



Relativistic effects in *K*-shell ionizations: SAC-CI general-*R* study based on the DK2 Hamiltonian

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ABSTRACT

Relativistic effects in *K*-shell ionizations were studied using the symmetry adapted cluster–configuration interaction (SAC-CI) general-*R* method based on the spin-free part of the second-order Douglass–Kroll–Hess (DK2) Hamiltonian. The core–electron binding energies (CEBEs) of F, Si, P, S, and Cl atoms of several molecules were calculated. The relativistic effect in the CEBEs of the second-row atoms was 4–9 eV. The relativistic effect was mostly overestimated by the Koopmans' theorem and was reduced to the extent of 0.15–0.4 eV by including the orbital relaxation and electron correlations. The present method provides a simple and reliable computational tool for calculating the CEBEs of molecules containing heavy elements.

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1. Introduction

Core–electron binding energies (CEBEs) contain information not only about inner-core electrons but also about valence electrons and chemical bonds. Extensive experimental studies have provided the CEBEs of numerous molecules. Siegbahn et al. [1] summarized the electron spectroscopy for chemical analysis (ESCA) data in 1969 and Bakke et al. [2] reported further ESCA data in 1980. They also clarified the important chemical implications involved in the CEBE data. The spectroscopy of the CEBE lies in the soft X-ray region, and the recent development of high-resolution soft X-ray photoelectron spectroscopy (XPS) has enabled accurate experimental observations of the CEBEs, resolving the vibrational structure.

Theoretically, Bagus and Schaefer [3,4] performed pioneering work by calculating the core–electron processes using the Hartree–Fock method. They calculated the CEBEs of some diatomic molecules. After their work, the Δ SCF method was used most fre-

quently; however, the Δ SCF method even with sufficiently large basis set uniformly underestimated the CEBEs. Electron correlation and core–valence correlation were found to be important for describing the inner-shell excited and ionized states accurately. These correlation effects of the core–electron processes were investigated by configuration interaction (CI) [5,6] and Green's function calculations [7,8]. Density functional theory (DFT) was also applied to calculate the CEBEs with the unrestricted general-ized transition-state (uGTS) method [9].

The SAC (symmetry adapted cluster) [10]/SAC-CI (configuration interaction) [11,12] method is now established as a reliable and useful tool for investigating a wide variety of chemistry [13–15], molecular spectroscopy, biological quantum chemistry, surface chemistry, and magnetic chemistry. There are two options in the SAC-CI method: the SAC-CI SD-*R* method [11,12] is useful for ordinary single-electron excitation and ionization processes and the SAC-CI general-*R* method [16–18] is a powerful tool for multiple-electron processes such as shake-up satellite states. Recently, we have successfully applied the general-*R* method to various types of core–electron processes. In the core–electron processes, the orbital relaxation is much larger than the valence electron processes and the general-*R* method describes both electron correlations and orbital relaxation. The method was applied to the CEBEs of C 1s and N 1s for many molecules [19] and to the inner-shell shake-up satellite spectra of CH₄, NH₃ [19], H₂O [20], and formaldehyde [21]. The *g*–*u* splitting of homonuclear

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molecules were predicted satisfactorily [19]. The overlapping vibrational spectra of the low-lying shake-up satellite states of CO [22] and N₂ [23] were also successfully interpreted by calculating the potential energy curves and Franck–Condon factors. The valence–Rydberg coupling [24] and its thermal effect [25] were also investigated for the inner-shell excitation spectra of N₂O.

The orbital relaxation of the core–electron processes can be treated in a more efficient manner. In the open-shell reference (OR)-SAC-CI method [26], the orbital relaxation effect is described in the reference ROHF function and therefore, this method describes the core–electron processes more effectively than the method of starting from the closed-shell reference function. The valence universal coupled cluster method developed by Jana and Mukherjee [27] can also describe this orbital relaxation of the core–electron processes effectively. These methods were applied to the CEBEs of molecules containing first-row atoms and shown to be useful for studying the core–electron processes of atoms and molecules.

