03, Gaussian, Inc., Pittsburgh, PA, 2003.
- ³³B. Levy, P. Mille, J. Ridard, and J. Vinh, *J. Electron Spectrosc. Relat. Phenom.* **4**, 13 (1974).
- ³⁴B. Kempgens, K. Maier, A. Kivimaki, M. Neeb, L. S. Cederbaum, and A. M. Bradshaw, *Phys. Rev. Lett.* **79**, 3617 (1997).
- ³⁵U. Hergenhahn, O. Kugeler, A. Rudel, E. E. Rennie, and A. M. Bradshaw, *J. Phys. Chem. A* **105**, 5704 (2001).
- ³⁶L. J. Aarons, M. Barber, M. F. Guest, I. H. Hillier, and J. H. McCartney, *Mol. Phys.* **26**, 1274 (1973).
- ³⁷D. Nordfors, A. Nilsson, N. Mårtensson, S. Svensson, U. Gelius, and H. Ågren, *J. Electron Spectrosc. Relat. Phenom.* **56**, 117 (1991).
- ³⁸S. Svensson, H. Ågren, and U. I. Wahlgren, *Chem. Phys. Lett.* **38**, 1 (1976).