High-precision Ab Initio Core-level Spectroscopy

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Abstract. High-precision ab initio theoretical spectroscopy of the core-electronic processes has been achieved by the symmetry-adapted cluster–configuration interaction (SAC–CI) general-R method. In this article, we review the SAC–CI theory and introduce some recent applications to the inner-shell processes. The general-R method reproduced the fine details of the high-resolution spectra providing quantitative assignments and clarifying the essence of the phenomena. We explain the inner-shell shake-up satellite spectrum of CO, geometry relaxation and vibrational spectra of the inner-shell satellites of N\textsubscript{2}, strong valence–Rydberg coupling of O1s excited states of N\textsubscript{2}O, and thermal effects in the inner-shell excitation spectrum.

1. Introduction
Development of state-of-the-art theories has made it possible to obtain precise knowledge of the excited and ionized states of molecules. Theoretical information is valuable in interpreting recent high-resolution molecular spectra. Theory predicts the fine details of the excitation and ionization processes and even supports the design of new molecular spectroscopies. Thus, the interplay between experiment and theory has become standard in modern molecular spectroscopy so that the predicting ability of a theory is an essential issue.

Theoretical spectroscopy has been achieved by various kinds of electronic structure theories. Peyerimhoff et al. performed pioneering work using the multi-reference single and double configuration interaction (MRSDCI) method [1]. Cederbaum and coworkers have greatly contributed to molecular spectroscopy, in particular for ionization spectra and inner-shell electronic processes using the Green’s function method called the algebraic diagrammatic construction (ADC) approach [2]. The symmetry-adapted cluster–configuration interaction (SAC–CI) method, which is based on the cluster expansion, was originally developed by Nakatsuji [3–5]. The method has become established as a reliable methodology through many applications in a wide variety of molecular spectroscopy, biological chemistry, and surface photochemistry [5,6] areas.

The SAC–CI general-R method [7,8] was proposed for investigating multielectron processes and has been successfully applied to processes such as shake-up satellites in the valence ionization spectra [6]. The general-R method is also useful for the inner-shell electronic processes. We have investigated various kinds of core-electronic processes using the general-R method [9–17]; for example, core-electron binding energies (CEBE), inner-shell shake-up satellite spectra, vibrational spectra and geometry relaxation of satellites, g–u splitting, valence–Rydberg coupling, and its vibration-induced suppression. We also examined the relativistic effect in K-shell ionizations using the scalar relativistic method. These series of studies clarified the essence of the core-electron processes.
In this article, we review the SAC–CI theory and introduce our recent challenges to the high precision \textit{ab initio} calculations of the inner-shell electronic processes.

2. Theory

2.1. SAC/SAC–CI theory

The SAC wave function describes the ground state and is defined as
\[
\Psi_{g}^{\text{SAC}} = \exp\left(\sum C_{i} S_{i}^{g}\right) |0\rangle ,
\]
where $|0\rangle$ is the Hartree–Fock wave function and $S_{i}^{g}$ is the spin-symmetry- and space-symmetry-adapted excitation operator. In the SAC method, to solve for $C_{i}$ we require that the Schrödinger equation is satisfied within the configuration space of $\{|0\rangle, S_{i}^{g} |0\rangle\}$ as
\[
\langle 0|H - E_{g}|\Psi_{g}^{\text{SAC}}\rangle = 0 ,
\]
\[
\langle 0|S_{i}^{g} (H - E_{g})|\Psi_{g}^{\text{SAC}}\rangle = 0 .
\]
This SAC equation is called a nonvariational method [3–5].

The SAC theory defines not only the SAC wave function for the ground state, but also the excited functions that span the basis for the excited states [3–5]. Using the correlated ground-state SAC wave function, we define the excited functions $\{\Phi_{k}\}$ as
\[
\Phi_{k} = P R_{k}^{R} |\Psi_{g}^{\text{SAC}}\rangle ,
\]
where $P$ is an operator that projects out the ground state and $\{R_{k}^{R}\}$ represents a set of the excitation, ionization, and electron-attachment operators. These functions $\{\Phi_{k}\}$ constitute a basis for the excited state. Therefore, we describe the excited state by a linear combination of these functions as
\[
\Psi^{\text{SAC–CI}} = \sum_{k} d_{k} \Phi_{k} ,
\]
which is the SAC–CI expansion. The nonvariational SAC–CI solution is obtained by projecting the Schrödinger equation to the $\{R_{k}^{R} |0\rangle\}$ configuration space,
\[
\langle 0|R_{k}^{R} (H - E_{g})|\Psi_{g}^{\text{SAC–CI}}\rangle = 0 .
\]
The electron correlation of the ground state is well described by SAC and the SAC–CI wave function describes a modification of the electron correlation by excitation. Therefore, the convergence of the SAC–CI expansion is much faster than calculating the excited-state correlations from the beginning [5].