It is now generally recognized that the relativistic effect is important in chemistry in particular for the molecular properties of the heavy elements [28–30]. The methodologies of relativistic quantum chemistry have been developed and established. In this field, Professor Kutzelnigg has deeply contributed to the development of the relativistic method using perturbation theory [31–33]. The relativistic effect is also important in core–electron processes. Although the spin–orbit splitting of the inner-shell P and D states has been intensively investigated, the relativistic effect has not been so much focused in the accurate calculation of the CEBEs for the heavy elements. Most calculations including both electron correlations and relativistic effect have been performed for molecules containing first-row atoms except for the recent work of Barysz and Leszcynski for the rare gas atoms [34], to the best of our knowledge. Experimentally, the spectroscopy of the inner-shell processes of molecules containing heavy elements needs high energy.

In this work, we investigated the CEBEs of molecules containing the second-row atoms, Si, P, S, and Cl as well as the F atom. We performed the SAC-CI general-*R* calculations based on the spin-free part of the second-order Douglas–Kroll–Hess (DK2) Hamiltonian [35–37]. Because the relativistic effect has not been extensively studied in this area, we examined the effect in the CEBEs for molecules including heavy elements at both the SCF level and SAC-CI calculations.

2. Method

The SAC-CI calculations of the CEBE are based on the general-*R* method. The wavefunction for the general-*R* method [16,18] is

$$\psi_{\text{general-}R}^{\text{SAC-CI}} = \left(\sum_i R_i + \sum_{ija} R_{ij}^a + \sum_{ijkab} R_{ijk}^{ab} + \sum_{ijklabc} R_{ijkl}^{abc} + \dots \right) \times \exp \left(\sum_T S_T \right) \Phi_{\text{HF}}$$

where *R* and *S* represent the *R*- and *S*-operators in the SAC-CI expansion, respectively, and Φ_{HF} is the closed-shell ground-state Hartree–Fock wavefunction. In the present calculation, we used the spin-free part of the DK2 Hamiltonian [35–37] to calculate the reference function. For the calculations of the CEBE, *R*-operators up to triples were included, that is, we used an SDT-*R* calculation. Although the SD-*R* calculation is accurate for describing one-electron processes, the triple *R*-operators are necessary for describing orbital relaxations, as well as electron correlations. In this sense, this reference function is not efficient for calculating the electron correlations in the core–electron processes. However, the general-*R* calculation is

stable when calculating the core–hole state and is also useful to calculate the *g*–*u* splitting. To calculate the two-electron processes such as inner-shell shake-up satellite states, we use the SDTQ-*R* calculations. Note that the OR-SAC and OR-SAC-CI methods [26], in which the reference function is based on the ROHF orbitals of the core–hole state, describe the core–electron processes more efficiently: the OR-SAC with single and doubles can describe the core–hole state and the OR-SAC-CI with SDT-*R* can describe the inner-shell shake-up satellite spectrum.

The SAC-CI wavefunction is generally solved by a non-variational method [12]. In the present calculations, we used the approximate variational SAC-CI-V method [12]. Many valence ionized states like single-hole states and shake-up satellite states also appear in the solutions. To obtain only the core–hole state, the initial vector in the Davidson diagonalization was adopted for the core–hole state and the correction vectors producing the valence ionized state were excluded.

In the present study, we calculated the vertical core-ionization processes, and so the molecular geometries were the experimental geometries for the ground state. The molecules studied were CH₃F*, HF*, ClF*, F₂*, Si*H₄, P*H₃, H₂S*, OCS*, and CH₃Cl*, where the asterisk designates the atom in which 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 (GTOs) of Shafer and Ahlrichs [38], (10s6p)/[6s3p] and (12s9p)/[8s5p] were used for the first-row and second-row atoms, respectively, augmented with two polarization d-functions [39] and the diffuse functions [2s2p2d] [40]. For the atoms, in which the 1s electron was ionized, these basis sets were further augmented by the first derivatives [41,42] of three s-functions, which describe the polarizations and the angular correlations of the 1s electrons [43,44]. It also describes the orbital reorganization due to the core–electron ionizations. For the H atom, the VTZ (6s1p)/[3s1p] set [39] was used. The resultant basis sets for the CEBE calculations were [8s8p4d] for the F atom and [10s10p4d] for the second-row atoms in which the 1s electron was ionized, and [8s5p4d/10s7p4d/3s1p] for the other atoms.