2.2. SAC–CI general-$R$ method

The SAC–CI method is applicable to the electronic processes over a wide energy region. There are two approaches in SAC–CI for studying the inner-shell electronic processes. One is based on the general-$R$ method [7,8] in which the neutral ground-state Hartree–Fock wave function is adopted for the reference function. The wave function for core ionization, for example, is given by,
\[
\Psi_{g}^{\text{SAC–CI}, \text{general-}R} = \Phi_{HF} \exp\left(\sum_{j} R_{j} + \sum_{jk} R_{jk} + \sum_{jkl} R_{jkl} + \sum_{jklm} R_{jklm} + \cdots\right) ,
\]
where $R$ and $S$ represent the $R$- and $S$-operators in the SAC–CI expansion, respectively, and $\Phi_{HF}$ is the closed-shell ground-state Hartree–Fock wave function. In this method, the higher $R$-operators such as triples and quadruples are necessary for describing both orbital relaxation and electron correlations of the core-electronic processes. Although the SD-$R$ method is accurate for the one-electron processes of the valence excitations and ionizations, higher-order operators are indispensable for the core-
electronic processes. For example, for calculating the core-electron binding energy, $R$-operators up to triples are necessary and for the shake-up satellite states, SDTQ-$R$ calculations are required. Thus, this method is simple and accurate; however, its computational cost is relatively high because it usually includes higher operators for accurate calculations. This method is applicable to the general core-electronic processes.

The other approach is the open-shell reference (OR) SAC–CI method, in which the core-ionized ROHF is used for the reference. Because the OR–SAC–CI method starts from the core–hole state, the method is efficient and accurate. However, it introduces a complex expansion because of the de-excitation operators. For example, it is difficult to calculate the $g$–$u$ splitting accurately because it starts from different reference functions for the $g$ and $u$ states.

In the present applications, the former type of method, the SAC–CI general-$R$ method, has been adopted and applied to various kinds of core-electronic processes.

3. Applications to core-electronic processes

3.1. Inner-shell shake-up satellite spectra

The shake-up satellite spectrum is a challenging spectroscopic subject from both theoretical and experimental viewpoints. Theoretically, a precise description of the satellite states is possible only with advanced theoretical methods because the spectra reflect complex electron correlation and orbital reorganization. In this section, we show a cooperative study by SAC–CI and XPS on the inner-shell satellite spectra of CO [14]. The valence and Rydberg excitations accompanying the inner-shell ionizations make the satellite spectra complex.

Figure 1 shows the observed XPS and SAC–CI general-$R$ spectra of the C1s satellites for CO. Theory reproduces the shape of the experimental satellite spectrum satisfactorily. To reproduce the inner-shell satellite spectrum, it was necessary to include $R$-operators up to quadruples, that is, an SDTQ-$R$ calculation. The conventional SAC–CI SD-$R$ method gives errors greater than 10 eV for these satellites and even qualitative assignment is impossible. The SAC–CI SDTQ-$R$ spectrum enables reliable assignments for the 16 satellite bands. Satellite band 1 was assigned to a $\pi\pi^*$ shake-up state, while the strongest band 2 was a $\pi\pi^*$ shake-up state strongly interacting with the three-electron process of C1s$^1\pi^2\pi^2$. Weak satellite peak 3 was also assigned to the double excitation $n^2\pi^2$ transition. The continuous sharp peaks above peak 4 in the higher energy region were dominantly assigned to the nun

![Figure 1. C1s shake-up satellite spectrum of CO.](image)