In the SAC-CI calculations, all of the MOs were included in the active space. To reduce the computational effort, perturbation selection [45] was performed in the state-selection scheme. The threshold of the linked terms for the ground state was set to $\lambda_g = 1.0 \times 10^{-6}$ au. 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 $\lambda_e = 1.0 \times 10^{-7}$ au for the core–electron ionized states. 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. Previously, we examined the threshold dependence of the results; the energy difference was as small as $\Delta E = 0.03$ eV [19].

The SAC/SAC-CI calculations were performed with the Gaussian03 suite of programs [46] with some modifications for calculating inner-shell ionization spectra.

3. Results and discussion

3.1. F 1s CEBEs

First, the F 1s CEBEs of CH₃F, HF, ClF, and F₂ were calculated by the SAC-CI SDT-*R* method. The calculated values with and without including the relativistic effect are summarized in Table 1 along with the experimental values [2] and are plotted in Fig. 1. The F 1s CEBE of these molecules ranges from 692.7 to 696.7 eV, showing a chemical shift of about 4 eV. In general, the CEBE is shifted to higher energy when the adjacent atom is electron-withdrawing.

Table 1
Calculated and observed CEBE (eV) of CH₃F, HF, ClF, and F₂.

Molecule	Exptl. ^a	Relativistic SAC-CI	Non-relativistic SAC-CI	Relativistic effect (eV)	
				SAC-CI ^b	Koopmans' theorem
CH ₃ F	692.66	692.98	692.41	0.57	0.60
HF	694.22	694.38	694.00	0.38	0.60
ClF	694.44	694.11	693.59	0.52	0.59
F ₂	696.69	696.61	696.07	0.54	0.59
Average deviation	–	0.22	0.49	–	–

^a Ref. [2].

^b $\Delta E = E(\text{Non-relativistic SAC-CI}) - E(\text{relativistic SAC-CI})$.

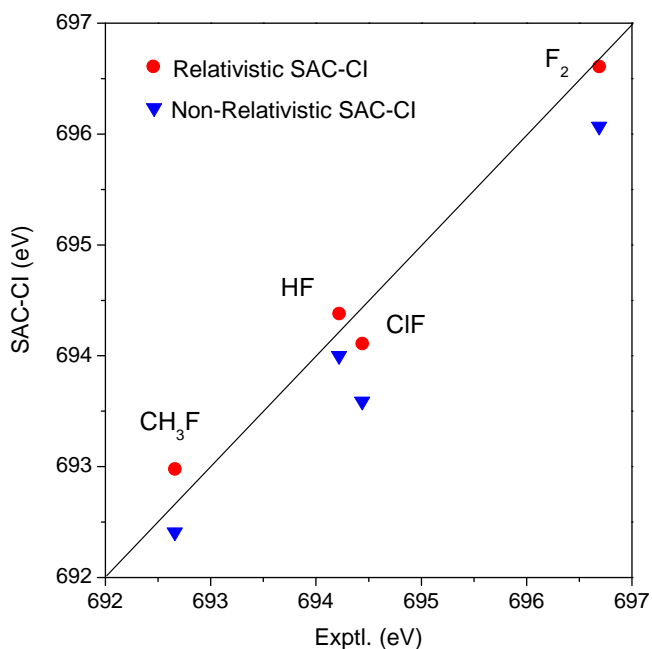


Fig. 1. F 1s CEBE: SAC-CI values plotted to experiment.

The calculated F 1s CEBE of F₂ without including the relativistic effect was 696.07 eV, while the experimental value was reported as 696.69 eV. The CEBE of F₂ was calculated as the average value of the g- and u-states. On the other hand, the SAC-CI method including the relativistic effect gave 696.61 eV, in good agreement with the experimental value. The same trend was obtained for the F 1s CEBE of other molecules. The average deviation of these four

Table 2
Calculated and observed Si, P, S, and Cl 1s CEBE (eV).