3.2. Geometry changes and vibrational spectra of inner-shell satellites
Vibrational spectra reflecting geometry relaxation can be observed for the inner-shell shake-up satellite states. The \( \pi\pi^* \) and \( \sigma\pi^* \) shake-up satellites were analyzed in detail for CO and \( \text{N}_2 \) by experiment and theory [13,14]. The correlation satellites can be classified into two groups phenomenologically. The first group includes satellites whose excitation cross sections relative to the single-hole ionization cross section stay constant, while the second group includes those whose excitation cross sections sharply decrease with an increase in energy. These two different types of energy dependence have been attributed to the two lowest-order correlation terms, often called the direct and conjugate shake-up terms. The low-lying shake-up satellite states of \( \text{N}_2 \) have electron configurations \( 1\sigma_u - 1\pi_u - 1\pi_g (^2\Sigma_g^+) \), \( 1\sigma_g - 1\pi_u - 1\pi_g (^2\Sigma_u^+) \), \( 1\sigma_g - 3\sigma_g - 1\pi_g (^2\Pi_g) \), and \( 1\sigma_u - 3\sigma_g - 1\pi_g (^2\Pi_u) \). The transitions leading to the \( ^2\Sigma_g^u \) states are dominated by the direct shake-up term and the transitions leading to the \( ^2\Pi_g,u \) states are dominated by the conjugate shake-up contribution.

The SAC–CI potential energy curves of the N1s shake-up states in the energy region of \( \pi\pi^* \) and \( \sigma\pi^* \) satellites are shown in Figure 2 [13]. The potential curves of the counterpart ungerade states almost overlap with the corresponding gerade states. The geometry relaxation by the shake-up ionization of \( \text{N}_2 \) is large for the \( ^2\Sigma_g^+ \) state. The calculated \( r_e \) of \( ^2\Sigma_g^+ \) was 1.259 Å, which is 0.164 Å longer than the ground state. Because the gerade state \( ^2\Sigma_g^+ \) has a hole in the \( 1\sigma_u \) orbital, it is located slightly lower in energy than the ungerade state \( ^2\Sigma_u^+ \). The calculated g–u splitting for these satellites was about 40 meV, which is smaller than the single-hole state (101 meV). The geometry relaxation for the \( ^2\Pi_g,u \) states is much smaller than for the \( ^2\Sigma_g^u \) states. The equilibrium distances of the lower and higher \( ^2\Pi_g \) states were \( r_e = 1.161 \) Å and 1.186 Å, respectively. The geometry changes for these states, 0.066 and 0.091 Å, were larger than the corresponding changes for CO of 0.042 and 0.068 Å. This is because the \( ^2\Pi_g,u \) states of \( \text{N}_2 \) have the character of \( \sigma\pi^* \) transitions and the \( ^2\Pi \) states of CO are \( \pi\pi^* \) transitions.

![Figure 2. Potential energy curves of N1s shake-up satellite \(^2\Sigma_g^+, ^2\Pi_g, ^2\Sigma_u^-, \) and \(^\Delta_g \) states of \( \text{N}_2 \).](image-url)
above. The higher $\Sigma_{g,u}$ states (singlet satellites) are repulsive in the Franck–Condon region and have a shallow minimum at about 1.57–1.59 Å; no vibrational structure is expected for these states.

Figure 3. Experimental and SAC–CI spectra of N1s satellites of N$_2$ in $\Sigma$ (left) and $\Pi$ (right) symmetry.

3.3. Strong valence-Rydberg coupling in inner-shell excited states

Angle-resolved ion yield (ARIY) spectra were also measured in the O K edge of N$_2$O [15]. Figure 4 shows the ARIY spectra measured at angles of 0° and 90° along with the total ion yield measurement. The measurement at 0° mainly observes the $\Sigma$ states, while the measurement at 90° observes $\Pi$ states. In the 4s$\sigma$ state, irregular excitation to the higher vibrational levels was observed [15], while the vibrational spectrum of the 3p$\pi$ state was a normal Rydberg spectrum.

To clarify this irregular vibrational progression, the potential energy surfaces of the O1s core–excited states were examined [15]. Figure 5 show the potential energy curves and the electronic part of the second moments $<r^2>$ of the O1s excited states of $\Sigma$ and $\Delta$ symmetry along the $R_{NO}$ distance. The second moment $<r^2>$ of the 4s$\sigma$ state drastically decreases at large $R_{NO}$ distance and this shows that strong valence–Rydberg coupling occurs in the 4s$\sigma$ state having a $\sigma^*$ component. Because of this...

Figure 4. Angle-resolved ion yield (ARIY) spectra of O1s excitation of N$_2$O measured at 0° and 90°.
strong valence–Rydberg coupling, the 4sσ state has a potential minimum at a large $R_{NO}$ distance. This shows that the irregular Rydberg behavior in the 4sσ state is caused by the strong valence–Rydberg coupling.

Figure 5. Potential curves (left) and second moments $\langle r^2 \rangle$ (right) of the O1s excited states of N$_2$O.

Franck–Condon analysis based on the SAC–CI two-dimensional potential energy surfaces was performed for the 4sσ and 3pπ states. Theory reproduced the observed vibrational excitations accurately, as shown in Figure 6. The higher vibrational levels are excited in the 4sσ state, while the vibrational spectrum of the 3pπ state shows the standard Rydberg-type vibrational progression.

Figure 6. Vibrational spectra of a) O1s–4sσ and b) O1s–3pπ excited states of N$_2$O. The SAC–CI predicted spectra are shown by the vertical solid lines.

3.4. Thermal effects in inner-shell excitation spectra
Absorption spectra of vibrationally excited “hot” molecules were observed for the O1s excitation of N$_2$O. The absorption spectra were measured at 300/700 K and the vibrationally excited absorption spectrum was extracted assuming the Boltzmann distribution (Figure 7) [16]. Comparing the spectra of (0,0,0) and (0,ν$_2$,0), the intensity of the nσs Rydberg series is significantly suppressed, while that of the A’(π) state is enhanced for the excitation from the vibrationally excited states, (0,ν$_2$,0). These observations suggest that the decrease in the bond angle causes a decrease in the mixing of the valence character that enhances the transition probability to the Rydberg states. An energy shift was also observed in the spectra from the vibrationally excited states.

To understand these phenomena, we performed SAC–CI calculations of the energies and the second moment $\langle r^2 \rangle$ of the O1s excited states varying the bond angle [16]. Figure 8 shows a cut of the
calculated potential energy surfaces of the O1s excited states of \(A'\) symmetry. The \(1A'\) state is correlated to the \(\pi^*\) state and stabilizes along the bending coordinate. All other states are stable in the linear structure. A characteristic curve crossing occurs between the \(\sigma\) and \(\pi\) Rydberg states along the bending coordinate. These potential curves explain the red shift of the \(\pi^*\) state and the blue shift of the \(3s\sigma\) and \(4s\sigma\) states. To analyze the mixing of the valence character in the Rydberg states, we examined the electronic part of the second moment \(<r^2>\), which is anticorrelated to the amount of valence character (Figure 8). The second moments of the \(3s\sigma\), \(4s\sigma\), and \(5s\sigma\) states become larger as the molecule becomes bent. This indicates that the mixing of the valence character in these states becomes less as the bond angle decreases. Consequently, the absorption oscillator strength to the \(ns\sigma\) Rydberg states becomes small. These results confirm the interpretation of the intensity changes observed for excitation from vibrationally excited molecules.

![Figure 7](image_url) **Figure 7.** ARIY spectra in the \(N_2O\) O1s excitation region: blue and red lines show the spectra from the vibrational ground and excited states, respectively.

![Figure 8](image_url) **Figure 8.** Potential energy curves (left) and second moments \(<r^2>\) (right) of the low-lying O1s excited states of \(N_2O\) along the bending coordinate.

The \(A'(\pi^*)\) state stabilizes along the bending coordinate whereas the \(3s\alpha'\) state destabilizes more than the \(A''(\pi^*)\) state. This anticorrelation indicates that the \(A'(\pi^*)\) and \(3s\alpha'\) states are strongly coupled. This coupling opens a flow of the valence character from the \(3s\alpha'\), \(4s\alpha'\), and \(5s\alpha'\) Rydberg states to the \(A'(\pi^*)\) state. Analyzing the MOs that contribute to the excitations, we conclude that the counterpart of the decrease in the mixing of the valence character in the \(3s\), \(4s\), and \(5s\) states is an increase in the \(s\sigma\)-type character of the \(a'(\pi^*)\) orbital.
Based on the SAC–CI calculations of the second moment $<r^2>$, the suppression is interpreted as being due to a decrease in the mixing of the valence character in the $ns\sigma$ Rydberg states with decreasing bond angle.

4. Summary
High-precision ab initio theoretical spectroscopy of the core-electronic processes have been achieved by the SAC–CI general-$R$ method. In this article, we have reviewed SAC–CI theory and introduced some recent applications to inner-shell spectroscopy. The general-$R$ method has reproduced the fine details of the high-resolution spectra providing quantitative assignments and clarifying the essence of the phenomena. We have explained our recent work on the inner-shell shake-up satellite spectrum of CO, geometry relaxation and vibrational spectra of the inner-shell satellites of $N_2$, strong valence–Rydberg coupling of $O1s$ excited states of $N_2O$, and thermal effects in the inner-shell excitation spectra.

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