Molecule	Exptl.	Relativistic SAC-CI	Non-relativistic SAC-CI	Relativistic effect (eV)	
				SAC-CI ^e	Koopmans' theorem
SiH ₄	1847.1 ^a	1848.24	1843.96	4.28	3.97
PH ₃	2150.5 ^b	2151.25	2146.32	4.93	5.30
H ₂ S	2478.5 ^c	2479.51	2472.98	6.53	6.94
OCS	2480.3 ^a	2481.84	2475.06	6.78	6.93
CH ₃ Cl	2829.4 ^d	2832.15	2823.35	8.80	8.95

^a Ref. [48].

^b Ref. [2].

^c Ref. [49].

^d Ref. [50].

^e $\Delta E = E(\text{Non-relativistic SAC-CI}) - E(\text{Relativistic SAC-CI})$.

molecules was 0.49 eV without the relativistic effect and 0.22 eV with the relativistic effect. The relativistic SAC-CI calculation reproduced the chemical shift of these F 1s CEBS except for the order of HF and ClF where the energy difference is very small. The relativistic effect in the F 1s CEBS of these molecules amounted to about 0.6 eV based on Koopmans' theorem, while it was 0.50 eV on average by the SAC-CI calculation. Koopmans' theorem gave the right order of magnitude of the relativistic effect with slight overestimation. Recent theoretical work of the inner-shell ionizations of the rare gas atoms also showed the same trends [34]. The orbital relaxation and electron correlations affect the scalar relativistic effect. The effect of these factors on the CEBS was clearly shown in the work by Kotsis and Staemmler for the O 1s hole states [47].

3.2. CEBS of second-row atoms

Next, we examined the K-shell ionization potentials of molecules containing second-row atoms, SiH₄, PH₃, H₂S, OCS, and CH₃Cl. The Si, P, S, and Cl 1s ionization potentials are presented in Table 2 along with the experimental values [2,48–50]. The non-relativistic SAC-CI calculations underestimated the CEBS compared with the experimental values, as in the case of the F 1s; however, the deviations are much larger, at about 3–6 eV. The relativistic effect amounted to 4–9 eV for the CEBS of these molecules. The relativistic SAC-CI calculations improved the CEBS but slightly overestimated the values. For example, the S 1s CEBS of H₂S was measured as 2478.5 eV [49] and our theoretical value without including the relativistic effect was 2472.98 eV, which is much smaller than the experimental value. The relativistic SAC-CI calculation for this CEBS gave 2479.51 eV. The deviations from the experimental values were about 1 eV for the molecules containing Si, P, and S. These errors amount to 0.03–0.06% of the absolute values of the CEBS. The CASPT2 calculations also gave the same order of deviations [34]; the errors were large for the inner-shell ionizations of the heavy elements. These errors may be attributed to the crudeness of the basis sets, the higher-order relativistic effects, and/or insufficiency of describing orbital relaxation. Kotsis and Staemmler discussed the difficulty of the basis set selection for the balanced description of the core and valence electron correlations [47]. For the CEBS of the second-row atoms, the difference in the relativistic effect between the Koopmans' theorem and the SAC-CI calculations is in the order of 0.15–0.4 eV; overestimation of the relativistic effect by the Koopmans' theorem also occurs as in the case of the F 1s CEBS, except for SiH₄. The effect of electron correlations is very small compared with the relativistic effect in those molecules containing the second-row atoms.

4. Summary

The SAC-CI SDT-R method based on the spin-free part of the DK2 Hamiltonian was used to calculate the K-shell ionization potentials of molecules containing F, Si, P, S, and Cl atoms. For the F 1s CEBS, the relativistic effect was 0.4–0.6 eV and the relativistic SAC-CI calculations reproduced the values accurately; the average deviation from the experimental values was 0.22 eV. The relativistic effect of the K-shell ionization potentials of molecules containing second-row atoms is as large as 4–9 eV. The relativistic SAC-CI calculation reproduced the CEBS of the second-row atoms with the errors of about 1 eV that amount to 0.03–0.06% of the absolute values. The relativistic effect was mostly overestimated by the Koopmans' theorem and was reduced to the extent of 0.15–0.4 eV by including orbital relaxation and electron correlations. The present method provides a simple and reliable tool for calculating the CEBS of molecules containing heavy elements.

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